Analytical chemistry

Lecture №21

REDOX titration

A lot of titrimertic methods used in quantitative analysis are based on the oxidation-reduction reactions (redox reactions). They are commonly named as ***oxidimetry (redox)*** methods.

With the help of oxidimetry used in clinical and biochemical research one can determine the catalase and peroxidase activity, the presence of ascorbic acid, sugar in blood and other biological liquids, uric acid in urine, urea in blood and urine, calcium ions in blood serum and so on.

With the help of oxidimetry methods used in hygiene and sanitary investigations one can determine the oxidability of water, the content of active chlorine in drinking water, dissolved oxygen and organic admixtures in the water and so on.

The redox reactions include a partial or a complete electron transfer from one group of atoms or ions to another group. These transfers are resulted in the change of oxidation states of the atoms of certain elements. According to the electron theory of oxidation-reduction processes, oxidation is the process of the loss of electrons. The substance which has lost electrons is called a reducing agent (reducer). Reducer transforms into its oxidized form in the course of the reaction. Each reduced formed is, actually, the oxidizing agent that is coupled with the initial reducing agent. For example,

$$Sn^{2+} - 2e^- \leftrightarrow Sn^{4+}$$

reducing agent 1 – ne^- ↔ oxidizing agent 1

Reduction is the process of the gain of electrons. The substance taking the electrons in redox reactions is called the oxidizing agent. Oxidizer transforms into its coupled reduced form during the redox reaction. For example,

$$Fe^{3+} + e^- \rightarrow Fe^{2+}$$

$$\text{oxidizing agent 2} + ne^- \rightarrow \text{reducing agent 2}$$

The processes of oxidation and reduction occur simultaneously and they should be considered inseparably, besides, the total number of electrons lost by the reducing agent is equal to the total number of the electrons gained by the oxidizing agent.

$$\begin{cases} \text{reducing agent 1} - ne^- \rightarrow \text{oxidizing agent 1} \\ \text{oxidizing agent 2} + ne^- \rightarrow \text{reducing agent 2} \end{cases}$$

$$\text{reducing agent 1} + \text{oxidizing agent 2} \rightarrow \text{oxidizing agent 1} + \text{reducing agent 2}$$

$$\begin{cases} Sn^{2+} - 2e^- \rightarrow Sn^{4+} \mid 2 \mid 1 \\ Fe^{3+} + e^- \rightarrow Fe^{2+} \mid \quad \mid 2 \end{cases}$$

$$Sn^{2+} + 2Fe^{3+} \rightleftarrows Sn^{4+} + 2Fe^{2+}$$

So, any redox reaction is the combination of two coupled processes — so-called half-reactions: oxidation of the reducing agent and the reduction of the oxidizing agent.

Redox titration - a titration in which the reaction between the analyte and titrant is an oxidation/reduction reaction.

Redox titrations were introduced shortly after the development of acid–base titrimetry. The earliest methods took advantage of the oxidizing power of chlorine. In 1787, Claude Berthollet introduced a method for the quantitative analysis of chlorine water (a mixture of Cl_2, HCl, and HOCl) based on its ability to oxidize solutions of the dye indigo.

In 1814, Joseph Louis Gay-Lussac (1778–1850), developed a similar method for chlorine in bleaching powder.

In both methods the end point was signaled visually. Before the equivalence point, the solution remains clear due to the oxidation of indigo. After the equivalence point, however, unreacted indigo imparts a permanent color to the solution.

The number of redox titrimetric methods increased in the mid-1800s with the introduction of MnO_4^-, $Cr_2O_7^{2-}$ and I_2 as oxidizing titrants, and Fe^{2+} and $S_2O_3^{2-}$ as reducing titrants. Even with the availability of these new titrants, however, the routine application of redox titrimetry to a wide range of samples was limited by the lack of suitable indicators. Titrants whose oxidized and reduced forms differ significantly in color could be used as their own indicator. For example, the intensely purple MnO_4^- ion serves as its own indicator since its reduced form, Mn^{2+}, is almost colorless. The utility of other titrants, however, required a visual indicator that could be added to the solution. The first such indicator was diphenylamine, which was introduced in the 1920s. Other redox indicators soon followed, increasing the applicability of redox titrimetry.

A redox titration permits us to determine the concentration of a form Ox_1 or Red_1 by adding antagonistic solution of Red_2 or Ox_2. The redox reaction between the antagonistic species, which is the titration reaction, induces a change in the equilibrium potential of the titrand solution for each added volume of titrant solution.

$$n_2\mathrm{Red}_1 + n_1\mathrm{Ox}_2 \rightleftharpoons n_2\mathrm{Ox}_1 + n_1\mathrm{Red}_2,$$

The necessary conditions to obtain a satisfactory titration.
There are two kinds: thermodynamic and kinetic.

The thermodynamic condition is an absolute necessity: A titration reaction must be as complete as possible, regardless of the kind of titration: acid–base, redox, etc. This condition must be satisfied in order to weaken the titration error.

From a practical standpoint, a titration reaction must be achieved as fast as possible. It is not always the case for redox titrations. Recall that the rate of a redox reaction may be considerably increased with the use of ***catalysts***. Additionally, some titrations imply them.

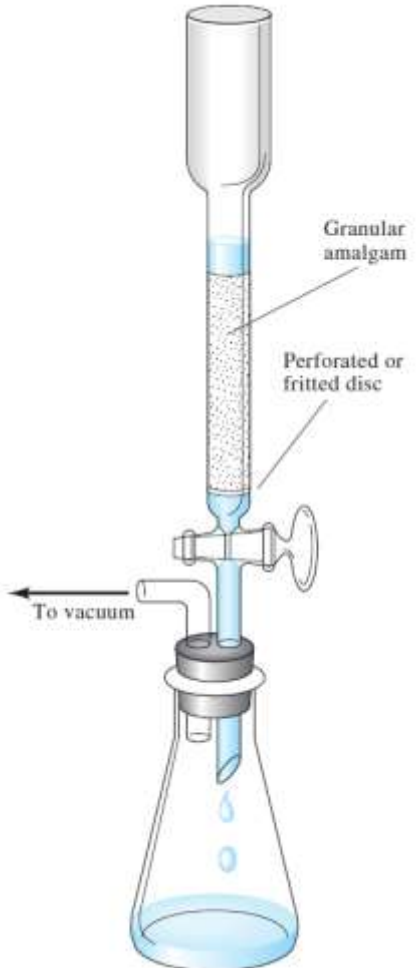
The requirements to the reactions used in oxidimetry are as follows:

- the reaction should be fast and irreversible;
- the products should have definite composition;
- there should not be any side reactions;
- there should be a method to fix the end of the reaction.

The number of reactions which satisfy these criterions is very small. The difference between redox potentials of two substances ($E = E_{ox} – E_{red}$) should be higher than 0.4 to make the process almost irreversible. Otherwise, there will be no drastic redox potential jump at the equivalence point.

Preparing the Solution—Getting the Analyte in the Right Oxidation State before Titration

When samples are dissolved, the element to be analyzed is usually in a mixed oxidation state or is in an oxidation state other than that required for titration. There are various oxidizing and reducing agents that can be used to convert different metals to certain oxidation states prior to titration. The excess preoxidant or prereductant must generally be removed before the metal ion is titrated.



A Jones reductor

REDUCTION OF THE SAMPLE PRIOR TO TITRATION

The reducing agent should not interfere in the titration or, if it does, unreacted reagent should be readily removable. Most reducing agents will, of course, react with oxidizing titrants, and they must be removable. **Sodium sulfite, Na_2SO_3, and sulfur dioxide** are good reducing agents in acid solution *($E^0 = 0.17$ V), and the excess can be removed* by bubbling with CO_2 or in some cases by boiling.

Stannous chloride, $SnCl_2$, is usually used for the reduction of iron(III) to iron(II) for titrating with cerium(IV) or dichromate. The reaction is rapid in the presence of chloride (hot HCl).

A number of **metals** are good reducing agents and have been used for the prereduction of analytes. Included among these reductants are zinc, aluminum, cadmium, lead, nickel, copper, and silver (in the presence of chloride ion). In the reductor, the finely divided metal is held in a vertical glass tube through which the solution is drawn under a mild vacuum. A typical Jones reductor has a diameter of about 2 cm and holds a 40- to 50-cm column of amalgamated zinc. Amalgamation is accomplished by allowing zinc granules to stand briefly in a solution of mercury(II) chloride.

Uses of the Walden Reductor and the Jones Reductor*

Walden $Ag(s) + Cl^- \rightarrow AgCl(s) + e^-$	Jones $Zn(Hg)(s) \rightarrow Zn^{2+} + Hg + 2e^-$
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$
$Cu^{2+} + e^- \rightarrow Cu^+$	$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$
$H_2MoO_4 + 2H^+ + e^- \rightarrow MoO_2^+ + 2H_2O$	$H_2MoO_4 + 6H^+ + 3e^- \rightleftharpoons Mo^{3+} + 3H_2O$
$UO_2^{2+} + 4H^+ + 2e^- \rightarrow U^{4+} + 2H_2O$	$UO_2^{2+} + 4H^+ + 2e^- \rightleftharpoons U^{4+} + 2H_2O$
	$UO_2^{2+} + 4H^+ + 3e^- \rightleftharpoons U^{3+} + 2H_2O^\dagger$
$V(OH)_4^+ + 2H^+ + e^- \rightarrow VO^{2+} + 3H_2O$	$V(OH)_4^+ + 4H^+ + 3e^- \rightleftharpoons V^{2+} + 4H_2O$
TiO^{2+} not reduced	$TiO^{2+} + 2H^+ + e^- \rightleftharpoons Ti^{3+} + H_2O$
Cr^{3+} not reduced	$Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$

OXIDATION OF THE SAMPLE PRIOR TO TITRATION

Sodium bismuthate is a powerful oxidizing agent capable, for example, of converting manganese(II) quantitatively to permanganate ion.

$$NaBiO_3(s) + 4H^+ + 2e^- \rightleftharpoons BiO^+ + Na^+ + 2H_2O$$

Ammonium peroxydisulfate, $(NH_4)_2S_2O_8$, is also a powerful oxidizing agent. In acidic solution, it converts chromium(III) to dichromate, cerium(III) to cerium(IV), and manganese(II) to permanganate.

$$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-} \qquad 2S_2O_8^{2-} + 2H_2O \rightarrow 4SO_4^{2-} + O_2(g) + 4H^+$$

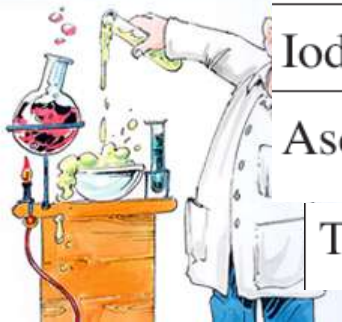
Peroxide is a convenient oxidizing agent either as the solid sodium salt or as a dilute solution of the acid.

$$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O \qquad E^0 = 1.78\ V$$

$$2H_2O_2 \rightarrow 2H_2O + O_2(g)$$

Oxidation-reduction titrations can be classified according to the titrant

Agent	Redox half-reaction	Standard reduction potential (v)
Oxidizing agents		
Cerium IV Ce^{4+} IV	$Ce(ClO_4)_6^{2-} + e^- = Ce^{3+} + 6\ ClO_4^-$	+ 1.7
Permanganate MnO_4^-	$MnO_4^- + 8\ H^+ + 5\ e^- = Mn^{2+} + 4\ H_2O$	+1.49
Bromate BrO_3^-	$BrO_3^- + 6\ H^+ + 6\ e^- = Br^- + 3\ H_2O$	+ 1.42
Dichromate $Cr_2O_7^{2-}$	$Cr_2O_7^{2-} + 14\ H^+ + 6\ e^- = 2\ Cr^{3+} + 7\ H_2O$	+ 1.33
Iodine I_2	$I_2 + 2\ e^- = 2\ I^-$	+ 0.521
Reducing agents		
Ferrous Fe^{2+}	$Fe^{3+} + e^- = Fe^{2+}$	+ 0.771
Iodide I^-	$I_2 + 2\ e^- = 2\ I^-$	+0.521
Ascorbic acid $C_6H_6O_6$	$3\ C_6H_6O_6 + 6\ H^+ + 6e^- = 3\ C_6H_8O_8$	+ 0.185
Thiosulphate $S_2O_3^{2-}$	$S_4O_6^{2-} + 2\ e^- = 2\ S_2O_3^{2-}$	+ 0.09



Redox titration curve

Consider the titration of 100 ml of 0,1 M iron(II) sulfate $FeSO_4$ solution with 0,1 M potassium permanganate solution, monitored potentiometrically.

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

The redox reaction between the antagonistic species, which is the titration reaction, induces a change in the equilibrium potential of the titrand solution for each added volume of titrant solution. A redox titration curve is the diagram of the solution's potential/added volume of titrant solution.

There are three distinct regions in the titration of iron(II) with potassium permanganate solution, monitored potentiometrically.

1) Before the equivalence point, where the potential is dominated by the analyte redox pair.

2) At the equivalence point, where the potential at the indicator electrode is the average of their conditional potential.

3) After the equivalence point, where the potential was determined by the titratant redox pair.

Before the equivalence point:

During the addition of the $KMnO_4$ solution up to the equivalence point, its only effect will be to oxidize the Fe^{2+}, and consequently change the ratio $[Fe^{3+}]/[Fe^{2+}]$.

Prior to the equivalence point, the half-reaction involving analyze is used to find the voltage because the concentrations of both the oxidized and the reduced forms of analyte are known.

After adding X mL of $KMnO_4$ the voltage can be calculated using Nernst equation as follows

$$E = E^0_{Fe^{3+}/Fe^{2+}} + \frac{0.059}{1}\lg\frac{[Fe^{3+}]_{formed}}{[Fe^{2+}]_{leftover}}$$

$$E = 0{,}77 + \frac{0.059}{1}\lg\frac{c(\tfrac{1}{5}KMnO_4)V(KMnO_4)}{c(Fe^{2+})V(Fe^{2+})_{initial} - c(\tfrac{1}{5}KMnO_4)V(KMnO_4)}$$

After adding 1 ml of 0,1 M $KMnO_4$:

$$E = 0{,}77 + \frac{0.059}{1}\lg\frac{0.1\cdot 1}{0.1\cdot 100 - 0.1\cdot 1} = 0.65\,V$$

E = 0,65 Volts

After adding 91 ml of 0,1 M $KMnO_4$:

$$E = 0{,}77 + \frac{0.059}{1}\lg\frac{0.1\cdot 91}{0.1\cdot 100 - 0.1\cdot 91} = 0{,}83\,V$$

E = 0,83 Volts

After adding 99,9 ml of 0,1 M $KMnO_4$:

$$E = 0{,}77 + \frac{0.059}{1}\lg\frac{0.1\cdot 99{,}9}{0.1\cdot 100 - 0.1\cdot 99{,}9} = 0{,}994\ B$$

E = 0,994 Volts

At the equivalence point

At the equivalence point, both half-reactions are used simultaneously to find the voltage.

$$aOx_1 + b\,\mathrm{Re}\,d_2 = a\,\mathrm{Re}\,d_1 + bOx_2$$

The electrode potential is given by:

$$E = \frac{bE^0{}_{Ox} + aE^0_{\mathrm{Re}\,d}}{b+a}$$

$$E = \frac{1\cdot E^0{}_{Fe^{3+}/Fe^{2+}} + 5\cdot E^0_{MnO_4^-/Mn^{2+}}}{5+1} = \frac{0{,}77 + 5\cdot 1{,}51}{6} = 1{,}39\ V$$

E = 1,39 Volts

After the equivalence point:

The subsequent addition of the $KMnO_4$ solution will merely increase the ratio $[MnO_4^-]/[Mn^{2+}]$.

$$E = E^0_{MnO_4^-/Mn^{2+}} + \frac{0.059}{5}\lg\frac{c(MnO_4^-)c(H^+)^8}{c(Mn^{2+})}$$

$$E = E^0_{MnO_4^-/Mn^{2+}} + \frac{0.059}{5}\lg\frac{c(MnO_4^-)_{added}V(MnO_4^-)_{added} - c(Fe^{2+})V(Fe^{2+})}{c(Fe^{2+})V(Fe^{2+})}$$

$$E = E^0_{MnO_4^-/Mn^{2+}} + \frac{0.059}{5}\lg\frac{c(MnO_4^-)V(MnO_4^-)_{added} - c(Fe^{2+})V(Fe^{2+})}{c(Fe^{2+})V(Fe^{2+})}$$

After adding 100,1 ml of 0,1 M $KMnO_4$:

$$E = E^0_{MnO_4^-/Mn^{2+}} + \frac{0.059}{5}\lg\frac{0.1\cdot 100.1 - 0.1\cdot 100}{0.1\cdot 100} = 1.475\,V$$

E = 1,475 Volts

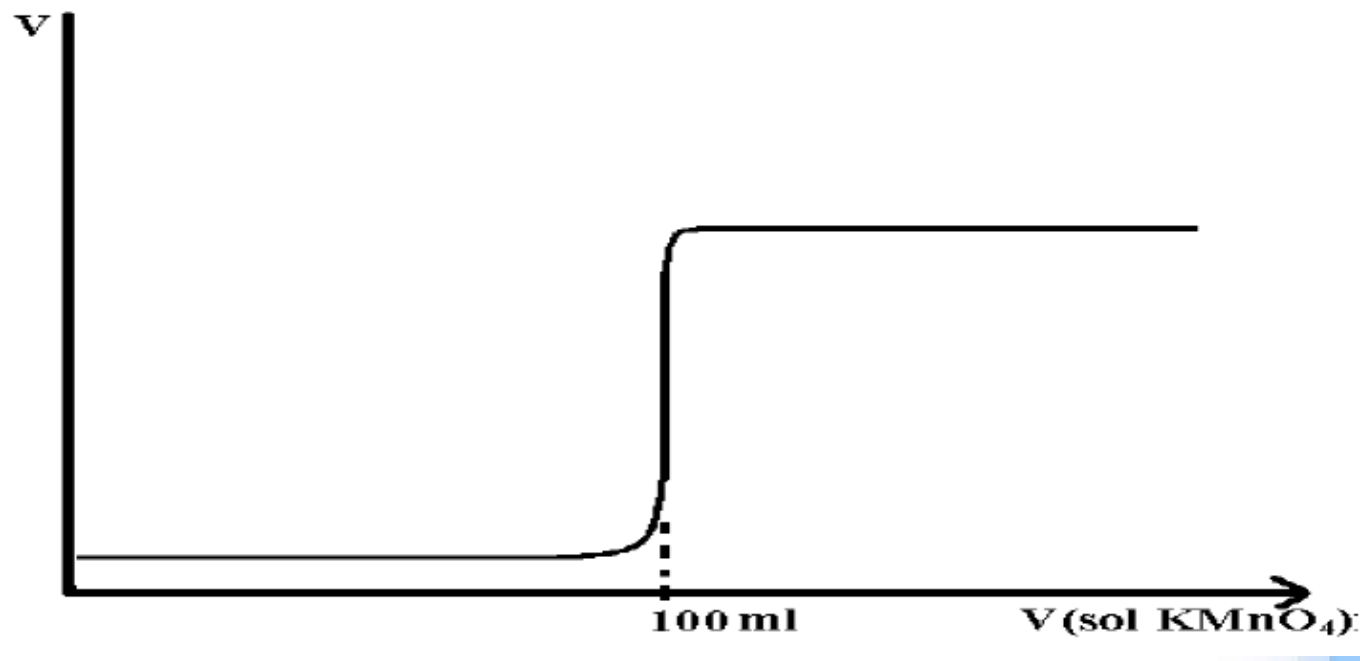
After adding 110 ml of 0,1 M $KMnO_4$:

$$E = E^0_{MnO_4^-/Mn^{2+}} + \frac{0.059}{5}\lg\frac{0.1\cdot 110 - 0.1\cdot 100}{0.1\cdot 100} = 1.498\,V$$

E = 1,498 Volts

Thus E (Volt) changes from 0,994 to 1,475 between 0,1 ml before and 0,1 ml after the stoichiometric endpoint. These quantities are of importance in connection with the use of indicators for the detection of the equivalence point.

№	$V(KMnO_4)$	E, V
1	1	0,65
2	50	0,77
3	91	0,83
4	99	0,89
5	99,9	0,994
6	100	1,39
7	100,1	1,475
8	101	1,487
9	110	1,498



Conclusions:

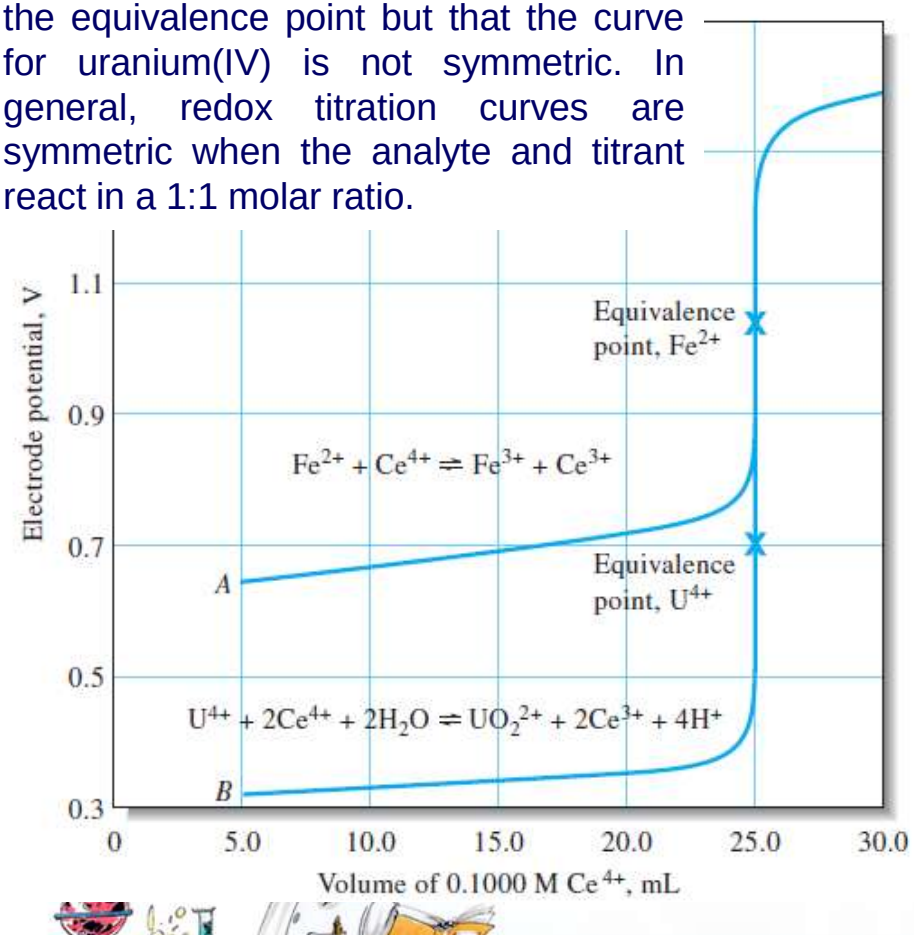
• It is evident that the abrupt change of the potental in the neighbourhood of the equivalence point is dependent upon the standard potentials of the two oxidation-reduction systems that are involved. The greater the difference in reduction potential between analyze and titrant, the sharper will be the end point.

• The voltage at any point in this titration is independent of dilution and of the concentrations unless these are extremely small.

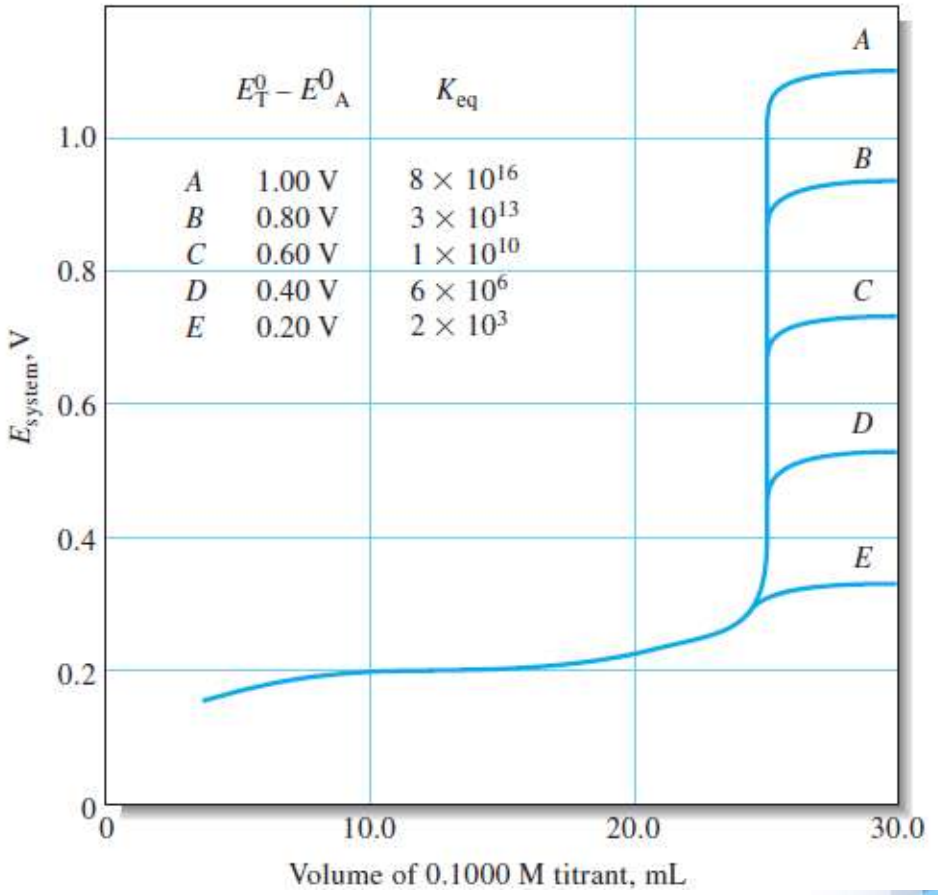
- **Completeness of the Reaction**

The change in potential in the equivalence-point region of an oxidation/reduction titration becomes larger as the reaction becomes more complete.

the curve for iron(II) is symmetric around the equivalence point but that the curve for uranium(IV) is not symmetric. In general, redox titration curves are symmetric when the analyte and titrant react in a 1:1 molar ratio.



Titration curves for 0.1000 M Ce^{4+} titration.
A: Titration of 50.00 mL of 0.05000 M Fe^{2+}.
B: Titration of 50.00 mL of 0.02500 M U^{4+}.



The greatest change in potential of the system is associated with the reaction that is most complete, and curve *E illustrates the opposite extreme.*

Detection of Endpoint in Redox Titration

At the equivalence point of a satisfactory redox titration, there is a sharp change in the equilibrium potential of the titrated solution. Several means exist for its detection.

They are based on the current use

- of internal ***redox*** indicators;
- **SELF-INDICATION** or of special redox species. The latter are purely and simply one (or several) of the reactants of the redox titration under consideration. They also play the role of indicators. For example, it is the case with iodine–iodide and of potassium permanganate solutions;
- of specific indicators that exhibit a particular color in the presence of a given reactant or product. It is the case for a starch solution in the presence of iodine and iodide;
- of several ***physical methods of analysis***, the most important of which is probably zero-current potentiometry. This is an electrochemical method that, as a rule, measures the potential of a solution.

Two types of chemical indicators are used for obtaining end points for oxidation/reduction titrations: **general redox indicators and specific indicators**.

General Redox Indicators

The ideal oxidation-reduction indicator will be one with an oxidation potential intermediate between that of the solution titrated (analyte) and that of the titrant, and which exibits a sharp, readily detectible colour change. An redox indicator is a compound which exhibits different colours in the oxidized and reduced forms.

These are highly colored dyes that are weak reducing or oxidizing agents that can be oxidized or reduced; the colors of the oxidized and reduced forms are different. The oxidation state of the indicator and hence its color will depend on the potential at a given point in the titration. The oxidation and reduction should be reversible. A half-reaction and Nernst equation can be written for the indicator:

$$Ind_{Ox} + ne \Leftrightarrow Ind_{Red} \quad E = E^0 + \frac{0.059}{n} \lg \frac{c(Ind_{Ox})}{c(Ind_{Red})}$$

Typically, a change from the color of the oxidized form of the indicator to the color of the reduced form requires a change of about 100 in the ratio of reactant concentrations, that is, a color change appears when

$$\frac{[In_{red}]}{[In_{ox}]} \leq \frac{1}{10} \qquad \frac{[In_{red}]}{[In_{ox}]} \geq 10$$

$$E = E^0 \pm \frac{0{,}058}{n}$$

Indicator range

This equation shows that a typical general indicator exhibits a detectable color change when a titrant causes the system potential to shift from E^0_{In} + 0.0592/*n to* E^0_{In} - 0.0592/*n or about (0.118/n) V. For many indicators, n 5 2, and a change of* 0.059 V is thus sufficient.

E^0_{In} must be near the equivalence point potential. A potential change of at least 120mV is needed for a color change for *n = 1 (of the* indicator half-reaction) and 60mV for *n = 2.*

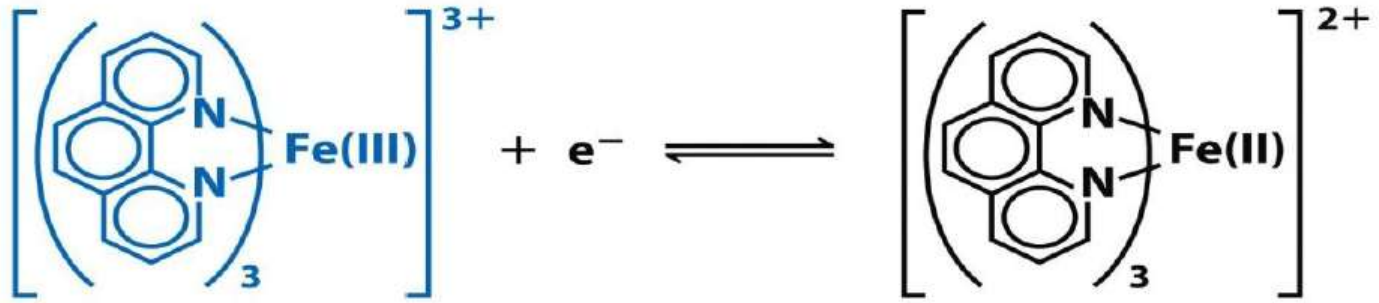
Protons participate in the reduction of many indicators. Thus, the range of potentials over which a color change occurs (the *transition potential)* is often ***pH dependent***.

The most commonly used internal redox indicators are derivatives of 1,10-phenanthroline, diphenylamine, phenothiazine, and diphenylpyrazine.

Iron(II) Complexes of Orthophenanthrolines

A class of organic compounds known as 1,10-phenanthrolines, or orthophenanthrolines, form stable complexes with iron(II) and certain other ions. The parent compound has a pair of nitrogen atoms located in such positions that each can form a covalent bond with the iron(II) ion.

Ferroin



Oxidized ferroin (pale blue) In(oxidized)

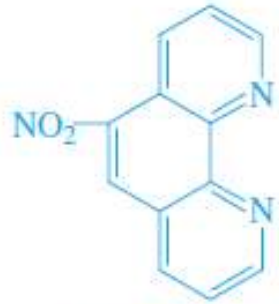
Reduced ferroin (red) In(reduced)

$$E^0 = 1{,}147\ V$$

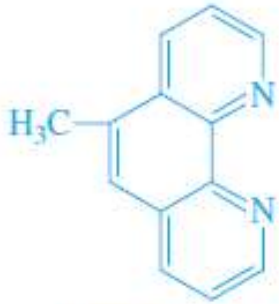
$$E = 1{,}06 \pm \frac{0{,}058}{1} = (1{,}088 \div 1{,}206)\ V$$

$E < 1{,}088\ V$ red (Reduced form)

$E > 1{,}206\ V$ Pale blue (Oxidized form)



5-nitro-1, 10-phenanthroline

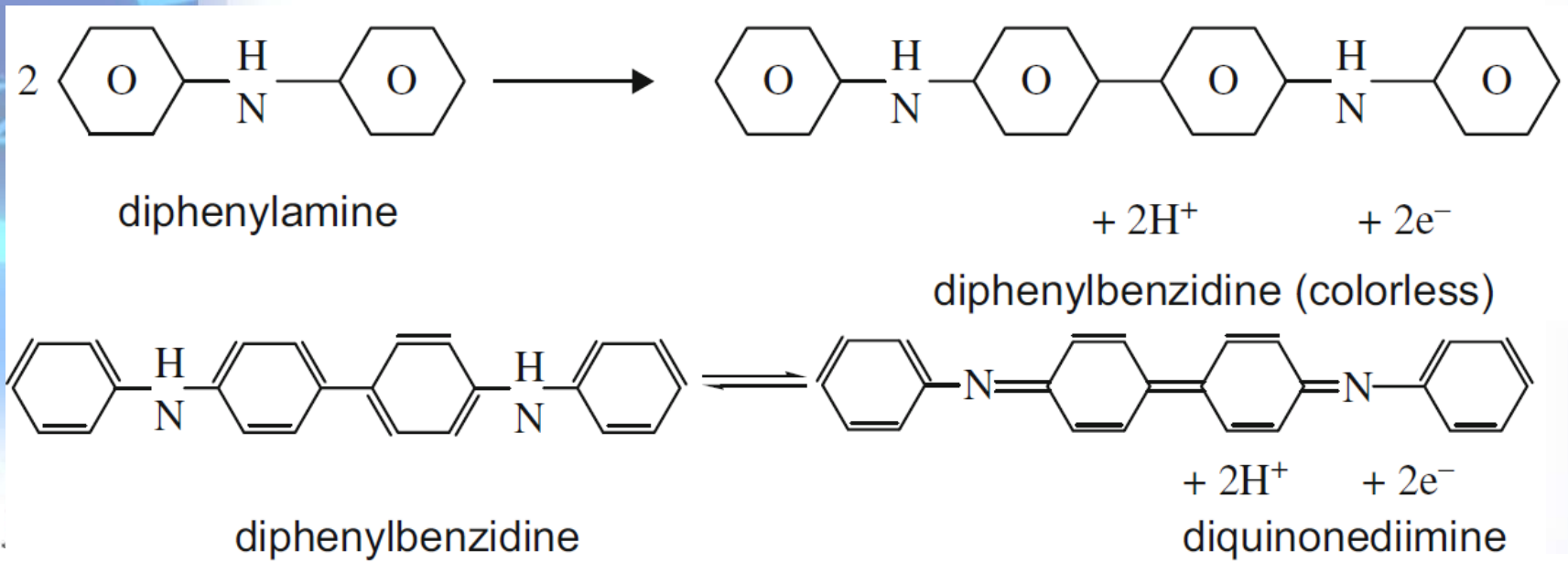


5-methyl-1, 10-phenanthroline

Diphenylamine

$E^0 = 0{,}76\ V$

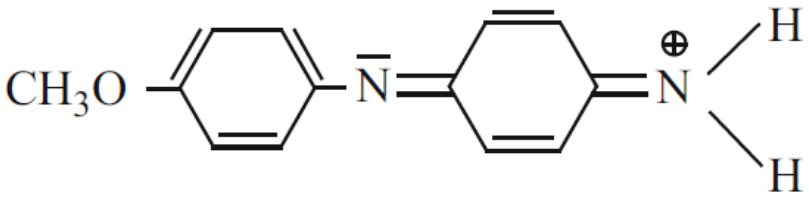
Some derivatives of diphenylamine are internal redox indicators that have been used very often. Diphenylamine dissolved in diluted acidic medium. *In the presence of a strong oxidizing agent, it first undergoes* an irreversible chemical oxidation to give the colorless diphenylbenzidine. Diphenylbenzidine can be reversibly oxidized according to a bielectronic process to give a colored diquinonediimine. Finally, the formed diquinonediimine can be oxidized once more, but this time irreversibly when it stays too long in the presence of the oxidizing solution. Diphenylamine can be used in the case of the titration of ferrous ions by potassium dichromate. It is poorly soluble in water.



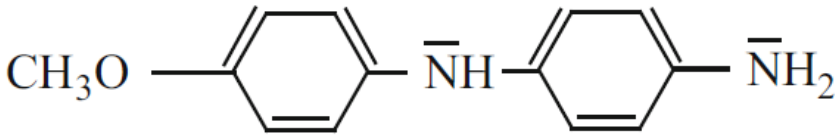
$$E = 0{,}76 \pm \frac{0{,}058}{2} = (0{,}73 \div 0{,}79)\ B$$

$E < 0{,}73\ V$ colourless (Reduced form)

$E > 0{,}79\ V$ bluish violet (Oxidized form)



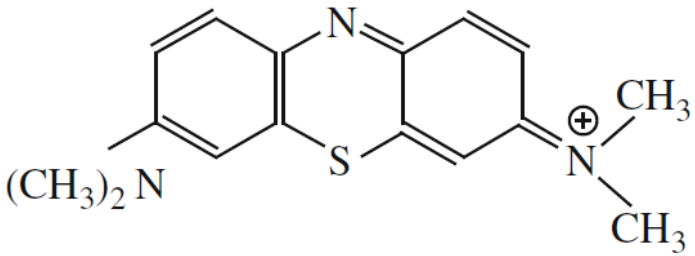
Oxidized form of blue variamine



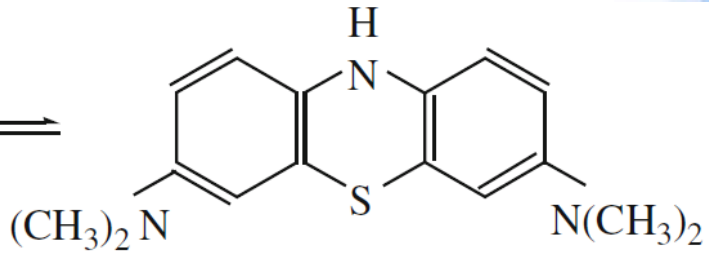
reduced form

variamine blue

Methylene blue derives from phenothiazine. (The reduced form can also undergo two further protonations on the dimethylamino rests depending on the medium's pH.) The standard potential of methylene blue is $E^\circ = 0.53\ V$.



methylene blue (oxidized form)



reduced form

A redox titration is feasible if the difference between analyte and titrant is > 0.2 V. If the difference in the formal potential is > 0.4 V, then a redox indicator usually gives a satisfactory end point.

Percent by mass, mass percentage, mass fraction (ω). The percent by mass (also called the percent by weight or the weight percent) is defined as ω = mass fraction of a solute = m (solute) / m (solution).

Molality (C_m). Molality is the number of moles of a solute (S) dissolved in 1 kg (1000 g) of a solvent. Cm = n (solute) / m (solvent).
Thus molality has the units of mol/kg.

Molarity (C). Molarity is defined as the number of moles of solute in 1 liter of a solution; that is, C = n (solute) / V (solution).
Thus, molarity has the units of mol/L or M.

Titer (T). Titer is defined as a mass of a solute in 1 milliliter of a solution; that is,
T = m (solute) / V (solution).
Thus, titer has the units of g/mL.

Normality (C_N). Normality is defined as the number of moles of the equivalent of a solute (neq) in 1 liter of a solution; that is,
C_N = neq (solute) / V (solution).
Thus, normality has the units of mol/L or N.

Solutions' concentration can be represented by **titer (T)** in the volumetric analysis - it is the number of solute's grammes in the one cm^3 (ml) of the solution (g/ml).

In chemical reactions the molar ratio of reacting substances is not always 1:1. It is determined by stoichiometric coefficients. For example, in the reaction written below the molar ratio between base and acid will be 2:1.

$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O$.

The coefficients can be replaced by equivalence factors: actually, for the base you need to divide number one (1) by the coefficient before acid, for the acid you need to divide number one by the coefficient before base. So, in the abovementioned reaction the equivalence factor for NaOH is 1, while for H_2SO_4 it is equal to 1/2.

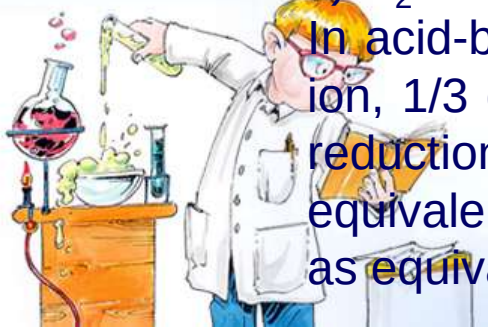
As substances behave differently in the complex formation reactions, chemists avoid using the notion of equivalent for them and use only molar masses instead. Thus, in this textbook the notion of equivalent will be used only for the substances taking part in oxidation-reduction and acid-base reactions.

Let‘s consider the following reactions:

a) $H^+ + OH^- = H_2O$; d) $2H^+ + S^{2-} = H_2S$;

b) $H^+ + NH_3 = NH_4^+$; e) $3OH^- + H_3PO_4 = PO_4^{3-} + 3H_2O$;

c) $H_2^0 - 2e^- = 2H^+$; f) $Al^{3+} + 3e^- = Al^0$.



In acid-base reactions (a, b, d, e) 1 OH^- ion, 1 NH_3 molecule, 1/2 S^{2-} ion, 1/3 of H_3PO_4 molecule are equivalent to one H^+ ion. In oxidation-reduction reactions (c, f) 1/2 of H_2 molecule, 1/3 of Al^{3+} ion are equivalent to one electron. The enumerated particles are considered as equivalents of substances taking part in these reactions.

From another point of view *the equivalent is some real or hypothetical particle which interacts with the carrier of one elementary charge in the ion exchange or oxidation-reduction reactions.*

Equivalent is that comparative quantity by weight of an element, which possesses the same chemical value as other elements, as determined by actual experiment and reference to the same standard.

Equivalence factor $f_{eq}(X)$ is the number indicating which part of the real particle of substance X is equivalent to one hydrogen ion in the given acid-base reaction or to one electron in the oxidation-reduction reaction. This value is dimensionless and is calculated on the basis of stoichiometric coefficients of a definite reaction.

Equivalence factor is often written as 1/z ratio, where z is the overall charge of ions from a molecule taking part in the given exchange reaction or the number of electrons which are gained or lost by a molecule (an atom) of the substance in oxidation-reduction reaction; z is always a positive integer and the equivalence factor is less or equal to 1: $f_{eq}(X) = 1/z \leq 1$.

Equivalence factor of the same substance can have different values in different reactions. Let‘s consider this using the following examples.

The mass of one mole of chemical equivalent is defined as equivalent molar mass (Meq), g/mol. The equivalent molar mass relates to the molar mass of a substance as follows: $M_{eq} = M \times f_{eq}$, where f_{eq} is the factor of equivalence.

In acid-base reactions Na_2CO_3 can be neutralized by an acid until the formation of an acidic salt or until the emission of CO_2:

a) $Na_2CO_3 + HCl = NaHCO_3 + NaCl$, $f_{eq}(Na_2CO_3) = 1$;

b) $Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2$, $f_{eq}(Na_2CO_3) = 1/2$.

In oxidation-reduction reactions $KMnO_4$ is always an oxidizing agent:

c) $5Na_2SO_3 + 2KMnO_4 + 3H_2SO_4 = 5Na_2SO_4 + 2MnSO_4 + 3H_2O + K_2SO_4$,

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$, $f_{eq}(KMnO_4) = 1/5$;

d) $3Na_2SO_3 + 2KMnO_4 + H_2O = 3Na2SO4 + 2MnO2 + 2KOH$,

$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$, $f_{eq}(KMnO_4) = 1/3$;

e) $Na_2SO_3 + 2KMnO_4 + 2KOH = Na_2SO_4 + 2K_2MnO_4 + H_2O$,

$MnO_4^- + e^- \rightarrow MnO_4^{2-}$, $f_{eq}(KMnO_4) = 1$.

The **equivalent mass of an** acid or base is the mass of the compound that reacts with or contains one mole of protons.

Thus, the equivalent mass of KOH (56.11 g/mol) is equal to its molar mass. For $Ba(OH)_2$, it is the molar mass divided by 2.

$$56.11 \frac{g}{\text{mol } \cancel{KOH}} \times \frac{1 \text{ mol } \cancel{KOH}}{\text{mol protons reacted}} = 56.11 \frac{g}{\text{mol protons reacted}}$$

$$171.3 \frac{g}{\text{mol } \cancel{Ba(OH)_2}} \times \frac{1 \text{ mol } \cancel{Ba(OH)_2}}{2 \text{ mol protons reacted}} = 85.6 \frac{g}{\text{mol protons reacted}}$$

$H_3PO_4 + NaOH \rightarrow NaH_2PO_4 + H_2O$

$f_{eq} = 1$ $f_{eq}=1$

$H_3PO_4 + 2NaOH \rightarrow Na_2HPO_4 + 2H_2O$

$f_{eq} = 1/2$ $f_{eq} = 1$

$H_3PO_4 + 3NaOH \rightarrow Na_3PO_4 + 3H_2O$

$f_{eq} = 1/3$ $f_{eq}= 1$

$Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O$

$f_{eq}= 1/3$ $f_{eq}= 1$

The equivalent factor for oxidizing and reducing agents into redox reactions is calculated as: feq = 1/Z, where Z is an amount of electrons gained or lost by one mole of a substance.

For example: $MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$

$f_{eq}= 1/2$ $f_{eq}= 1$

The law of equivalence: the masses of chemical substances which are involved into a reaction and masses of its products are directly proportional to their equivalent molar masses.

There's a transition between molar concentration of equivalent and titer:

$$T = \frac{n \cdot E}{1000} \quad (g/cm^3),$$

Where: E - solute's equivalent.

Oxidizer's (reducer's) equivalent is calculated using this formula:

$$E = \frac{M}{e},$$

Where: M - compound's molar mass;
e - attached by oxidizer or released by reducer electron number.