

ENZYMES driven **Electrochemical** reactions across Cell membranes **Electric potential** acidosis, oxidative stress

Anniversary Nernst's Nobel Prize in 1920:

Electrode is the **Metal immersed** into **solution**

Electrochemical reaction is movement of charged **ions** across cellular membranes on surface of **interface** between phases like lipid bilayer and water solutions both side.

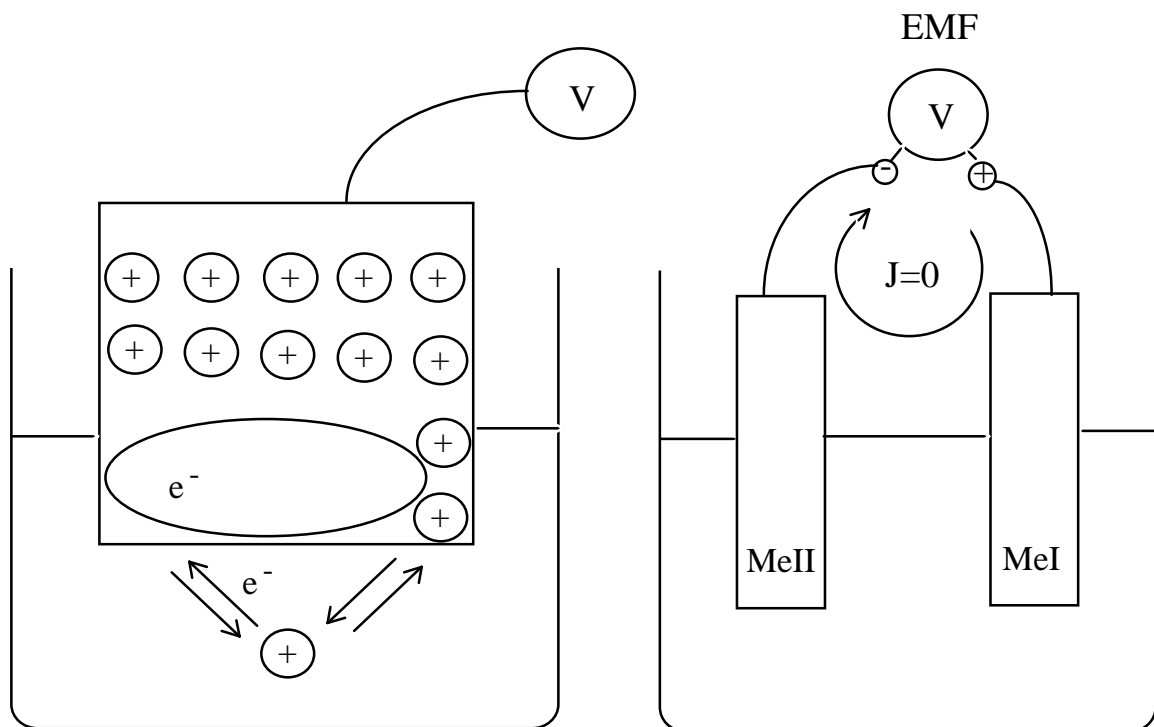
On the **electrode** immersed into solution interface start **Electrochemical reactions**.

Metallic Electrode is carrier of Reduction–Oxidation **electrochemical reactions** transferring through **interface** charged **ions** and **electrons** to make electric **potential**.
Are classified such Type **electrodes**:

Type I,
Type II and
Red-Ox electrode.

Electrochemical reactions driven charged ions gradient through **Membrane** channels form **Membrane potential** E_M .

Metal consist of electron e^- gas and crystalline metallic Me^+ ions lattice frame.

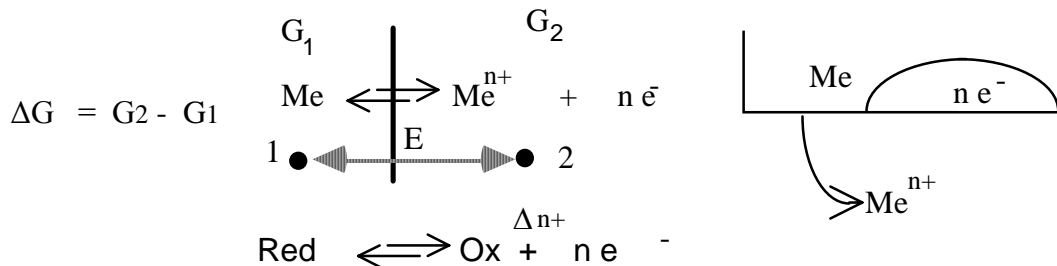


Voltmeter with minus "-" and plus "+" clamps measures difference of potentials or **EMF** (Electric Motion Force) between two **MeI (Indicator)** and **MeII (Standard)** on electric circuit linked electrodes :

$$EMF = E_I - E_{II} \quad ; \quad E_I = EMF + E_{II}$$

Indicator electrode having E_I – has reactivity with solution - electrode of investigations,
Standard Reference } electrode having E_{II} = constant– has no reactivity with environment into solution.

The obtaining of Nernst's equation for the Reduction - Oxidation equilibrium.



One 1 mol of the reduced form **Red** transfer from left side to right side in equilibrium to oxidised form **Ox** is the standard free energy change performed work W of one mol Me^{n+} transfer from point 1 into metal to point 2 into solution applied with negative value $-\Delta G^\circ$ at electric potential value E . One mole Me^{n+} charge is $q = nF$, and work calculated as $W = qE = nFE = -\Delta G^\circ = W_{work} = nFE = RT \ln K_{eq}$.

Red-Ox equilibrium constant $K_{eq} = \frac{[Ox] \cdot [e^-]^n}{[Red]}$ so

$$E = \frac{RT}{nF} \cdot \ln \left(\frac{[Ox] \cdot [e^-]^n}{[Red]} \right) = \frac{RT}{F} \cdot \ln([e^-]) + \frac{RT}{nF} \cdot \ln \left(\frac{[Ox]}{[Red]} \right) \quad \text{if } \frac{[Ox]}{[Red]} = 1 \text{ then}$$

$$E^\circ = \frac{RT}{F} \cdot \ln([e^-]) ; \ln([e^-]) = \frac{E^\circ F}{RT} = \text{const on metal surface unite and therefore } E^\circ = \text{const.}$$

Nernst's equation in natural (number $e=2,7$) logarithm \ln and decimal (number 10) logarithm \lg form $\ln(a) = \ln(10) \cdot \lg(a) = 2,3 \dots \cdot \lg(a)$:

$$E = E^\circ + \frac{RT}{nF} \cdot \ln \left(\frac{[Ox]}{[Red]} \right) ; \frac{\ln(10) \cdot R \cdot T}{F} = \frac{2.3 \cdot R \cdot T}{F} = 0,0591 \text{ V} ; E = E^\circ + \frac{0.0591}{n} \cdot \lg \left(\frac{[Ox]}{[Red]} \right)$$

Second (correct) approach to obtaining Nernst's expression.

When equilibrium is established reactant and product chemical potential sum becomes equal. As positive potential E charge on Left side is compensated by Red potential $\mu_{Red} + nE = \mu_{Ox} + n\mu_{e^-}$ positive charge on Right side Ox form compensates number electron negative charge in reaction products $n\mu_{e^-}$ but each chemical compound chemical potential is: $\mu = \Delta G^\circ + RT \ln(N_A)$, were N_A is substance A concentration in mol fraction units. ΔG° is given compound A standard potential. In chemical equilibrium given compounds have ΔG°_{Ox} , $\Delta G^\circ_{e^-}$ and ΔG°_{Red} .

$$\Delta G^\circ_{Red} + RT \ln(N_{Red}) + nE = \Delta G^\circ_{Ox} + RT \ln(N_{Ox}) + n\Delta G^\circ_{e^-} + RT \ln(N^n_{e^-})$$

Expressing E from equilibrium conditions of the chemical potentials μ :

$$E = \frac{\Delta G^\circ_{Ox} + n\Delta G^\circ_{e^-} - \Delta G^\circ_{Red}}{nF} + \frac{RT}{nF} \cdot \ln \left(\frac{N_{Ox} \cdot N^n_{e^-}}{N_{Red}} \right) \quad \text{pure compound mol fraction is } N_A = 1.$$

Free electrons in separate phase (so called electron gas) of metal is just pure compound $N_{e^-} = 1$ therefore

$$E = \frac{\Delta G^\circ_{Ox} + n\Delta G^\circ_{e^-} - \Delta G^\circ_{Red}}{nF} + \frac{RT}{nF} \cdot \ln \left(\frac{N_{Ox}}{N_{Red}} \right).$$

As seen standard potential E° expression is $E^\circ = \frac{\Delta G^\circ_{Ox} + n\Delta G^\circ_{e^-} - \Delta G^\circ_{Red}}{nF}$.

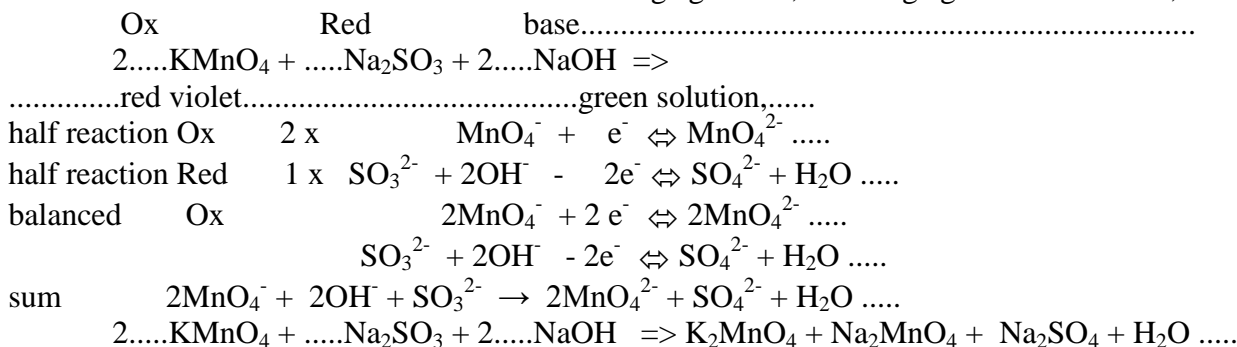
conversion to molar concentrations and decimal logarithm we obtain

Reducing form $\leftarrow Ox^{\Delta n+} + ne^-$ $E = E^\circ + \frac{0.0591}{n} \cdot \lg \left(\frac{[Ox]}{[Red]} \right)$

in reaction ne^- electron lose (left at metal) exert towards solution transfer Δn^+ positively charged ions $Ox^{\Delta n+}$. Electrons ne^- leaves at metal electron gas. Such Δn^+ positive charge entrance into solution as oxidised form $Ox^{\Delta n+}$ in products brings the chemical potential electrical part of negative electrons which is $n\mu_{electr} = -nFE$.

3rd. Pour into test tube 1 cm (1 mL) potassium permanganate KMnO_4 and 3 cm 3 mL sodium hydroxide NaOH solution add 1 drop sodium sulfite Na_2SO_3 solution; Confirm observations in Table Nr2 and over given initial compounds write:

Which is oxidising agent Ox, reducing agent Red and acid, water, base!



Described in table Nr2 observations and manganese oxidation step in products!

Balancing electrons in half reactions for oxidising (Ox) and reducing (Red) forms

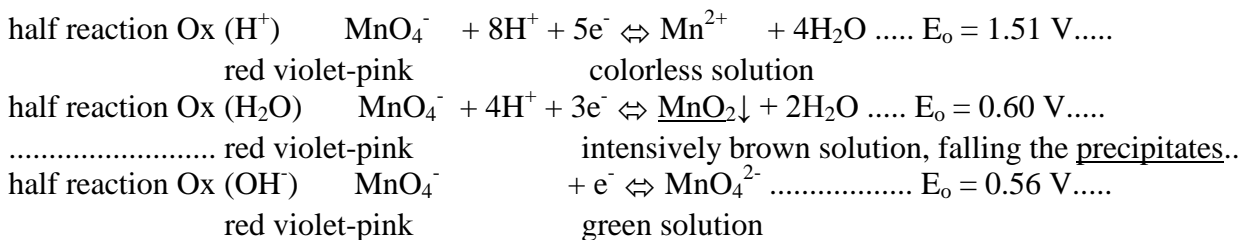
complete whole oxidation – reduction reaction in acidic 1), neutral 2) and basic 3) medium.

Compare power of oxidants and reductants which add and donate electrons in reaction.

Estimate power of oxidants and reductants using standard potential values E_0 !

When oxidised form is stronger in acid, neutral or basic medium?

Show influence according experiments 1), 2) and 3) !



Acidosis increases the:

- 1) hydrogen ion H^+ molar concentration $[\text{H}^+] = 10^{-\text{pH}}$ mols/Litre ;
- 2) consumed electrons number $+ 1e^-$, $+ 3e^-$, $+ 5e^-$;
- 3) standard potential E_0 in Volts $E_0 = 0.56 \text{ V}$, $E_0 = 0.60 \text{ V}$, $E_0 = 1.51 \text{ V}$.

Data collection

Colour change of oxidation – reduction reaction in acidic, neutral and basic environment.

Table Nr 2

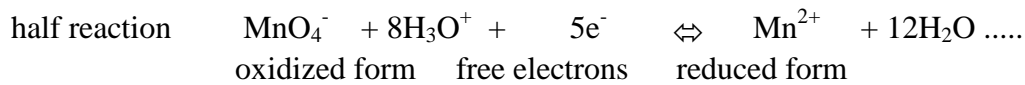
Nr. of test tube	Colour of mixture	Environment acidic, basic, neutral	Colour of mixture when + Na_2SO_3	Colour of product ion or substance in reaction	Oxidation number of manganese in product
1 st	$\text{KMnO}_4 + \text{H}_2\text{SO}_4$	acidic	colorless	Mn^{2+}	+2
2 nd	$\text{KMnO}_4 + \text{H}_2\text{O}$	neutral	brown sediment	$\text{MnO}_2\downarrow$	+4
3 rd	$\text{KMnO}_4 + \text{NaOH}$	basic	Green	MnO_4^{2-}	+6

Conclusions Acidosis palielina osidētāja spēju oksidēt – pievienot brīvos elektronus.

Nernst's potential expression practical studies for permanganate half reaction

General Nernst's expression for half reaction awarded 1920. Nobel prize:

a conversion between Ox and Red forms in redox half reaction can be in the most popular permanganate oxidized form in acidic medium with manganese:



$$E = E^\circ + \frac{0.0591}{5} \cdot \lg \left(\frac{[\text{MnO}_4^-][\text{H}^+]^8}{[\text{Mn}^{2+}] \cdot [\text{H}_2\text{O}]^{12}} \right); [\text{H}_2\text{O}] = 55,3 \text{ M} = \frac{996 \text{ g/L}}{18 \text{ g/mol}}$$

Water concentration $[\text{H}_2\text{O}]^{12}$ included in standard potential value E° as logarithm:

$$E_o = 1,51 \text{ V} = E^\circ + \frac{0.0591}{5} \cdot \lg \left(\frac{1}{[\text{H}_2\text{O}]^{12}} \right) = E^\circ + \frac{0.0591}{5} \cdot \lg \left(\frac{1}{55,3^{12}} \right) = E^\circ + \frac{0.0591 \cdot (-12)}{5} \cdot \lg(55,3)$$

$$E^\circ = E_o - 1,7427 \cdot 0,1418 = E_o - 0,2472; E^\circ = 1,51 \text{ V} + 0,2472 \text{ V} = 1,76 \text{ V} \text{ thermodynamic potential}$$



$$E = E_o + \frac{0.0591}{n} \cdot \lg \left(\frac{[\text{MnO}_4^-][\text{H}^+]^8}{[\text{Mn}^{2+}]} \right) = 1,51 \text{ V} + \frac{0.0591}{5} \cdot \lg \left(\frac{[\text{MnO}_4^-][\text{H}^+]^8}{[\text{Mn}^{2+}]} \right)$$

If acid amount increases as hydrogen ions concentration $[\text{H}^+]^8 = 1^8 = 1 = 10^0$ times 10 grater that's make hundred million greater value $10^8 = 100000000$ and increase initial potential for + 0.09456 Volts :

$$E = E_o + 0.01182 \cdot \lg(10^8) = 1.51 \text{ V} + 0.01182 \cdot 8 \text{ V} = 1.51 \text{ V} + \underline{0.09456 \text{ Volts}}$$

$$\text{If } [\text{H}^+]^8 = 1^8 = 1 = 10^0 \text{ then } E = E_o + 0.01182 \cdot \lg(10^0) = 1.51 + 0.01182 \cdot 0 = 1.51 \text{ Volts.}$$

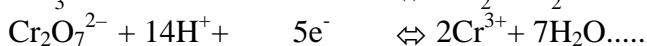
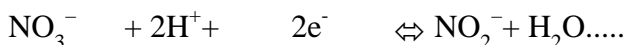
For electrochemistry powered acidosis oxidation power increase evaluated as potential increase as well of Latin term means **potencia**: might and force increases.

Potential increases: 1) $\Delta E = +0.0946 \text{ V}$ if acidosis increase hydrogen ion concentration $[\text{H}^+]$ 10 times;

2) about $\Delta E = +0.0118 \text{ V}$ if oxidized form concentration increase of $[\text{MnO}_4^-]$ 10 times;

3) about $\Delta E = +0.0118 \text{ V}$ if reduced form concentration decrease of $[\text{Mn}^{2+}]$ 10 times.

Give **Nernst's potential** expression and the analyze for selected half reactions!



- What component concentration (oxidizer [Ox], reducer [Red], acidity $[\text{H}^+]$ hydrogen cation) changes increase power of oxidiser as well as increase potential E as well increase power of reducer as well as decrease potential E?

- What are actual standard potential E_o values four given half reactions?

- Where in Nernst's potential equation included constant water concentration $[\text{H}_2\text{O}] = 55.3 \text{ M}$?

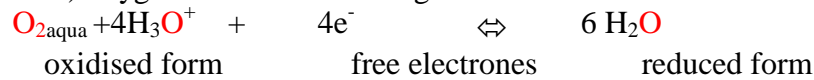
- How do You explain relative standard potential E_o values

for oxidizer reagents power in oxidation and reducer reagents power in reduction reaction?

Nernst's potential $O_{2(aqua)}/H_2O$ red-ox system physiologic mechanism of acidosis and oxidative stress

Note: Destructive hazard for life! Oxidative stress causes **non enzymatic** oxidation in multiple chain reactions and parallel products so destroying the organism!

In water medium (blood plasma) oxygen solution is strong oxidiser **1.229 V** for half reaction:



6th page: <http://aris.gusc.lv/BioThermodynamics/OxRedBiologicalW.pdf>

$$E = E_o + \frac{0.0591}{4} \lg([O_{2(aqua)}] \cdot [H^+]^4); E = 1.229 V + 0.01478 \cdot \lg([O_{2(aqua)}] \cdot [H^+]^4) \dots$$

Note: hydrogen ions are oxidised form $O_{2(aqua)} + 4H_3O^+$ components ;

reduced form 6 water molecules diminish thermodynamic potential from **1.383 V** to standard **1.229 V**:

$$E_o = E^\circ + \frac{0.0591}{4} \cdot \lg\left(\frac{1}{[H_2O]^6}\right) = ; [H_2O] = 55.3 M = \frac{996 \text{ g/L}}{18 \text{ g/mol}}$$

$$E_o = E^\circ + \frac{0.0591}{4} \cdot \lg\left(\frac{1}{[H_2O]^6}\right) = 1.388 + 0.01478 \cdot \lg\left(\frac{1}{[55.3]^6}\right) = 1.229 V; -0.01478 \cdot 10.456 = -0.15449 \dots$$

Water concentration diminish thermodynamic potential about **1.383-1.229 = -0.15449**..... V volts.

Constant water concentration $[H_2O]^6$ included in standard potential value E_o as sum of inverse constant with exponent six logarithm and of thermodynamic potential E° value.

If increases hydrogen ion concentration of $[H^+]$ 10 times total rise is $[H^+]^4 = 10000 = 10^4$ times.

If physiologic pH=7.36 hydrogen concentration is $[H^+]^4 = 10^{-7.36 \cdot 4} M = 10^{-29.44} M$ than increase 10^4 times rises value $(10 \cdot 10^{-7.36})^4 = 10^{-29.44+4} = 10^{-25.44}$ increases potential about + 0.2364 V:

$$E = E_o + 0.014775 \cdot \lg(10^4) = 1.23V + 0.014775 \cdot 4 V = 1.229 V + 0.2364 V = 1,465 \text{Volts.}$$

Electrochemical oxidation potential increases acidosis and oxygen concentration provoking potential

increase as Latin **potencia** is power, force which rises as oxidative stress with positive $\Delta E > 0$ increase:

1) about $\Delta E = +0.236$ V if increases hydrogen ion concentration $[H_3O^+]$ 10 times ;

$$E = E_o + 0.014775 \cdot \lg(5) = 1.23V + 0.014775 \cdot 0,699 V = 1.229 V + 0.0103 V = 1,24 \text{ Volti.}$$

Replacing air 20.95% oxygen to pure 100% $[O_{2(aqua)}]$ concentration increases 5 times.

It increases potential about: $+0.01478 \cdot \lg(4.773) = +0.01478 \cdot 0.6788 = +0.01$ Volts

2) $\Delta E > 0$ increase about $\Delta E = +0.01$ V if increases oxygen concentration 5 times ;

3) water concentration $[H_2O] = 55.3 M$ diminishing oxidative stress risk potential about

$$\Delta E = -0.154 \dots \dots \dots V \text{ from } E^\circ = 1,383 V \text{ to } E_o = 1,229 V.$$

Which concentration (oxidiser [Ox], reducer [Red], acid $[H^+]$ hydrogen cations) changes increase power of oxidation as well as increase potential E and opposite increase power of reduction as well as decrease potential E value?

- What is the standard potential E_o value in given half reaction?

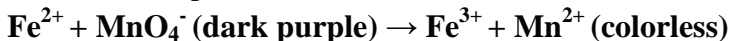
- Where included constant water concentration $[H_2O] = 55,3 M$?

- How do You explain relative standard potential E_o values

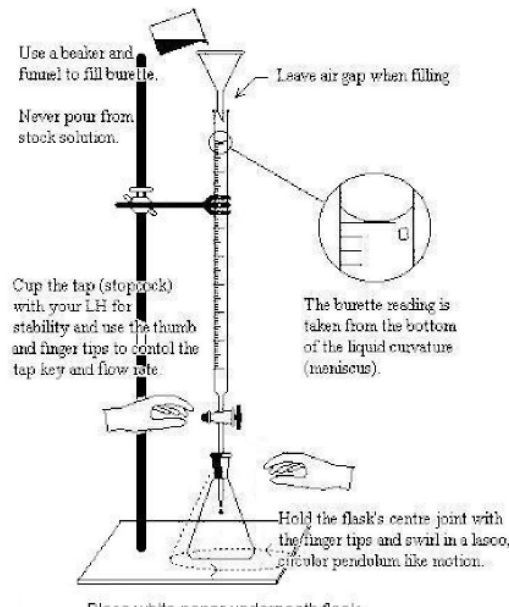
for oxidizer reagents power in oxidation and reducer reagents power in reduction reaction?

Part 2. Oxidation – reduction titration.

In this lab, a redox titration is performed. In this redox reaction, Fe^{2+} is converted into Fe^{3+} and MnO_4^- (dark purple) is converted into Mn^{2+} . The change in the oxidation state of manganese in MnO_4^- to Mn^{2+} causes a change in colour. When the reaction is complete and excess MnO_4^- is added to the reaction mixture, the solution turns pink and the titration is done.

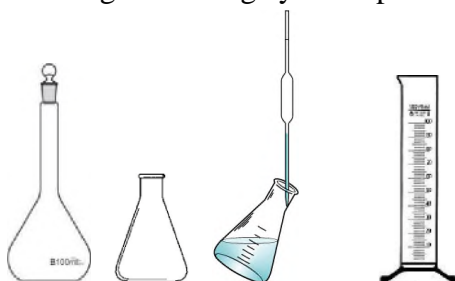


(unbalanced equation) Fe^{2+} from FeSO_4 solution and MnO_4^- - from 0.02 M KMnO_4 solution.

<p style="text-align: center;">Materials</p> <ul style="list-style-type: none"> • Burette and stand • Funnel • 3 Conical (Erlenmeyer) flasks • Waste beaker • Pipette 10 mL • Pipette filler • Measuring cylinder • 100 mL volumetric flask with FeSO_4 solution ($C_M=?$) • Potassium permanganate KMnO_4 solution ($C_M=0,02$ M) • Sulfuric acid H_2SO_4 ($C_M=3,0$ M) • Eye protection • Waste beaker 	
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Procedure

1. Dilute the given FeSO_4 sample solution in volumetric flask up to mark.
2. Using safety filler, transfer 10,0 mL of FeSO_4 into 50÷200 mL conical flask.
3. Using measuring cylinder pour 10,0 mL of sulfuric acid H_2SO_4 into conical flask.
4. Add enough 0.02 M KMnO_4 solution to fill the burette above the zero level. Open the stopper and allow a small amount of the solution to drain into a waste beaker (Enough to reach the volume to the zero mark of the burette). Record the initial volume of the KMnO_4 in your data table.
5. Titrate Fe^{2+} solution in conical flask with 0,02 M potassium permanganate KMnO_4 solution.



Volumetric - Conical flask; Measuring cylinder

(Erlenmeyer flask + pipette volume 10 mL)

6. After ~7 mL has been added, slow down the titration.
7. When the excess KMnO_4 is added to the reaction mixture, the solution turns pink from **1 drop** reaction complete.
8. Note the final reading point of volume on burette!
9. **Just on demand of lecturer!** Repeat the titration **several times** and calculate average volume

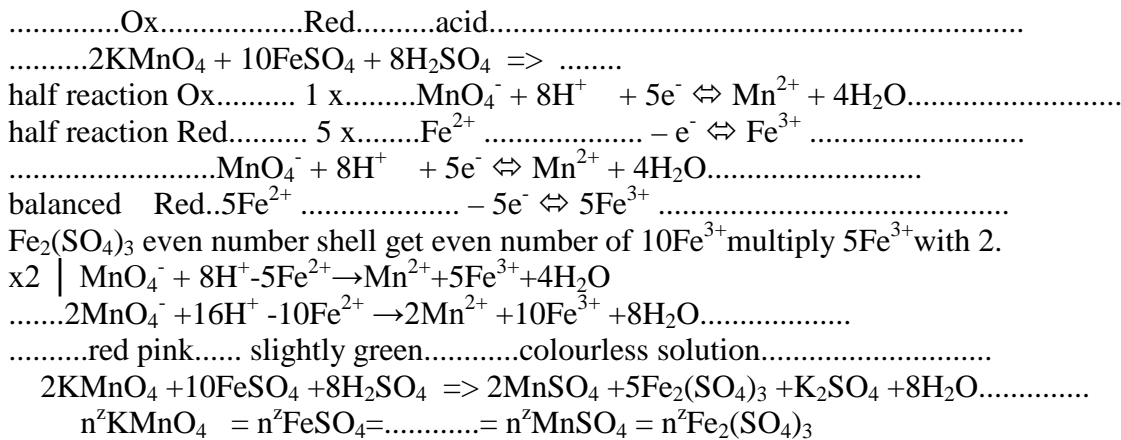
Data Table

Trial	Data Table Initial KMnO_4 volume, mL	Final KMnO_4 volume, mL	Volume of KMnO_4 needed to titrate Fe^{2+} (the difference between the final and initial volume), mL
1			$V_1=$
2			$V_2=$
3			$V_3=$
4			$V_4=$
5			$V_5=$

Average :

Permanganometry is a method of volume analysis, where **KMnO₄** solution serves as the titrant in acidic environment only because of 3 reasons :

- 1) In acidic environment permanganate add maximum 5 electrons;
- 2) In acidic environment the pink color of **MnO₄⁻** disappears **Mn²⁺** colorless .
- 3) Standard potential is maximal **E^o = +1.51 V**.



Initial compounds and products reaction in equivalent amounts. CALCULATION OF RESULTS.

Iron(II) ion Fe²⁺ in sulfate FeSO₄ loses one electron **1e⁻** : **Fe²⁺ - e⁻ ⇌ Fe³⁺** as one equivalent.

Potassium permanganate **KMnO₄** add five electrons **5e⁻** as five equivalents.

Compounds reaction in equivalent amounts. Added electrons number + 5e⁻ = -5 e⁻ is equal to removed electrons number. One mol **KMnO₄** is equivalent to five mols of FeSO₄ **5•n_{MnO4} = n_{Fe2+}** . In titration the used FeSO₄ mol numbers are five times greater as **KMnO₄** mol numbers. Therefore at equivalence point the compounds are expressed in equivalent amounts as **5•V_{MnO4} • C_{M_MnO4} = V_{Fe2+} • C_{M_Fe2+}**

Fe²⁺ solution molarity is calculated using V_{Fe2+} in expression:

$$C_{M_{Fe2+}} = \frac{5 \cdot V_{KMnO_4} \cdot C_{M_{KMnO_4}}}{V_{Fe^{2+}}} = \dots\dots\dots M$$

where the volume of permanganate is the one , read from the burette, the volume V_{Fe2+} is the one, that was taken for titration 10 mL (it depends on pipett) from the total volume 100 mL of Fe²⁺ solution).

The mass of reducing agent in all the volume of sample can then be calculated as:

$$m_{Fe} = M_{Fe2+} \cdot V_{Fe2+kopējais} \cdot C_{M_{Fe2+}} = \dots\dots\dots g$$

m_{Fe} is the equivalent mass of the reducing agent in the whole sample (in grams) ,

Statistic

- 1) molarity of FeSO₄ sample solution;
- 2) mass of Fe²⁺ ions in the total volume mL.
- 3) the standard deviation: **s_v** , where V_i are the individual measurements,

$$s_{\bar{v}} = \sqrt{\frac{\sum (V_i - \bar{V})^2}{n \cdot (n - 1)}} = \dots\dots\dots$$

\bar{V} is the average value of all the measurements,

n is the number of measurements, and with the security interval of your results $\Delta V = s_{\bar{v}} \cdot t_{\alpha,n}$

where **t_{α,n}** is Student's coefficient values 4.3, 3.2, and 2.8

for 3, 4 and 5 measurements corresponding.

Calculations

1. Calculate molar concentration of Fe²⁺ ions in 10 mL of solution (used for titration).
2. Calculate mass of Fe²⁺ in 100 mL of solution.