Water Harmony
Erasmus+

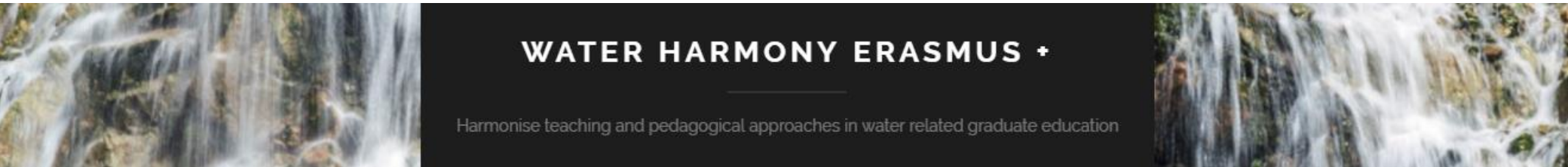
Co-funded by the
Erasmus+ Programme
of the European Union

WATER CHEMISTRY

Prof. Lech Smoczyński

University of Warmia and Mazury

Chemistry Department
Plac Łódzki 4, 10-727 Olsztyn, PL
tel. 89-5234801, fax. 89-5234801,
email: lechs@uwm.edu.pl



Co-funded by the
Erasmus+ Programme
of the European Union

CONTENT*

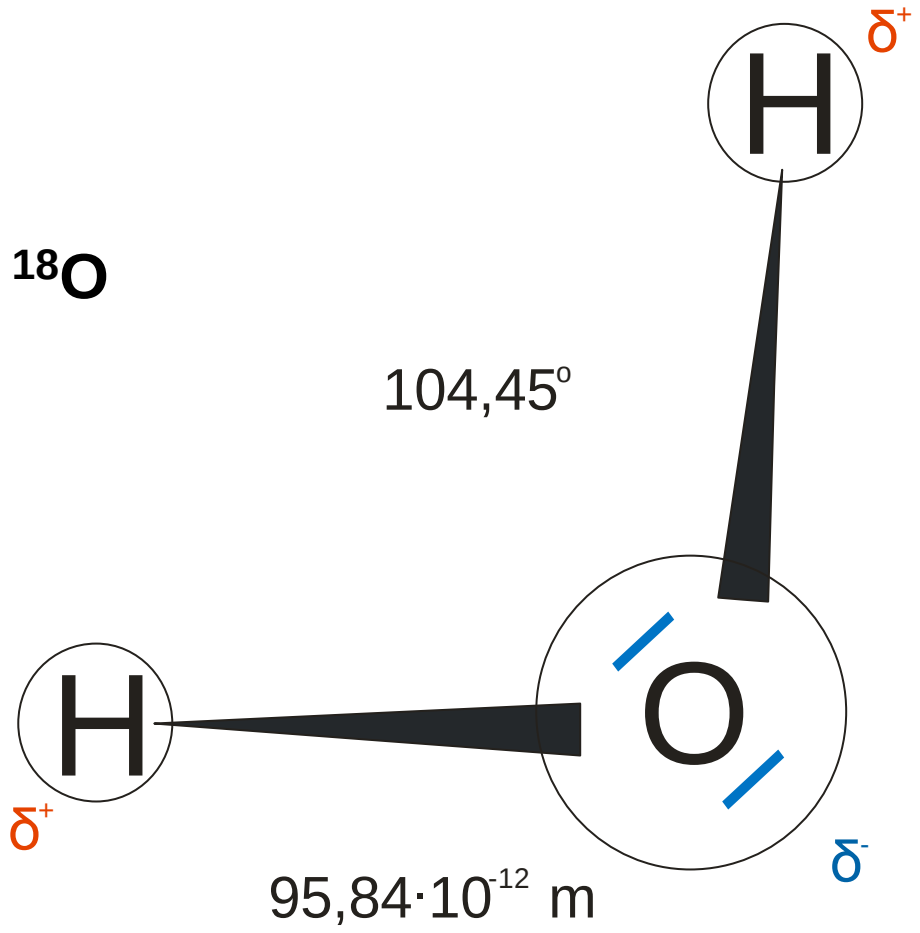
1. Water properties
2. Kinetics and mass balance
3. Acid, base, and salt pH.
4. Solubility
5. Basic coordination chemistry
6. EDTA and water hardness
6. Redox reactions

Co-funded by the
Erasmus+ Programme
of the European Union

oxygen (8)

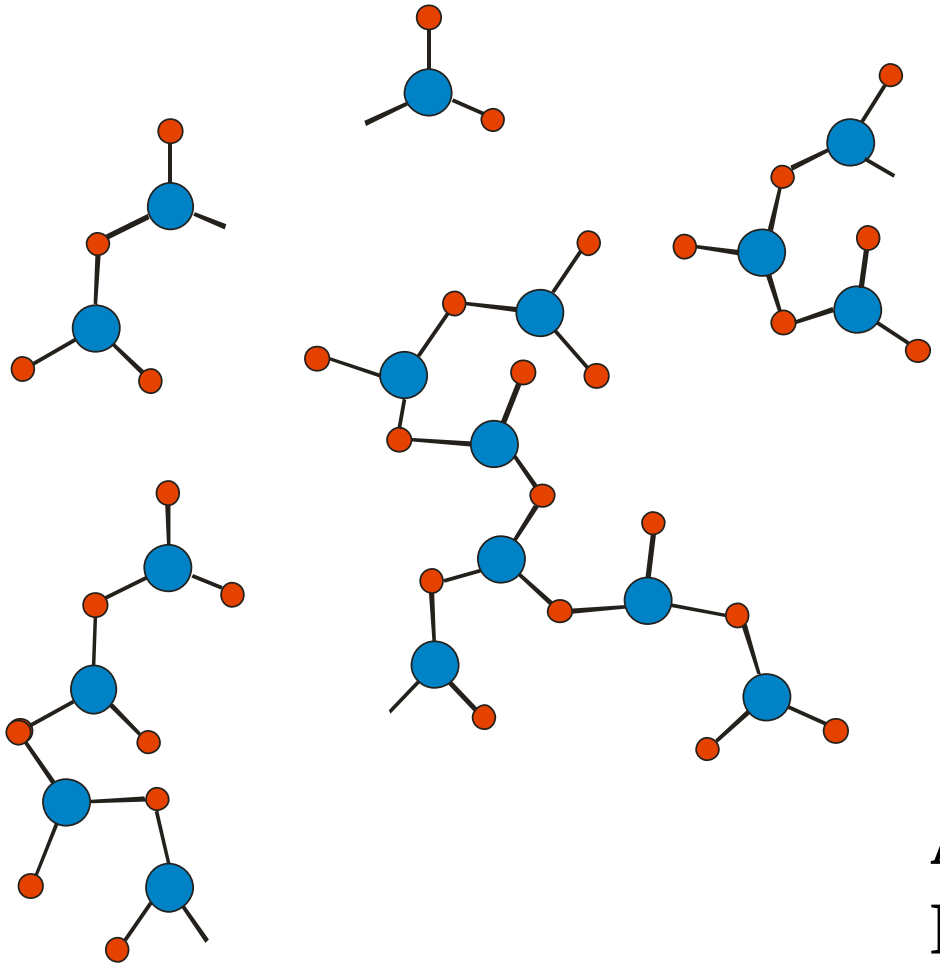
isotopes (^{15}O), ^{16}O, ^{17}O, ^{18}O

electrons: $1s^2$; $2s^2$ $2p^4$



water dipole structure*

Co-funded by the
Erasmus+ Programme
of the European Union



Association* of H_2O molecules

Co-funded by the
Erasmus+ Programme
of the European Union

Chemical Properties of Water (some selected)

1. electrolysis: $2H_2O \rightarrow 2H_2 + O_2$
2. reaction with Metal Oxides: $CaO + H_2O \rightarrow Ca(OH)_2$
3. reaction with Nonmetal Oxides*: $SO_2 + H_2O \rightarrow H_2SO_3$
4. reaction with Active Metals: $2Na + H_2O \rightarrow 2NaOH + H_2$
5. formation of Hydrates: $BaCl_2 + 2H_2O \leftrightarrow BaCl_2 \cdot 2H_2O$
6. hydrolysis**: a) $CO_3^{2-} + H_2O \leftrightarrow HCO_3^- + OH^-$
   b) $C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$
   c) $Al^{3+} + H_2O \leftrightarrow AlOH^{2+} + H^+$

Co-funded by the
Erasmus+ Programme
of the European Union

Water impurities

a. dissolved and suspended materials, gases

b. bacteria and other microorganisms

Purification and other treatment of Water

1) distillation (-a and -b) and...
   boiling at least for 15 min. (b. and...part of a.)
2) sedimentation (coagulation), filtration (sand)
   and disinfection (chlorine or aeration)
3) hard water and its softening
4) *med.* fluoridation of water against the dental caries

Co-funded by the
Erasmus+ Programme
of the European Union

Many nuclear reactors use water as a moderator, a substance that slows down neutrons.

Water pollutants:

a) oxygen-demanding wastes (both plants and animals)
b) disease causing agents (pathogenic microorganisms; cholera)
c) radioactive material (leakage from nuclear power plants)
d) heat = high temperature = thermal pollution (coolant; oxygen)
e) plants nutrients (excess of „trophic" N and P)
f) synthetic organic chemicals (detergents, pesticides, food additives)
g) inorganic chemicals and minerals (sulphates exchanging to H_2S)

Co-funded by the
Erasmus+ Programme
of the European Union

In the body, WATER acts as:

a) a component of cell and/or tissue fluid

b) a solvent

c) a transporting agent that facilitates the digestibility, decomposition and excretion of substances

---

if the water intake is greater than water output, a condition known as *endema* results.

if water intake is less than output *dehydration* occurs

Co-funded by the
Erasmus+ Programme
of the European Union

Chemical kinetics searches **the rate and mechanism of chemical reactions.**

The rate of the reaction use to be mathematically expressed as:

$$v = -\frac{dc}{dt} = \frac{dx}{dt}$$

where: c – the substrate concentracion*

x – the product concentration*

Co-funded by the
Erasmus+ Programme
of the European Union

In nature the most common are the first order reactions:

$$v = -\frac{dc}{dt} = k \cdot c$$

$$-\int_{c_0}^{c} \frac{dc}{c} = k \cdot \int_{0}^{t} dt$$

$$\ln c = \ln c_0 - k \cdot t$$

Integrating* the kinecs equation in the range of time (***0,t***) and concentration of the substrate (***c_0,c***) we have obtained a final formula expressing linear relationship between ***lnc*** and ***t***, where the direction coefficient is ***–k***.

An example of 1-st order reaction is a hydrolysis process like: **$CH_3COOC_2H_5 + HOH \rightarrow CH_3COOH + C_2H_5OH$**

Co-funded by the
Erasmus+ Programme
of the European Union

In practice the half of a first order reaction time $t_{1/2}$ use to be often used

$t_{1/2}$ is defined as a time needed to react of half

of the primary concentration of the product

If c at $t_{1/2}$ is $0.5 \cdot c_o$

then $\ln\frac{0.5c_o}{c_o} = -k \cdot t_{1/2}$ and $\ln(0.5) = -k \cdot t_{1/2}$

hence finally $\frac{0.693}{k} = t_{\frac{1}{2}}$

makes possible of many simple calculations like below:

Example:

The half of a first order reaction time $t_{1/2}$ is 371.04 hours. How many hours are needed to react for 75% of the primary concentraction of the product?

for the 1st order reaction: $t_{\frac{1}{2}} = \frac{0.693}{k}$ then $k = \frac{0.693}{t_{\frac{1}{2}}} = \frac{0.693}{15.46} = 1.08$ hours^{-1}

therefore $t = \frac{1}{k} \cdot 2.303 \cdot \lg \frac{c_o}{c} = \frac{1}{0.045} \cdot 2.303 \cdot \lg \frac{100}{25} = \mathbf{739.2\ hours}$

==========

and not as from simple relationship like:

50% - 371.04 hours

75% - x and x = ~~556.56 hours~~*

Co-funded by the
Erasmus+ Programme
of the European Union

Chemical rection rate increases with a **temperature** increasing.

The simplest aproach to this phenomenon gives **Van't Hoff formula**:

$$k_{T+\Delta T} = k_T \cdot a^{(\Delta T/10)}$$

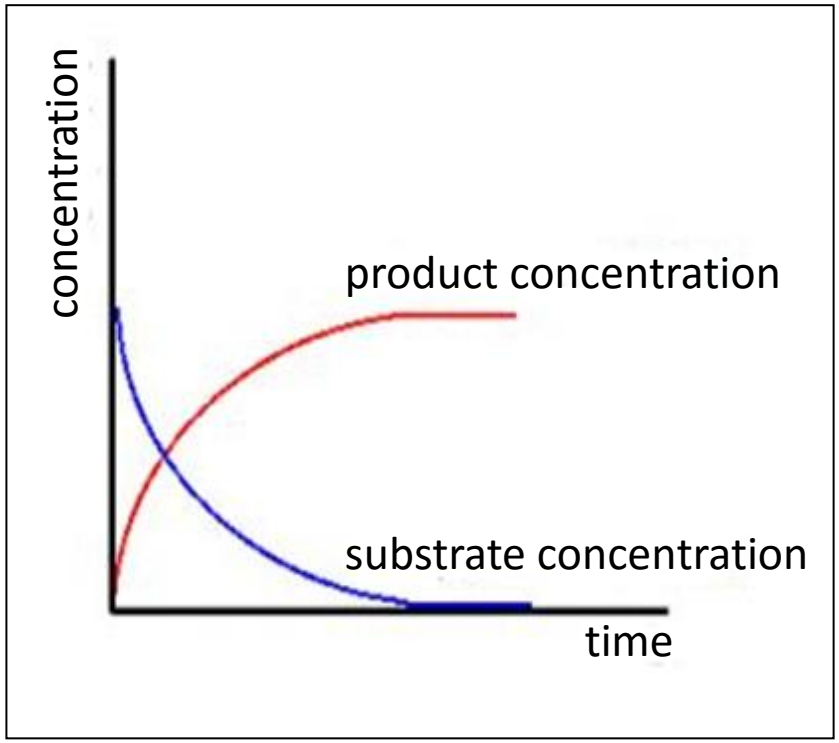
expressing that each increase of **10 degrees** in temperature speeds up

a reaction rate by **2 - 4 times**,

what means that any lab reaction carried at **200° C** can be finished after

1 minute instead of **72 minutes** in **20°C** for instance*

Co-funded by the
Erasmus+ Programme
of the European Union



Graph 2 shows changes of the substrate and product concentrations during so-called

reversible reaction. Such a situation was considered and described by two Norwegians

Gulberg and Waage in their genius* **law of mass action.**

Co-funded by the
Erasmus+ Programme
of the European Union

Law of mass action (Guldberg and Waage 1864)

chemical kinetics shows that: $\mathbf{V = -\Delta c/\Delta t = k \cdot c^p}$

where ***c*** means molar conc. of the reactant(s)

for such a reaction: $nA + mB \leftrightarrow xC + yD$

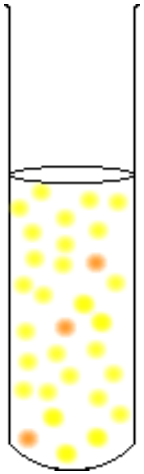
*$V_L = k_L \cdot [A]^n \cdot [B]^m$ (where n+m=p and […]=c) **$V_R = k_R \cdot [C]^x \cdot [D]^y$

at an equilibrium state **always*** $\mathbf{V_L = V_R}$ and finally at T=const

$$\frac{[C]^x \cdot [D]^y}{[A]^n \cdot [B]^m} = const = K$$

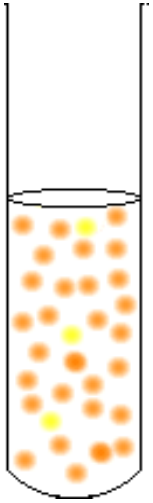
Co-funded by the
Erasmus+ Programme
of the European Union

$$2\ CrO_4^{2-}(aq) + 2\ H^+(aq) \leftrightarrow Cr_2O_7^{2-}(aq) + H_2O$$



$$const = \frac{K}{[H_2O]} = K' = \frac{[Cr_2O_7^{2-}]}{[CrO_4^{2-}]^2 \cdot [H^+]^2}$$

In a solution we call a **chromate solution***, there is also a little bit of dichromate, but the predominant color will be yellow.



In a solution we call a **dichromate solution***, there is also a little bit of chromate, but the predominant color will be orange.

Co-funded by the
Erasmus+ Programme
of the European Union

$$H_2O \leftrightarrow H^+ + OH^- \quad \text{or} \quad (2H_2O \leftrightarrow H_3O^+ + OH^-)^*$$

and according to **Guldberg and Waage Law**

$$K = \frac{[H^+]\cdot[OH^-]}{[H_2O]} = 1.8\cdot10^{-16}$$

Co-funded by the
Erasmus+ Programme
of the European Union

Let's calculate the concentration of **„water in water"** (expected to be constant)

if $dH_2O = 1\ g \cdot cm^{-3}$ then $1000\ cm^3$ of $H_2O \equiv 1000\ g$ of H_2O

(**a**)1000 cm^3 - (**b**)1M (solution*) - (**c**) (contain) 18g H_2O (1 mol of water)

(**d**)**1000 cm^3** - (**e**)**x** - (**f**) **1000g H_2O**

always: **a·b·f = d·e·c** , therefore here

$$x = \frac{1000cm^3 \cdot 1M \cdot 1000g}{1000cm^3 \cdot 18g} = \frac{10^2}{1.8}\text{M} = [H_2O]^{**}$$

Co-funded by the
Erasmus+ Programme
of the European Union

$$K = \frac{[H^+]\cdot[OH^-]}{[H_2O]} = 1.8\cdot10^{-16}$$

therefore $[H^+]\cdot[OH^-] = \frac{10^2}{1.8}\cdot1.8\cdot10^{-16}$

hence finally for any ***ionic product***:

$[H^+]\cdot[OH^-] = 10^{-14}$ **(at T=298K)**

Co-funded by the
Erasmus+ Programme
of the European Union

let $pH = -\lg[H^+]$ and $pOH = -\lg[OH^-]$

$[H^+][OH^-] = 10^{-14}$ then after $[\cdot(-\lg)]$ of a left and right side

finally we have a logharitmic version: **pH + pOH = 14**

Let's calculate ***pH of water.***

for water always $[H^+]=[OH^-]$; hence $[H^+]^2= 10^{-14}$

and then $[H^+]=10^{-7}$

therefore $pH = -\lg 10^{-7} = -(-7)\lg 10 =$ **7** ; **pOH=?***

Co-funded by the
Erasmus+ Programme
of the European Union

Example 1. Calculate *pH of 0.125 M HCl.*

notice, for strong acid like HCl

$$[HCl]^* = [Cl^-] = [H^+] = 0.125 = 1.25 \cdot 10^{-1}$$

$$pH = -\lg (1.25 \cdot 10^{-1}) = -(\lg 1.25 + \lg 10^{-1}) = 1 - \lg(1.25) =$$

$$= 1 - 0.097 = 0.903 \approx \mathbf{0.9}$$

Co-funded by the
Erasmus+ Programme
of the European Union

Example 2. Calculate $[OH^-]$ *in the solution of* $pH = 12.72$.

$$pOH = 14 - pH = 14 - 12.72 = 1.28$$

$$[OH^-] = 10^{-1.28} = 10^{-2} \cdot 10^{0.72} =$$

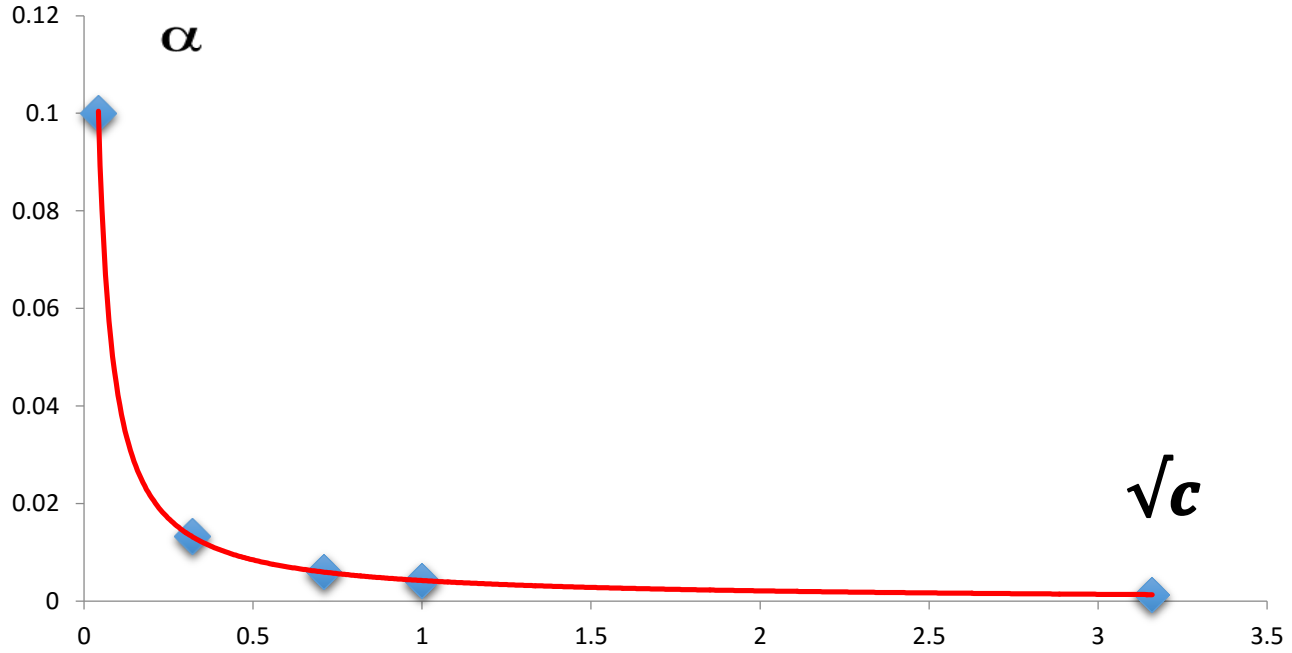
$$= 5.25 \cdot 10^{-2} = 0.0525^*$$

this is 0.0525 molar water solutions of OH^- anions

Co-funded by the
Erasmus+ Programme
of the European Union

Dissociation Degree

The dissociation degree is the fraction of original solute molecules that have dissociated. It is usually indicated by the Greek symbol **α**. *The values of α use to be not available (possible to calculate), because they depend on c*.*



Co-funded by the
Erasmus+ Programme
of the European Union

Example. $1.782 \cdot 10^{22}$ molecules of a weak acid HA were introduced to 1 dm^3 of the solution and pH = 3 was measured. Calculate **α** of the acid.

a) if pH = 3 then $[H^+] = 10^{-3} = 0.001$

b) 1 mol H^+ ≡ $6.023 \cdot 10^{23}$ molecules
10^{-3} mol ≡ x

---

and then x = $6.023 \cdot 10^{20}$ molecules/ions of H^+ ≡
≡ a number of the dissociated HA

c) therefore $\alpha = \frac{6.023 \cdot 10^{20}}{1.782 \cdot 10^{22}} = 3.38 \cdot 10^{-2} = 0.0338 \equiv 3.38\%$

Co-funded by the
Erasmus+ Programme
of the European Union

Ostwald's Law

$CH_3COOH \leftrightarrow CH_3COO^- + H^+$

$$K = \frac{[CH_3COO^-]\cdot[H^+]}{[CH_3COOH]}$$

if $[CH_3COO^-] = [H^+] = c_a \cdot \alpha$ and $[CH_3COOH] = c_a\,(1 - \alpha)$

then $K = \frac{c_a \cdot \alpha \cdot c_a \cdot \alpha}{c_a(1-\alpha)}$ and $K = \frac{c_\alpha \cdot \alpha^2}{(1-\alpha)}$

for $1 \gg \alpha$ $(1 - \alpha) \approx 1$ and $K = c_a \cdot \alpha^2$

exactly when $\alpha < 0{,}05$, or when $\frac{c}{K} > 400$

---

most cases $\alpha = \sqrt{\frac{K}{c_\alpha}}$ therefore „$\alpha = f(c_a)$" *

Co-funded by the
Erasmus+ Programme
of the European Union

Example. Calculate pH of 0.24 M NH_3. (K_b=1.78·10^{-5})

$$\frac{c}{K} = \frac{0.24}{1.78\cdot10^{-5}} = \frac{24\cdot10^{-2}}{1.78\cdot10^{-5}} = 13.48\cdot10^{3} = 13480$$

(FORTUNATELY!?)* 13480 > 400 therefore

$$K = c\cdot\alpha^2 \quad \text{and} \quad \alpha = \sqrt{\frac{K}{c}} = \sqrt{\frac{1.78\cdot10^{-5}}{0.24}}$$

$$\alpha = \sqrt{\frac{17.8\cdot10^{-6}}{0.24}} = \sqrt{(74.2\cdot10^{-6})} = 8.6\cdot10^{-3}$$

$$[OH^-] = \alpha\cdot c = 8.6\cdot10^{-3}\cdot0.24 = 2.07\cdot10^{-3}$$

pOH = -lg(2.07·10^{-3}) = 3-0.32 = 2.68, pH = 14 - 2.68 = **11.32****

Co-funded by the
Erasmus+ Programme
of the European Union

pH of salt

anionic hydrolysis runs: $CH_3COO^- + H_2O \leftrightarrow CH_3COOH + OH^-$

$$K=\frac{[CH_3COOH]\cdot[OH^-]}{[CH_3COO^-]\cdot[H_2O]} \quad \text{and} \quad K_h=\frac{[CH_3COOH]\cdot[OH^-]}{[CH_3COO^-]}$$

$$\frac{[CH_3COOH]\cdot[OH^-]}{[CH_3COO^-]}\cdot\frac{[H^+]}{[H^+]}=\frac{10^{-14}}{K_a}=\frac{[OH^-]^2}{c_s}$$

$$[OH^-]=\sqrt{\frac{c_s\cdot 10^{-14}}{K_a}}$$

Co-funded by the
Erasmus+ Programme
of the European Union

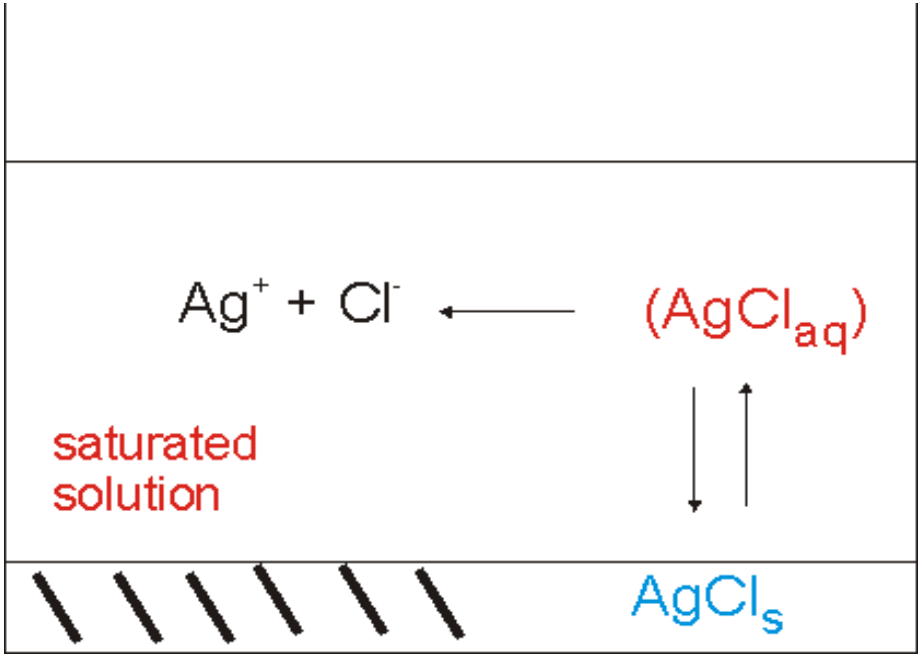
Example: Calculate pH of 0.1M **CH_3COOK**, if $K_a=1.8\cdot10^{-5}$.

$$[OH^-] = \sqrt{\frac{10^{-1} \cdot 10^{-14}}{1.8 \cdot 10^{-5}}} = 7.45 \cdot 10^{-6}$$

$$pOH = 6 - \lg 7.45 = 6 - 0.87 = 5.13$$

$$\text{therefore} \quad pH = 14 - 5.13 = \mathbf{8.87^*}$$

Co-funded by the
Erasmus+ Programme
of the European Union



precipitate

(Definition) **SOLUBILITY** is ***molarity*** (molar conc.) of the saturated solution*.

For poorly soluble substances (salts) use to be a small value and for **AgCl** the solubility is app. 0.00001 (10^{-5} mol·dm^{-3}) **(will be proved soon)**

Co-funded by the
Erasmus+ Programme
of the European Union

According to **Guldberg and Waage Law**

$$K = \frac{[Ag^+] \cdot [Cl^-]}{[AgCl_s]} \qquad where \quad [AgCl_s] = const,$$

$$and \;\; K \cdot [AgCl_s] = L$$

$$hence \qquad L = [Ag^+] \cdot [Cl^-]$$

Co-funded by the
Erasmus+ Programme
of the European Union

If d = 5.56 g·cm^{-3} of solid AgCl let's calculate a molar conc. of poorly soluble (solid) salt in a solid salt like AgCl (Ag-108; Cl-35.5).

(a) 1000 cm^3 – **(b)** 1 M („solution") – **(c)** 143.5g AgCl (always!)
(d) 1000 cm^3 - **(e)** x M - **(f)** 5560g AgCl (always!)

as at pH of water calculations remember that „always": **a·b·f=d·e·c ***

therefore, x = (1000·1·5560)/(1000·143.5) = const ≈ 39

Conclusion: **[$AgCl_s$] ≈** (always) **39** [mol·dm^{-3}] and is… **const!!**

Co-funded by the
Erasmus+ Programme
of the European Union

let consider the easiest case: $L=[Ag^+]\cdot[Cl^-]$

$$AgCl_s \leftrightarrow Ag^+_{aq} + Cl^-_{aq}$$

$$1mol = 1mol + 1mol$$

Let the solubility (remaining: means molar conc. of the saturated solution) is „**x**”, therefore

$$[AgCl_{aq}] = [Ag^+] = [Cl^-] = \mathbf{x}$$

and $L = \mathbf{x}\cdot\mathbf{x} = x^2$, hence $\mathbf{x} = \sqrt{L}$

$AgBr$; AgJ ; $AgCN$; $CaCO_3$; $AlPO_4$ etc.*

Co-funded by the
Erasmus+ Programme
of the European Union

$$Ag_2CrO_{4s} \leftrightarrow 2Ag^+ + CrO_4^{2-}$$

1mol = 2mol + 1 mol, and then

$$[Ag_2CrO_{4aq}] = [CrO_4^{2-}] = x \text{ , but } [Ag^+] = 2x$$

$$\text{therefore } L = [Ag^+]^2 \cdot [CrO_4^{2-}] = (2x)^2 \cdot x = 4x^3$$

$PbCl_2$

Ag_3PO_4: $L = (3x)^3 \cdot x = 27x^4$

$Ca_3(PO_4)_2$: $L = (3x)^3 \cdot (2x)^2 = 108x^5$

Fe_2S_3 : $L = (2x)^2 \cdot (3x)^3 = 108x^5$

Co-funded by the
Erasmus+ Programme
of the European Union

Some selected Solubility Constants *(Solubility products)*

$AgCl$	$1{,}1 \cdot 10^{-10}$
$CaCO_3$	$4{,}7 \cdot 10^{-9}$
CaC_2O_4	$2{,}1 \cdot 10^{-9}$
$AlPO_4$	$5{,}8 \cdot 10^{-19}$
Ag_2CrO_4	$2{,}4 \cdot 10^{-12}$
$PbCl_2$	$1{,}6 \cdot 10^{-5}$
$Fe(OH)_3$	$6{,}0 \cdot 10^{-38}$
Ag_3PO_4	$1{,}0 \cdot 10^{-21}$
$Ca_3(PO_4)_2$	$1{,}3 \cdot 10^{-32}$
Fe_2S_3	$1{,}0 \cdot 10^{-88}$

Co-funded by the
Erasmus+ Programme
of the European Union

Example 1: Will be any precipitate (like stone or „sand") formed when 50 cm^3 0.001M $C_2O_4^{2-}$ (oxalate) comes to the human kidney containing 100 cm^3 0.001M Ca^{2+} (L for CaC_2O_4 = **$2.1 \cdot 10^{-9}$**)?

In the kidney:

$[C_2O_4^{2-}] = 0.001 \cdot (50/150) = 3{,}33 \cdot 10^{-4}$

$[Ca^{2+}] = 0.001 \cdot (100/150) = 6.66 \cdot 10^{-4}$

$[C_2O_4^{2-}] \cdot [Ca^{2+}] = 3.33 \cdot 10^{-4} \cdot 6.66 \cdot 10^{-4} = 22.18 \cdot 10^{-8} = 2.2 \cdot 10^{-7}$

$2.2 \cdot 10^{-7}$ > (100-times) **$2.1 \cdot 10^{-9}$**

therefore "unfortunately" the **stone will be formed** in the kidney

Co-funded by the
Erasmus+ Programme
of the European Union

Example 2: Calculate the solubility of AgCl ($L=1\cdot10^{-10}$):
a) in water, b) in 0,1M HCl.

a) $L=[Ag^+]\cdot[Cl^-]=x^2$, hence **(„regular")** x = [AgCl] =
= **$[Ag^+] = [Cl^-]$** = $\sqrt{L} = \sqrt{10^{-10}} = 10^{-5}$ [mol·dm^{-3}]

b) in HCl solution **$[Ag^+] \neq [Cl^-]$**

$L = [Ag^+]\cdot[Cl^-]$, and hence **(„irregular")** x'= [AgCl] =
= **$[Ag^+] = L/[Cl^-]$** $=10^{-10}/10^{-1}= 10^{-9}$ [mol·dm^{-3}]

Finally: x in water (regular) **:** x' in 0,1M HCl („irregular") =

= $10^{-5}/10^{-9} = 10^4 = 10000$-fold better…..**in water!***

Co-funded by the
Erasmus+ Programme
of the European Union

Alfred Werner Nobel's experiment

heat up such a system gradually
and keep control of [Cl^-]

hexaamminecobalt(III) chloride

$$[Co(NH_3)_6]Cl_3 \rightarrow [Co(NH_3)_5H_2O]Cl_3 \rightarrow$$

$$\rightarrow ...[Co(H_2O)_6]Cl_3 \rightarrow$$

$$\rightarrow ...[Co(H_2O)_5Cl]Cl_2$$

Co-funded by the
Erasmus+ Programme
of the European Union

Important Assumptions are:

Na^{+} , K^{+} , Ca^{2+} , Mg^{2+} exist in water solution

but „Fe^{2+} , Fe^{3+} , Co^{3+} , Cu^{2+}„
do not exists (are not available in water solution)*

because the aquacomplexes like:

$Co(H_2O)_6^{3+}$, $Fe(H_2O)_6^{2+}$, $Fe(H_2O)_6^{3+}$

$Cu(H_2O)_4^{2+}$ exist and they

are the only available in water solution

Co-funded by the
Erasmus+ Programme
of the European Union

Configuration of electrons for coordination number 6

Atom (Element)	Ion (Cation)	Complex Ion
Cobalt Co (27)	Co^{3+}	$Co(NH_3)_6^{3+}$
		Krypton structure
$1s^2$	$1s^2$	$1s^2$
$2s^2\ 2p^6$	$2s^2\ 2p^6$	$2s^2\ 2p^6$
$3s^2\ 3p^6\ 3d^7$	$3s^2\ 3p^6\ 3d^6$	$3s^2\ 3p^6\ 3d^{10}$
$4s^2$	and	$4s^2\ 4p^6$
no octet here	no octet here either	

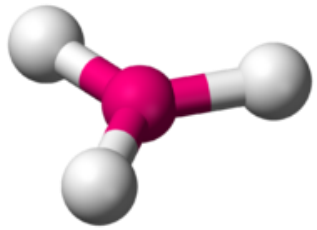
$\Delta = (d^{10} - d^6) + 4S^2 + 4p^6 = 4 + 8 = 12 = 6$ pairs of electrons = **6** NH_3

Co-funded by the
Erasmus+ Programme
of the European Union

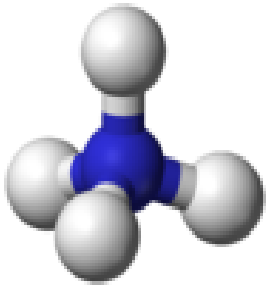
Coordination number	Angle	Shape
2	180°	linear

Ligand-----Metal Ion-----Ligand

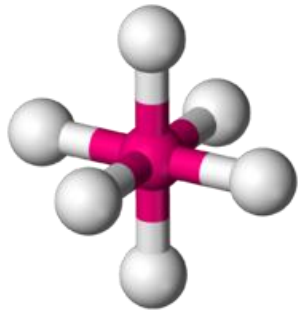
Coordination number	Angle	Shape
3	120°	trigonal planar



Coordination number	Angle	Shape
4	109° 28′	tetrahedron



Coordination number	Angle	Shape
6	90°	Octahedron



Co-funded by the
Erasmus+ Programme
of the European Union

Coordination Number

a) 4 : Cu, Zn, Ag, Cd, Sn, Hg, Pb

b) 6: very easy coordinating and forming the lasting complexes both simples and chelates

Ligands

a) containing oxygen (less selective): H_2O, OH^-, O^{2-}, CO_3^{2-}, SO_4^{2-}, $RCOO^-$, NO^- etc.

b) containing N and/or S (more selective and more common): NH_3, NH_2^-, H_2S, S^{2-}, $S_2O_3^{2-}$, SCN^-, RS^-

Co-funded by the
Erasmus+ Programme
of the European Union

Typical complexes (also aqua complexes):

$[Cu(H_2O)_4]^{2+}$; $[Cu(NH_3)_4]^{2+}$; $[Zn(NH_3)_4]^{2+}$; $[Ag(NH_3)_2]^{+}$;

$[Fe(H_2O)_6]^{2+}$; $[Fe(CN)_6]^{4-}$; $[Fe(CN)_6]^{3-}$; $[Ag(S_2O_3)_2]^{3-}$

$[Al(OH)_4(H_2O)_2]^{-}$; $[Pb(OH)_3]^{-}$

Co-funded by the
Erasmus+ Programme
of the European Union

Labile complexes (like aqua complex)
use to exchange easy to **stable** complexes:

$$[Ni(H_2O)_4]^{2+} + 4CN^- \rightarrow [Ni(CN)_4]^{2-} + 4H_2O$$

Some selected complexing reactions

$$\mathbf{Au + 4HCl + 3HNO_3 \rightarrow HAuCl_4 + 3NO_2 + 3H_2O}$$

$$\mathbf{[CuCl_2(H_2O)_2] + Cl^- \rightarrow [CuCl_3(H_2O)]^- + H_2O}$$

$$\mathbf{Zn(OH)_2 + 2OH^- \rightarrow [Zn(OH)_4]^{2-}}$$

$$\mathbf{HgS + S^{2-} \rightarrow [HgS_2]^{2-} \; ; \; As_2S_3 + 3\,S^{2-} \rightarrow 2[AsS_3]^{3-}}$$

Co-funded by the
Erasmus+ Programme
of the European Union

Significance of complexing in nature

1. Transportation of cations (Fe^{3+} for instance) from soil to a plant by so-called chelates.

2. Carrying Ni^{2+}, $Co^{2+,}$ czy Ca^{2+} in the organisms by amino acids as ligands.

3. Dissolving of some poorly soluble precipitates:

   a) $Cu(OH)_2\downarrow + 4NH_3 \cdot H_2O \rightarrow [Cu(NH_3)_4](OH)_2$

   b) vitamin C as a ligand protects silting (clogging) of the organism (human body for instance) and also is able to transform some precipitates into „assimilable" forms.

Co-funded by the
Erasmus+ Programme
of the European Union

4. Bioligands improve assimilability of some fertilizers as $Ca_3(PO_4)_2$ for instance. Chelates (so-called multi-pincers chelates particularly) like chlorophyll, hemoglobin or vitamin C make the system acid and then are increasing a solubility of many precipitates.

5. Nature prefers labile systems. Cis-isomers use to complex strongly, that's why in nature trans-maleic acid is common, opposite to cis-maleic one.

6. Chelatotheraphy is a significant medical branch:

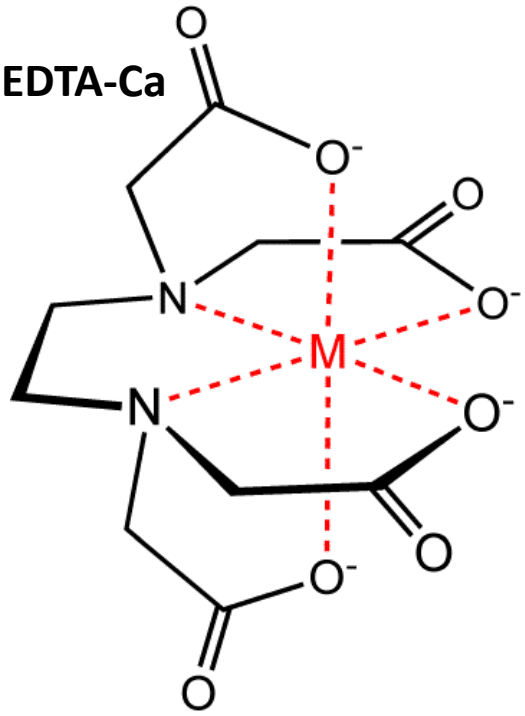
   a) cis-platinium inhibits a development of some cancer tissue

   b) excess of Cu^{2+} in food, so-called Wilsona disease use to be treated with a commonly known bioligand EDTA,

   c) BAL (2,3-ditio-1-propanol) is an antidote at poisoning with haevy metals

Co-funded by the
Erasmus+ Programme
of the European Union

multi-pincers chelate

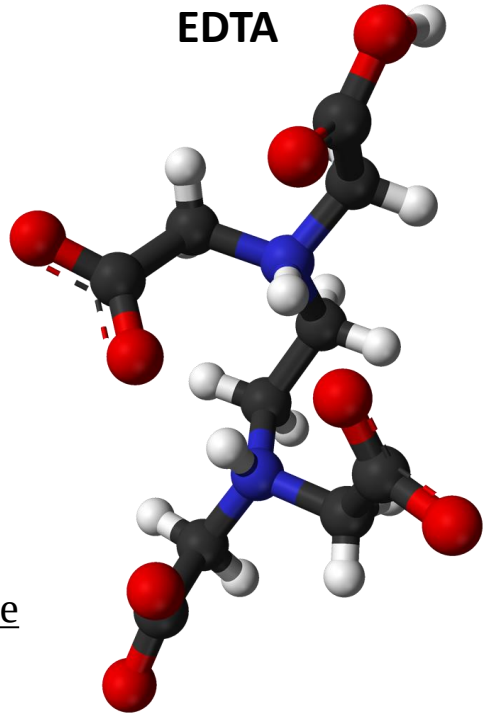


EDTA complexing reactions*:

$1EDTA + 1Na^{+} = (EDTA\text{-}Na)^{+}$

$1EDTA + 1Ca^{2+} = (ADTA\text{-}Ca)^{2+}$

$1EDTA + 1Fe^{3+} = (EDTA\text{-}Fe)^{3+}$



Any chemical reaction as neutralization for instance

$H_2SO_4 + 2NaOH = Na_2SO_4 + H_2O$

$Na_2CO_3 + 2HNO_3 = 2NaNO_3 + H_2O + CO_2$

By Ben Mills , https://commons.wikimedia.org/w/index.php?curid=3557118

Co-funded by the
Erasmus+ Programme
of the European Union

hardness forming: (rock) $CaCO_3\downarrow$ + (rain) $CO_2 + H_2O \rightarrow Ca(HCO_3)_{2(aq)}$

Carbonate Hardness (T_c)* + Permanent Hardness (T_p) = Total Hardness (T_t)

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3\downarrow + CO_2\uparrow + H_2O$$

$$Mg^{2+} + 2HCO_3^- \rightarrow Mg(OH)_2\downarrow + 2CO_2\uparrow$$

1°N is an equivalent of 10 mg CaO** per 1L of water

Co-funded by the
Erasmus+ Programme
of the European Union

Water hardness removal

$Ca^{2+} + CO_3^{2-}$ {from Na_2CO_3} $\rightleftharpoons$ $CaCO_3\downarrow$

$Mg^{2+} + 2OH^-$ {from $\underline{Ca(OH)_2}$} $\rightleftharpoons$ $Mg(OH)_2\downarrow$

Na - Kt - Na + Ca^{2+} {from $Ca(HCO_3)_2$}* $\rightleftharpoons$ ($\rightarrow$) Kt = Ca + $2Na^+$

Na - Kt - Na + Mg^{2+} {from $MgCl_2$} $\rightleftharpoons$ ($\rightarrow$) Kt = Mg + $2Na^+$

Kt = Ca + $2Na^+$ $\rightleftharpoons$ ($\rightarrow$) Na - Kt - Na + Ca^{2+} regeneration

Kt = Mg + $2Na^+$ $\rightleftharpoons$ ($\rightarrow$) Na - Kt - Na + Mg^{2+} regeneration

Co-funded by the
Erasmus+ Programme
of the European Union

Analytical Example: The water hardness is **18°N**. How many cm^3 of 0.02M **EDTA** is needed for complexing all Ca^{2+} and Mg^{2+} cations being responsible for that hardness in 1 dm^3 of that water. [Ca-40]

1°N – 10 mg of CaO in 1dm^3 (as a definition says)
18°N - x and x = 180 mg CaO per 1 dm^3

---

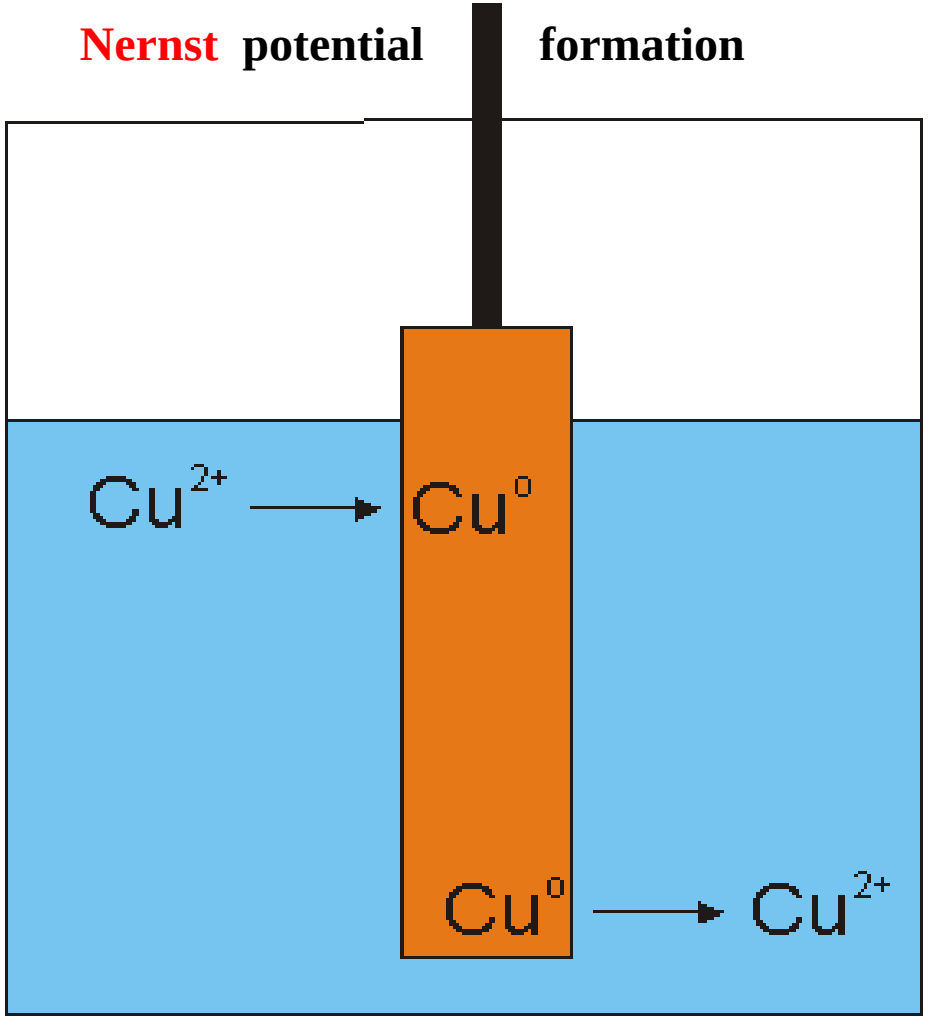
1 mol of EDTA ≡ (complexing) ≡ 1 mol Ca^{2+} ≡ 1 mol CaO

1000 cm^3 - 1 M EDTA - 56 000 mg CaO
y - 0.02 M - 180 mg CaO

$$y = \frac{1000 \cdot 1 \cdot 180}{0.02 \cdot 56\,000} = 161\ cm^3$$

Co-funded by the
Erasmus+ Programme
of the European Union

Nernst potential formation



$$\mathbf{E} = E_o' + \frac{R \cdot T}{z \cdot F} \ln K \,, \quad \text{but} \quad K = \frac{[Cu^{2+}]}{[Cu]} \,,$$

$$\text{or exactly} \quad * K = \frac{a_{Cu^{2+}}}{a_{Cu}}$$

so in standard conditions for **Cu ****

and at T = 298 K (Europe):

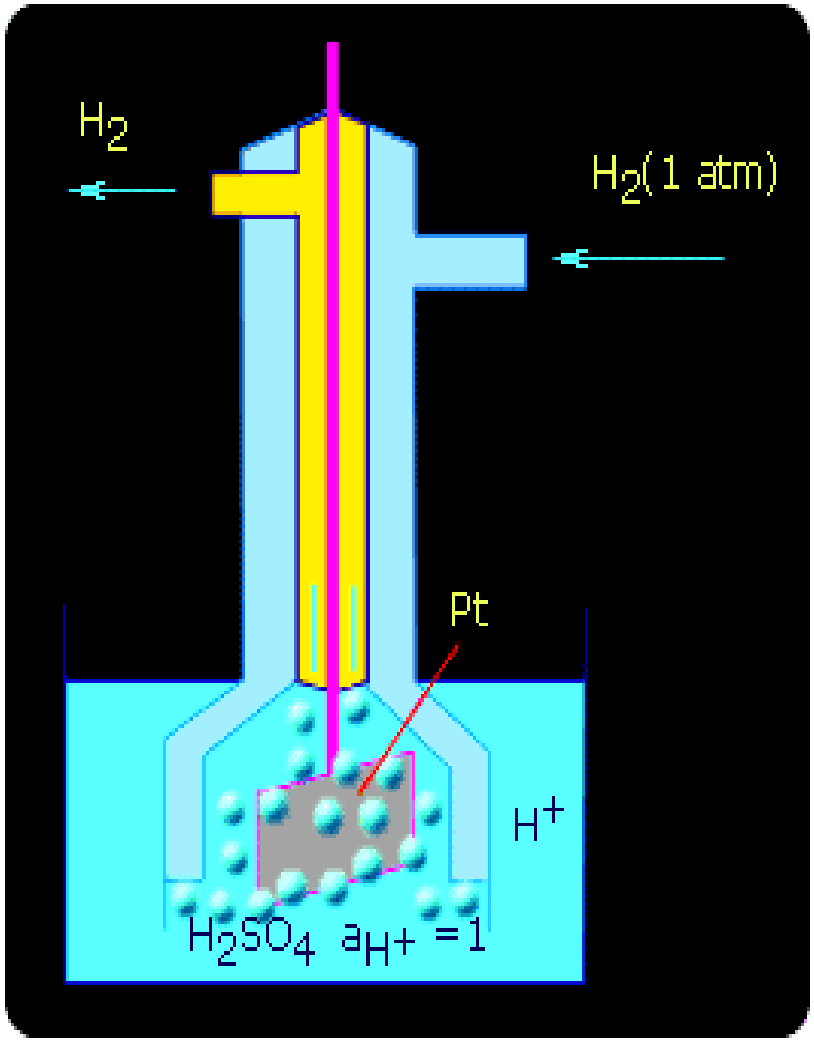
$$\frac{R \cdot T}{z \cdot F} \ln K = 0{,}0295 \cdot \log K$$

therefore $\mathbf{E = E_o + 0{,}0295 \cdot \log a_{Cu^{2+}}}$

where $E_o = E_o' - \log a_{Cu}$

notice: $\mathbf{E = E_o}$ **when** $\mathbf{a_{Cu^{2+}} = 1}$ **(!) *****

Co-funded by the
Erasmus+ Programme
of the European Union



For such an electrode

a standard potential is **0***

Co-funded by the
Erasmus+ Programme
of the European Union

$Au^{3+} + 2e = Au^{+}$	1,29
$Cl_2 + 2e = 2Cl^{-}$	1,385
$Cr_2O_7^{2-} + 14H^{+} + 6e = 2Cr^{3+} + 7H_2O$	1,36
$BrO_3^{-} + 6H^{+} + 6e = Br^{-} + 3H_2O$	1,44
$ClO_3^{-} + 6H^{+} + 6e = Cl^{-} + 3H_2O$	1,45
$PbO_2 + 4H^{+} + 2e = Pb^{2+} + 3H_2O$	1,456
$HClO + H^{+} + 2e = Cl^{-} + H_2O$	1,49
$MnO_4^{-} + 8H^{+} + 5e = Mn^{2+} + 4H_2O$	1,52
$Ce^{4+} + e = Ce^{3+}$	1,61
$Pb^{4+} + 2e = Pb^{2+}$	1,69
$H_2O_2 + 2H^{+} + 2e = 2H_2O$	1,77
$Co^{3+} + e = Co^{2+}$	1,84
$O_3 + 2H^{+} + 2e = H_2O + O_2$	2,07
$F_2 + 2e = 2F^{-}$	2,85

Co-funded by the
Erasmus+ Programme
of the European Union

Mn redox reactions*

$$MnO_4^- + 8H+ 5e = Mn^{2+} + 4H_2O \quad (\text{acid } H_2SO_4)$$

Examples

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 = 2MnSO_4 + 10CO_2 + K_2SO_4 + 8H_2O$$

$$Mn^{7+} + \underline{\mathbf{5e}} = Mn^{2+} \qquad 2$$

$$2C^{3+} - \underline{\mathbf{2e}} = 2C^{4+} \qquad 5$$

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

$$2MnO_4^- + 5H_2O_2 + 6H^+ = 2Mn^{2+} + 5O_2 + 8H_2O$$

Co-funded by the
Erasmus+ Programme
of the European Union

Example. 1,003 g **H_2O_2 solution was diluted to** 250 cm^3. Titrating 25 cm^3 of the diluted solution **17,4 cm^3 0,02 m $KMnO_4$** was used*. Calculate % concentration of the primary **H_2O_2 solution**.

$$2MnO_4^- + 5H_2O_2 + 6H^+ = 2Mn^{2+} + 5O_2 + 8H_2O$$

$2 \cdot 1000\ cm^3$ – 1 M - $5 \cdot 34$ g H_2O_2

17,85 cm^3 – 0,02 M - x and then x = 0,0303 g H_2O_2 **(in 25 cm^3)**

1,003 g of the solution - $10 \cdot 0{,}0303$ g H_2O_2 **(in 250 cm^3)**

therefore 100 g of the solution - **y**

---

then y = 30,2 % H_2O_2

Co-funded by the
Erasmus+ Programme
of the European Union

Redox reactions running in wastewater (another lecture)*

Aerobic conditions

organic matter + **O_2**+ **aerobic bacteria** → $CO_2 + H_2O$

Anoxic conditions

organic matter + **NO_3^-** + **denitrification bacteria** → $CO_2 + N_2$

Anaerobic conditions

organic matter + **fermentation bacteria** → CO_2 + **SO_4^{2-}** + acetic anions + hydrogen + organic acids + alcohols + **sulphate reducing bacteria** → $CO_2 + H_2S$**