Analytical Chemistry

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1. Quantities and Units

SI Base Units

Quantity	Formula Sym.	Base Unit	Symbol	Definition
Distance	l, s, r	Meter	m	One meter is equivalent to 1650763,73 x of the vacuum-wavelength of the radiation, which is emitted during the transition from the $2p^{10}$ to the $5d^5$ state of the element ^{86}Kr.
Time	t	Second	s	One second is defined as the duration of 9192631770 periods of the radiation, which corresponds to the transition between the two hyper-fine structure levels of the ground state of the element ^{133}Cs.
Mass	m	Kilogram	kg	One kilogram is the mass of the international kilogram-prototype, that is kept at the BIPM in Sèvres, France.
Electrical current	I	Ampere	A	One ampere is defined as the constant current, that will produce an attractive force of 2×10^{-7} newton per meter of length between two straight, parallel conductors of infinite length and negligible circular cross section placed one meter apart in a vacuum.
Temperature	T	Kelvin	K	The kelvin is defined as the fraction 1/273 of the thermodynamic temperature of the triple point of water.
Luminous intensity	I_K	Candela	cd	One candela is the luminous intensity a black body of the area 1/600000 m^2 emits perpendicular to its surface at the solidification temperature of platinum under the pressure of 101325 N/m^2.
Quantity of substance	n	Mol	mol	One mol of a substance contains as many particles as there are carbon atoms in exactly 0.012 kg of ^{12}C. The number of particles in one mol is given by the Avogadro constant: $N_A = 6.022045 \cdot 10^{23}$.

1. Quantities and Units

Derived SI-Base Units, SI-Prefixes and Some Fundamental Natural Constants

Quantity	Formula Symbol	SI-Unit	Derived Unit
Force	F	kg m s^{-2}	N
Energy	E	N m (kg m^2 s^{-2})	J
Power	P	J s^{-1} (kg m^2 s^{-3})	W
Pressure	p	N m^{-2}	Pa
Frequency	ν	s^{-1}	Hz
Electrical charge	Q	A s	C
Electrical potential	U	kg m^2 A^{-1} s^{-3}	V
Electrical resistance	R	kg m^2 A^{-2} s^{-3}	Ω
Molar Mass	M	g mol^{-1}	Da
Concentration	c	mol l^{-1}	-

Natural Constant	Symbol	Figure
Avogadro constant	N_A	$6.022045 \cdot 10^{23}$ particles·mol^{-1}
Bohr's radius	a_0	$5.2917706 \cdot 10^{-11}$ m
Bohr's magneton	μ_B	$9.274096 \cdot 10^{-24}$ JT^{-1}
Boltzmann constant	k	$1.380662 \cdot 10^{-23}$ J·K^{-1}
Elementary charge	e	$1.6021892 \cdot 10^{-19}$ C
Standard acceleration	g	9.80665 m·s^{-2}
Faraday constant	F	96485 C·mol^{-1}
Gravitational constant	G	$6.6729 \cdot 10^{11} m^3 kg^{-1} s^{-2}$
Speed of light in vacuum	c	$2.99792458 \cdot 10^{8}$ m·s^{-1}
Molar volume	V_m	22.414 l·mol^{-1}
Permittivity of the vacuum	ε_0	$8.854 \cdot 10^{-12}$ $AsV^{-1}m^{-1}$
Permeability of the vacuum	μ_0	$4\pi \cdot 10^{-7}$ $VsA^{-1}m^{-1}$
Planck's quantum of action	h	$6.626176 \cdot 10^{-34}$ J·s
Universal gas constant	R	8.31441 J·mol^{-1}·K^{-1}

Pow. of ten	Prefix	Abbreviation
10^{-24}	Yocto	y
10^{-21}	Zepto	z
10^{-18}	Atto	a
10^{-15}	Femto	f
10^{-12}	Pico	p
10^{-9}	Nano	n
10^{-6}	Micro	μ
10^{-3}	Milli	m
10^{-2}	Centi	c
10^{-1}	Deci	d
10^{1}	Deca	da
10^{2}	Hecto	h
10^{3}	Kilo	k
10^{6}	Mega	M
10^{9}	Giga	G
10^{12}	Tera	T
10^{15}	Peta	P
10^{18}	Exa	E
10^{21}	Zetta	Z
10^{24}	Yotta	Y

1. Quantities and Units

Designation of Quantities for Mixed Phases in Accordance to DIN 1310

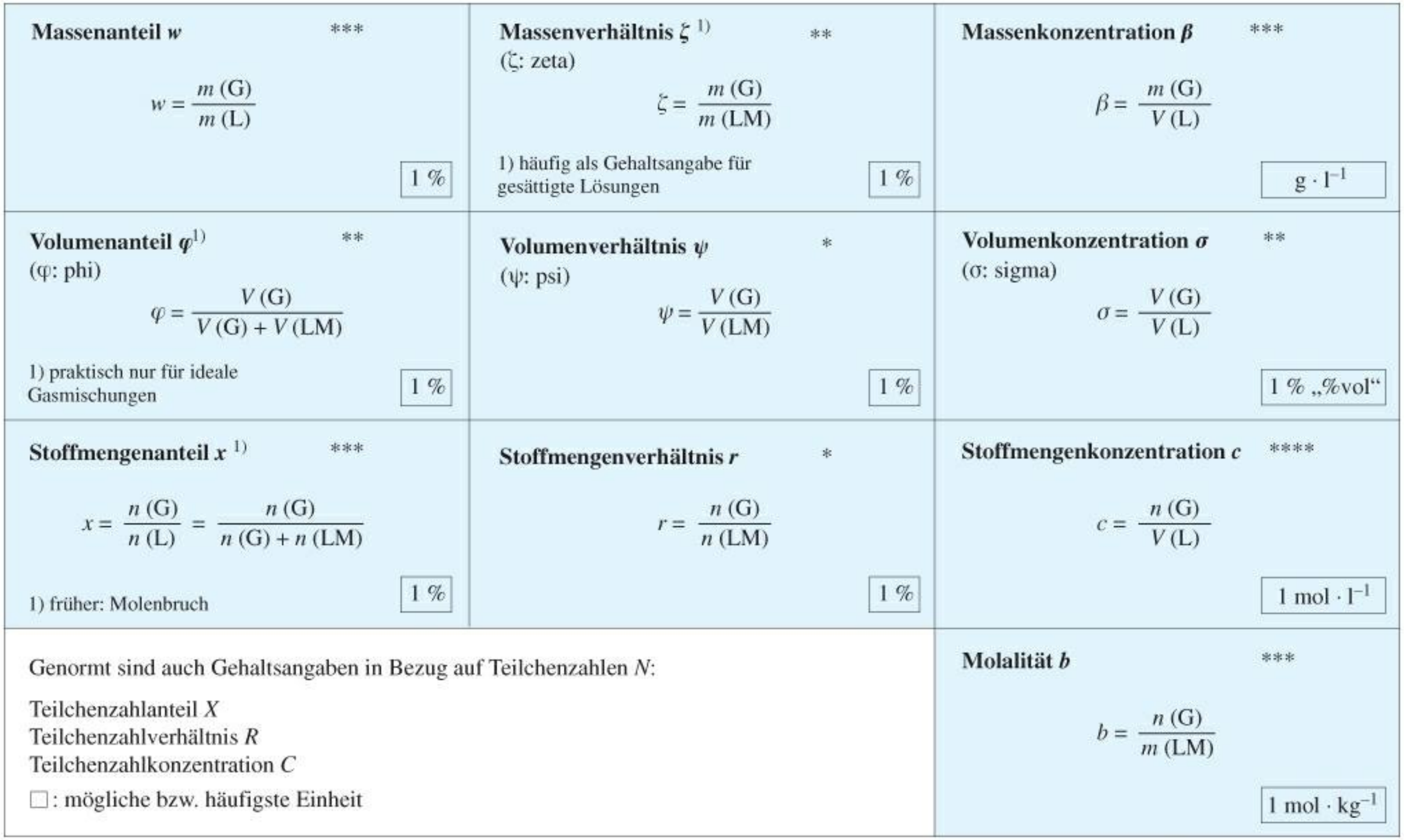
G = Dissolved substance

L = Solution

LM = Solvent

c = Molarity

b = Molality



Massenanteil w *** $w = \frac{m\,(\mathrm{G})}{m\,(\mathrm{L})}$ 1 %	**Massenverhältnis ζ 1)** ** (ζ: zeta) $\zeta = \frac{m\,(\mathrm{G})}{m\,(\mathrm{LM})}$ 1) häufig als Gehaltsangabe für gesättigte Lösungen 1 %	**Massenkonzentration β** *** $\beta = \frac{m\,(\mathrm{G})}{V\,(\mathrm{L})}$ $\mathrm{g \cdot l^{-1}}$
Volumenanteil φ 1) ** (φ: phi) $\varphi = \frac{V\,(\mathrm{G})}{V\,(\mathrm{G}) + V\,(\mathrm{LM})}$ 1) praktisch nur für ideale Gasmischungen 1 %	**Volumenverhältnis ψ** * (ψ: psi) $\psi = \frac{V\,(\mathrm{G})}{V\,(\mathrm{LM})}$ 1 %	**Volumenkonzentration σ** ** (σ: sigma) $\sigma = \frac{V\,(\mathrm{G})}{V\,(\mathrm{L})}$ 1 % „%vol“
Stoffmengenanteil x 1) *** $x = \frac{n\,(\mathrm{G})}{n\,(\mathrm{L})} = \frac{n\,(\mathrm{G})}{n\,(\mathrm{G}) + n\,(\mathrm{LM})}$ 1) früher: Molenbruch 1 %	**Stoffmengenverhältnis r** * $r = \frac{n\,(\mathrm{G})}{n\,(\mathrm{LM})}$ 1 %	**Stoffmengenkonzentration c** **** $c = \frac{n\,(\mathrm{G})}{V\,(\mathrm{L})}$ $1\ \mathrm{mol \cdot l^{-1}}$
Genormt sind auch Gehaltsangaben in Bezug auf Teilchenzahlen N: Teilchenzahlanteil X Teilchenzahlverhältnis R Teilchenzahlkonzentration C ☐: mögliche bzw. häufigste Einheit		**Molalität b** *** $b = \frac{n\,(\mathrm{G})}{m\,(\mathrm{LM})}$ $1\ \mathrm{mol \cdot kg^{-1}}$

Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung01-03.jpg

1. Quantities and Units

Areas of Application for Analytical Chemistry

Environmental analyses

• Soil	heavy metals, microorganisms
• Air	exhaust gases, airborne pollutants (micro- and nanoparticles)
• Water	heavy metals, herbicides, insecticides, pesticides, hormones, contrast agents, antibiotics, and so on

Process control and regulation

- Distillation and rectification processes
- Extraction processes
- Quality control
- Monitoring of product yield

Food analytics

• Milk	polychlorinated biphenyls
• Drinking water	herbicides, heavy metals
• Brazil nuts	lead, radium, thorium, uranium

2. General Principles

Areas of Application for Analytical Chemistry

Toxico-pharmacological , forensical analytics

Drug detection	ethanol, cannabis, cocaine, methadone, ...
Doping control	anabolic agents
Clinical trials	early diagnosis and screening of diseases
Forensic medicine	toxins, blood group determination, DNA-profiling (Single Nucleotide Polymorphisms SNPs)

Research and development

Bio analytics	humane genome project
Preparative chemistry	analysis of structure and properties
Material development	electronic, magnetic, and optical properties
Astronomy	high resolution spectral analysis
Space systems	planetary probes

2. General Principles

Classification of Analytical Chemistry

Qualitative analysis

Which chemical elements or substances are present within a sample?

- Separation processes
- Infrared spectroscopy (IR)
- Nuclear Magnetic Resonance spectroscopy (NMR)
- Mass Spectroscopy (MS)
- X-Ray Diffraction (XRD)

Quantitative analysis

How much of a chemical element or a substance is present within a sample?

- Gravimetric analysis
- Volumetric analysis
- Photometry
- Atomic Absorption Spectroscopy (AAS)
- X-Ray Fluorescence (XRF)
- Electron Spectroscopy for Chemical Analysis (ESCA)

2. General Principles

Steps of a Chemical Analysis

Sampling and probing

- Random samples (e.g. 100 tea leafs from a container)
- Homogenisation of samples (e.g. grinding of tea leafs)

Analysis of samples

- Preparation/transformation of sample to make it accessible for analysis (e.g. dissolution, digestion, enrichment)
- Mask substances that would otherwise interfere with the analysis
- Measurement of the concentration in aliquotes (repeated measurements)
- Interpretation of results and conclusions

3. Substances and Separation

Substances are Bodies which Chemical and Physical Properties are Independent of Size and Shape

Example: Stainless steel → scissors, drills, knifes, quill, ...

Substances

	Heterogeneous systems (microscopically distinguishable)	***Homogeneous systems (microscopically uniform)***
Solid-Solid	**mixtures (granite)**	**alloy (brass)**
Solid-Liquid	**suspension (lime milk)**	**solutions (salt solution)**
Solid-Gaseous	**aerosol (smoke)**	**-**
Liquid-Liquid	**emulsion (milk)**	**solutions (alcohol in water)**
Liquid-Gaseous	**aerosol (fog, foam)**	**solutions (oxygen in water)**
		pure elements

3. Substances and Separation

Substances can be Classified by a Range of Physical Properties

Physical property	Formula symbol	Unit
• Absorption strength (colour)	ε	$lmol^{-1}cm^{-1}$
• Refractive index	n	-
• Density	ρ	gcm^{-3}
• Dipole moment	μ	Cm
• Electrical conductivity	σ	$\Omega^{-1}\cdot m^{-1}$
• Hardness	-	-
• Isoelectric point	IEP	pH
• Solubility	L	$mol^{-n}l^{-n}$
• Magnetic moment	μ	μ_B
• Molar heat capacity	c_{vm}	$JK^{-1}mol^{-1}$
• Melting point	T_m	° K
• Boiling point	T_b	° K
• Heat conductivity	λ	$Jm^{-1}s^{-1}K^{-1}$
• Decomposition temperature	T_d	° K

3. Substances and Separation

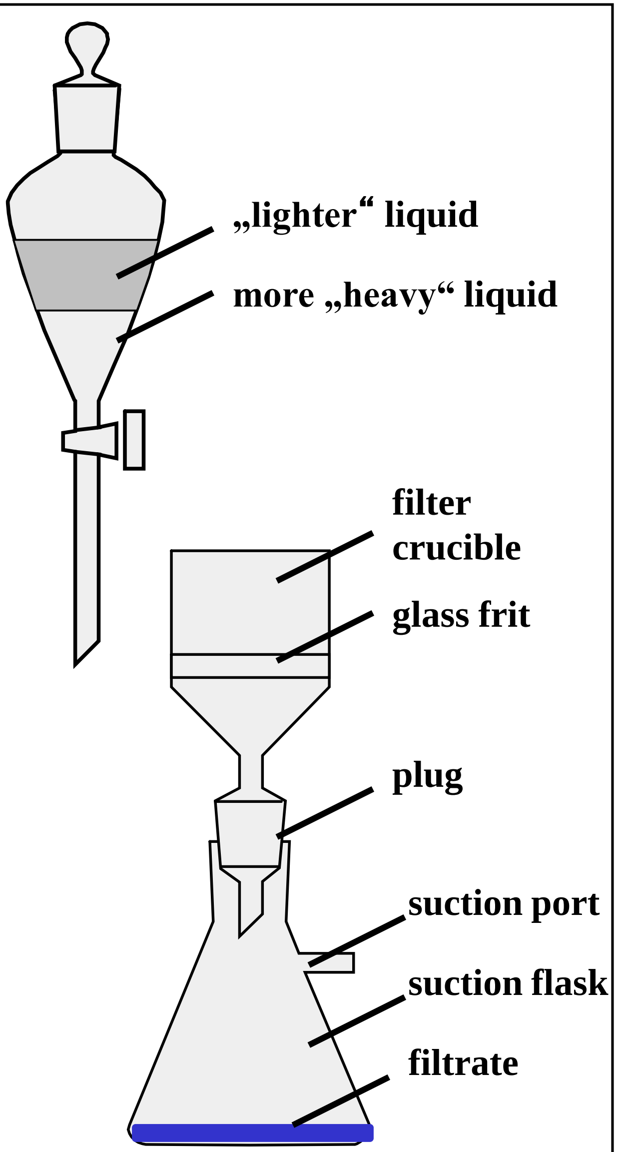
Physical Separation of Heterogeneous Systems

1. **Differences in density**

Solid-Solid	Re-slurry (washing of gold)
Solid-Liquid	sedimentation (1 G)
	centrifugation (up to 10^4 G)
Liquid-Liquid	separation (separating funnel)

2. **Differences in particle size**

Solid-Solid	sieve
Solid-Liquid	filtration (filter crucible)
Solid-Gaseous	filtration (air filter)



3. Substances and Separation

Separation of Homogeneous Systems

1. <u>Physical methods</u>

Vaporising and condensation:	seawater → rainwater
Cooling:	salt solutions → salt crystals
Condensation and vaporising:	air → N_2, O_2, noble gases
Adsorption and desorption	
Gas chromatography	dissolution of vaporisable substances
Liquid chromatography	dissolution of solid substances
Paper chromatography	dissolution of solid substances *(ß-carotine)*
Centrifugation (gases)	${}^{235/238}UF_6 \rightarrow {}^{235}UF_6 + {}^{238}UF_6$

2. <u>Chemical methods</u>

Precipitation	$Mg^{2+}, Hg^{2+} (aq) + S^{2-} \rightarrow HgS\downarrow + Mg^{2+} (aq)$
Gas purification	drying of Ar via $P_4O_{10} + 6\ H_2O \rightarrow 4\ H_3PO_4$

3. Substances and Separations

Classification of Substances

Heterogeneous substances	system consists of different phases
Homogeneous substances	system consists of only one phase
1. Solutions	phases consists of different types of molecules
2. Pure substances	phase consists of a single type of molecules
a. Compounds	mol. structure based on different types of atoms
b. Elements	mol. structure based on a single type of atoms

All substances can be cleaved into the corresponding elements through dissociation processes at sufficiently high temperatures:

$$2\ \mathrm{HgO(s)} \xrightarrow{400\,^{\circ}\mathrm{C}} 2\ \mathrm{Hg(s)} + \mathrm{O_2(g)}$$

$$\mathrm{MgO(s)} \xrightarrow{6000\,^{\circ}\mathrm{C}} \mathrm{Mg(g)} + \mathrm{O(g)}$$ (no formation of O_2, because oxygen exists almost exclusively dissociated at 6000 K)

4. Theoretical Foundations

The Law of Mass Action ⇒ Quantitative Description of Reactions in Equilibrium

General formulation for the reaction: $a\,A + b\,B \rightleftharpoons c\,C + d\,D$

Forward reaction: $v_1 = k_1 * c^a(A) * c^b(B)$

Reverse reaction: $v_2 = k_2 * c^c(C) * c^d(D)$

v = velocity

k = speed constant

Equilibrium is reached as soon as $v_1 = v_2$ ⇒ $k_1 * c^a(A) * c^b(B) = k_2 * c^c(C) * c^d(D)$

The equilibrium constant for concentration equilibria can thus be determined to:

$$\boxed{K_c = \frac{k_1}{k_2} = \frac{c^c(C) \cdot c^d(D)}{c^a(A) \cdot c^b(B)}}$$

K_c is dependant on pressure and temperature!

Assumption: The analytically determined concentration equals the effective concentration

4. Theoretical Foundations

Solubility Equilibria can be described by the Solubility Product

$A_mB_n(s) \rightleftharpoons m\, A^{n+}(aq) + n\, B^{m-}(aq)$

$$\boxed{K = \frac{c^m(A^{n+})\cdot c^n(B^{m-})}{c(A_mB_n)}}$$

This equation can be multiplied by $c(A_mB_n)$, due to the fact that the concentration of A_mB_n is constant at constant temperatures ⇒ **solubility product**

i.e. $K_L = K\cdot c(A_nB_m) \Rightarrow$ $\boxed{K_L = c^m(A^{n+})\cdot c^n(B^{m-})}$

$\boxed{\text{Unit: } [mol^{(m+n)} l^{-(m+n)}]}$

Example: $AgCl \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

$K_L = c(Ag^+)\cdot c(Cl^-) = 2\cdot 10^{-10}\ mol^2/l^2$ $pK_L = 9.7$ whereas $p = -\log_{10} \Rightarrow$ „operator“

Concentration of Ag^+ Ions: $c(Ag^+) = \sqrt{K_L} = 1.4\cdot 10^{-5}$ mol/l, with $c(Ag^+) = c(Cl^-)$

4. Theoretical Foundations

Solubility Products of poorly soluble Substances in H_2O at 25 ° C (in Reference to Activities)

Salt	pK_L Value	Salt	pK_L Value	Salt	pK_L Value
LiF	2.8	SnS	27.5	$MgCO_3$	7.5
MgF_2	8.2	PbS	52.7	$CaCO_3$	8.4
CaF_2	10.4	MnS	15.0	$SrCO_3$	9.0
BaF_2	5.8	NiS	19.4	$BaCO_3$	8.3
PbF_2	7.4	FeS	18.1	$PbCO_3$	13.1
$PbCl_2$	4.8	CuS	36.1	$ZnCO_3$	10.0
PbI_2	8.1	Ag_2S	59.1	$CdCO_3$	13.7
CuCl	7.4	ZnS	24.7	Ag_2CO_3	11.2
CuBr	8.3	CdS	27.0	$SrCrO_4$	4.4
CuI	12.0	HgS	52.7	$BaCrO_4$	9.7
AgCl	9.7	Bi_2S_3	71.6	$PbCrO_4$	13.8
AgBr	12.3	$CaSO_4$	4.6	Ag_2CrO_4	11.9
AgI	16.1	$SrSO_4$	6,5	$Al(OH)_3$	32.3
Hg_2Cl_2	17.9	$BaSO_4$	10.0	$Sc(OH)_3$	30.7
Hg_2I_2	28.3	$PbSO_4$	7.8	$Fe(OH)_3$	38.8

4. Theoretical Foundations

Rules of Thumb for the Solubility of Substances

- **Solubility is dependant on temperature (and pressure)**
- **Polar substances dissolve in polar solvents**
- **Non-polar substances dissolve in non-polar solvents**
- **All nitrates and alkaline metal salts dissolve readily in H_2O**
- **Salts of heavy metals are poorly soluble (in water)**
- **Solubility of hydroxides:**
  $NaOH > Mg(OH)_2 > Al(OH)_3 > Si(OH)_4 \Rightarrow$ **explanation: ionic charge density**

4. Theoretical Foundations

Activity and Activity Coefficient

Experimental investigations on the solubility of salts show that the solubility depends on the concentration of the salt itself and possible additional salts, respectively.

Activity: $a = \gamma \cdot c$ (effective concentration)

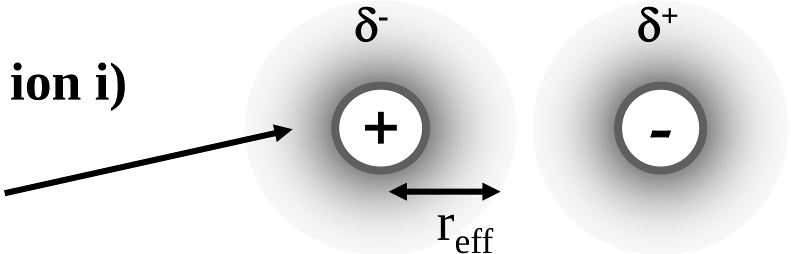
Magnitude of the activity coefficient γ

- **Highly diluted solutions** $\gamma \approx 1.0$ **i.e.** $a = c$
- **Concentrated solutions** $\gamma = 0.0 \ldots 1.0$ **i.e.** $a < c$

Dependence of the activity coefficient

- **Ionic strength** $I = 0.5\Sigma c_i \cdot z_i^2$ **(**z_i **= ionic charge of ion i)**

- **Effective ionic radius** r_{eff}**: ion + hydrate shell**
  (the hydrate shell weakens the attractive interaction)



4. Theoretical Foundations

Activity Coefficients in H_2O at 25 ° C

		Activity coefficient for a given ionic strength I [mol/l]		
Ion	**r_{eff} [pm]**	**I = 0.001**	**I = 0.01**	**I = 0.1**
H^+	900	0.967	0.914	0.830
Li^+	600	0.965	0.907	0.810
Na^+, HCO_3^-, HSO_4^-, $H_2PO_4^-$	400	0.964	0.901	0.770
K^+, Cl^-, Br^-, I^-, CN^-, NO_2^-, NO_3^-	300	0.964	0.899	0.755
Mg^{2+}, Be^{2+}	800	0.872	0.690	0.450
Ca^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+}	600	0.870	0.675	0.405
Sr^{2+}, Ba^{2+}, Cd^{2+}, Hg^{2+}, S^{2-}, WO_4^{2-}	500	0.868	0.670	0.380
Hg_2^{2+}, SO_4^{2-}, $S_2O_3^{2-}$, CrO_4^{2-}, HPO_4^{2-}	400	0.867	0.660	0.355
Al^{3+}, Fe^{3+}, Cr^{3+}, Sc^{3+}, Y^{3+}, La^{3+}	900	0.738	0.445	0.180
PO_4^{3-}, $[Fe(CN)_6]^{3-}$, $[Cr(NH_3)_6]^{3+}$	400	0.725	0.395	0.095

Calculation of activity coefficients according to Debye and Hückel

$$\boxed{\log\gamma = \frac{-0.51 \cdot z \cdot \sqrt{I}}{1 + (r_{eff}\sqrt{I}/305)}}$$

4. Theoretical Foundations

The Isoelectric Point IEP is defined as the pH-Value, whereat the average electrical Charge of a Polyprotic Acid equals to Zero

Al-salt in water

$[Al(H_2O)_6]^{3+}$

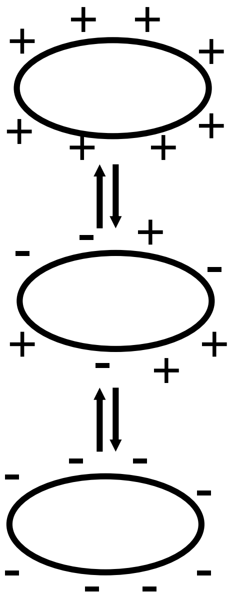
$\rightleftharpoons$ $\pm H^+$ pK_1

$Al(OH)_3$

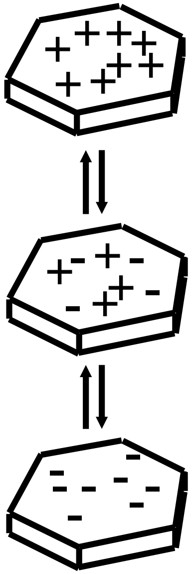
$\rightleftharpoons$ $\pm H^+$ pK_2

$[Al(OH)_4]^-$

Proteins (nano particles)



Powder (micro particles)



IEP at pH = $(pK_1 + pK_2)/2$

Even at the IEP there is an equilibrium: $Al(OH)_3 \rightleftharpoons [Al(OH)_2]^+ + [Al(OH)_4]^-$

5. Gravimetric Analysis

Through Gravimetric Analysis one can determine the Amount of an Analyte within a Sample by weighing a Reaction Product of the Analyte

Example: Determination of sulphur S (analyte) in pyrite FeS_2

Steps: $FeS_2 \xrightarrow{HNO_3/HCl} Fe^{3+} + SO_4^{2-} \xrightarrow{N_2H_4} Fe^{2+} + SO_4^{2-} \xrightarrow{Ba^{2+}} BaSO_4$

Weight pyrite: e [g]

Weight $BaSO_4$: a [g]

Stoichiometric factor: $F = A_S/M_{BaSO4}$

Mass fraction $\boxed{w = \frac{a \cdot F}{e} \cdot 100}$ [%]

5. Gravimetric Analysis

Course of a Gravimetric Analysis

1. Sampling
2. Initial Weighing e [g]
3. Dissolution
4. Separation + Possible Masking
5. Precipitation ⇒ Precipitation Product
6. Filtration + Washing
7. Heat Treatment ⇒ Weighing Product
8. Final Weighing a [g]
9. Calculations, i.e. Transformation of Measured Quantities into Sought Quantities
10. Evaluation of Analysis, e.g. Determination of Arithmetic Mean and Standard Deviation

5. Gravimetric Analysis

Sampling

- Product (1000 t) → Raw sample (100 g – 1 kg) → Lab sample (e.g. 3 x 10 g)
- Reduction of grain size and sieving

Initial Weighing

- Subtractive weighing: weigh empty vessel and vessel with analyte

Filtration

- Porcelain filter crucible (< 1000 ° C)
- Glass filter crucible(< 160 ° C)
- Paper filter (must be combusted)
  - 589 ash-free
  - 595 crude, thick
  - 597 crude, thin
  - 602 fine

5. Gravimetric Analysis

Precipitation and Weighing Product

A, B, C, D, … + X (precipitation reagent) ⟶ $BX \cdot H_2O + C + D + \ldots$

(precipitation product)

↓ Separation or masking of A

$\downarrow \Delta T$

BX / BY (weighing product)

Precipitation product

- Precipitation must be quantitative
- No impurities. i.e. extraneous matter must be removed
- Filtration must be applicable easily

Weighing product

- Must be stoichiometrically well defined
- Mass must be constant ($\Delta m < \pm 0.2$ mg)

5. Gravimetric Analysis

Precipitation

Schematic course

1. Oversaturation of solution through addition of precipitation reagent
2. Seed formation = f(saturation concentration, impurities)
3. Crystal growth = f(T) ⇒ slow growth leads to purer precipitates, because alien substances can be excluded more easily
4. Crystal order = f(T) ⇒ the higher the temperature the higher the order of the crystal

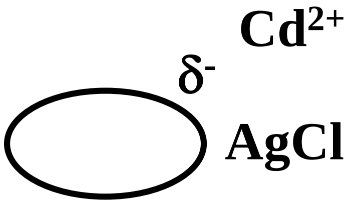
„Optimal precipitation“

- Diluted solution
- Precipitation reagent is added dropwise or the reagent must be formed homogeneously in solution
- Elevated temperatures
- Suspension should be annealed slowly

5. Gravimetrc Analysis

Entrainment Effects

1.	**Occlusion**	**mechanical inclusion**
2.	**Chemisorption**	**enrichment on surface**
3.	**Adsorption**	**on charged colloidal particles**
4.	**Incorporation into lattice**	$NH_4MgPO_4 + NH_4MgAsO_4 \Rightarrow$ **solid solutions**



Prevention of interfering ions during precipitation

- **Volatile precipitation agent, i.e. NH_3 instead of NaOH or H_2S instead of Na_2S**
- **Re-precipitation, i.e. filtrate, dissolve and precipitate again**
- **Precipitation from homogeneous solution, i.e. the reagent, e.g. OH^- or S^{2-}, is formed homogeneously in solution**

5. Gravimetric Analysis

Precipitation from Homogeneous Solution → „Homogeneous Precipitation“

The precipitation reagent is formed in solution, e.g. by thermal decomposition of a precursor: precursor → precipitation reagent

Precipitation of sulphides

Hydrolysis of thioacetamide	$CH_3\text{-}CS\text{-}NH_2 + 2\,H_2O \rightarrow H_2S + CH_3\text{-}COO^- + NH_4^+$
	$H_2S + 2\,H_2O \rightleftharpoons HS^- + H_3O^+ + H_2O \rightleftharpoons \boxed{S^{2-}} + 2\,H_3O^+$

Precipitation of hydroxides

Hydrolysis of urea	$H_2N\text{-}CO\text{-}NH_2 + H_2O \rightarrow 2\,NH_3 + CO_2$
Hydrolysis of potassium cyanate	$HOCN + 2\,H_2O \rightarrow NH_3 + CO_2$
Hydrolysis of urotropine	$N_4(CH_2)_6 + 6\,H_2O \rightarrow 4\,NH_3 + 6\,CH_2O$
	$NH_3 + H_2O \rightleftharpoons NH_4^+ + \boxed{OH^-}$

Precipitation of phosphates

Hydrolysis of tri-methylphosphate	$(CH_3O)_3P{=}O + 3\,H_2O \rightarrow 3\,CH_3OH + \boxed{PO_4^{3-}} + 3\,H^+$

5. Gravimetric Analysis

Precipitation of Hydroxides

$$\text{Charge density} = \frac{\text{Ionic charge}}{\text{Ionic volume}} = \frac{\text{Formal charge} \times 1.602 \times 10^{-19}\,[\text{C}]}{\frac{4}{3}\pi \times \text{Ionic radius}^3\,[\text{mm}^3]}$$

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

The pH-value / H^+-concentration, where a cation can be precipitated as a hydroxide depends on its ionic charge density:

Cation	Radius [pm]	Ionic charge density [C/mm³]
Na^+	116	24
Mg^{2+}	86	120
Al^{3+}	68	370
Cr^{3+}	76	270
Fe^{3+}	79	240
Si^{4+}	54	970

⇒ **values for octahedral coordination only**

$Me^{3+} + 3\,OH^- \rightarrow Me(OH)_3$ with Me = Fe, Cr, Al, (Sc, Y, La) at pH 7 - 9

$Mg^{2+} + 2\,OH^- \rightarrow Mg(OH)_2$ at pH 9 – 11

Na^+ can not be precipitated, even in highly alkaline solutions

5. Gravimetric Analysis

Precipitation of Phosphates

For Mg^{2+}, Zn^{2+} and Mn^{2+}-analysis

$NH_4H_2PO_4 + Me^{2+} \rightarrow NH_4MePO_4{\cdot}xH_2O\downarrow$ **precipitation product**

$2\ NH_4MePO_4{\cdot}xH_2O \rightarrow Me_2P_2O_7 + 2\ NH_3 + (2x+1)\ H_2O$ **weighing product**

Precipitation of Sulphates

For Ba^{2+}, Pb^{2+}-analysis

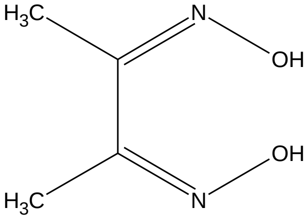
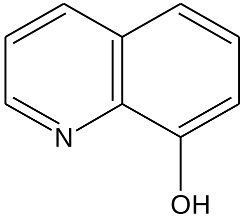
$Me^{2+} + SO_4^{2-} \rightarrow MeSO_4\downarrow$ **precipitation product = weighing product**

5. Gravimetric Analysis

Precipitation of Complexes with Organic Ligands

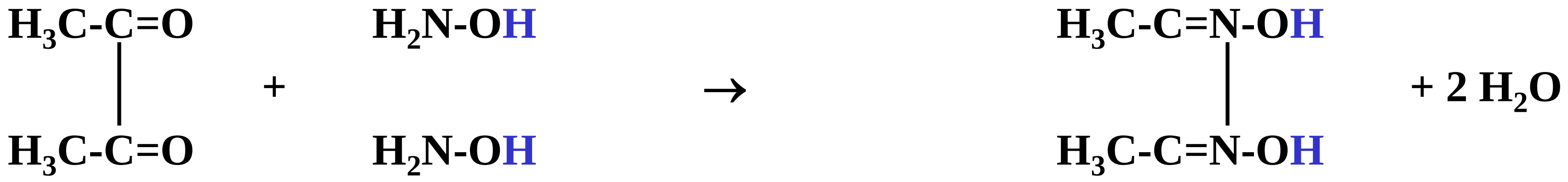
Advantages of organic reagents

- **Highly selective**
- **Precipitation product = weighing product**
- **Low stoichiometric factor**

Name	Structure	Precipitation of
Di-methylglyoxime (DMG)		Ni^{2+}, Pd^{2+}, Pt^{2+}
8-hydroxyquinoline		Mg^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, Al^{3+}, Fe^{3+}, Bi^{3+}, …
Sodium tetra-phenylborate	$Na^+[B(C_6H_5)_4]^-$	K^+, Rb^+, Cs^+, NH_4^+, Ag^+

5. Gravimetric Analysis

Precipitation with Di-methylglyoxime

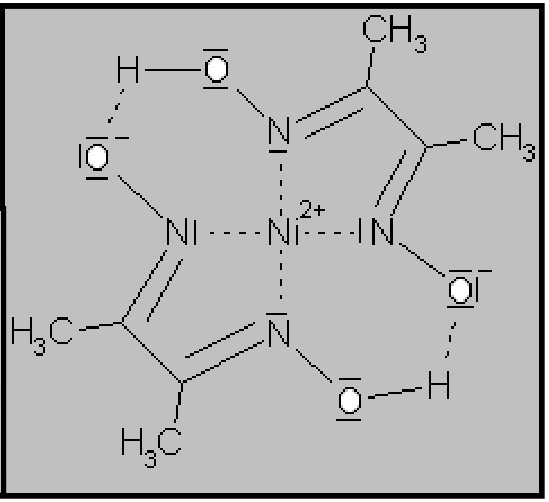


$$\begin{array}{c} H_3C-C=O \\ | \\ H_3C-C=O \end{array} + \begin{array}{c} H_2N-OH \\ \\ H_2N-OH \end{array} \rightarrow \begin{array}{c} H_3C-C=N-OH \\ | \\ H_3C-C=N-OH \end{array} + 2\ H_2O$$

di-methylglyoxale hydroxylamine di-methylglyoxime (H_2DMG)

$$2\ H_2DMG + Ni^{2+} + 2\ OH^- \rightarrow [Ni(HDMG)_2]\downarrow + 2\ H_2O$$

- The metal atom is coordinated in a square planar fashion thus forming a chelating complex
- $[Ni^{II}(HDMG)_2]$ is red
- $[Pd^{II}(HDMG)_2]$ is bright yellow
- Precipitation with di-phenylglyoxime
  → even lower stoichiometric factor

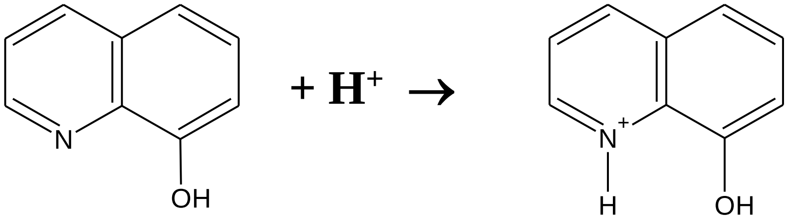


5. Gravimetric Analysis

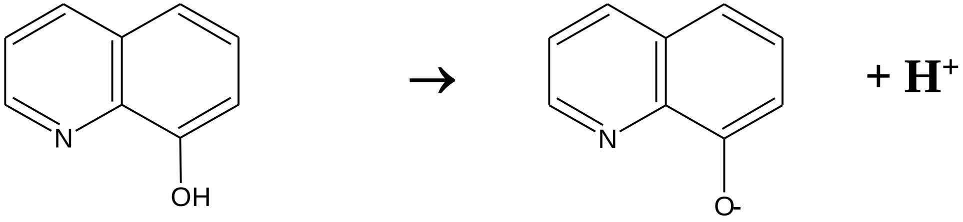
Precipitation with 8-Hydroxyquinoline (HOx) → Group Reagent

This bi-dentate ligand is amphoteric, i.e. can act as an acid or a base

Reaction as base



Reaction as acid



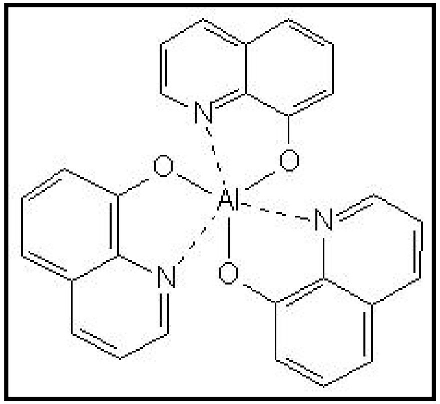
At IEP: $[H_2Ox^+] = [Ox^-]$

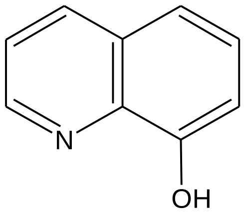
⇒ The pH-value equal to IEP is 7.43

⇒ At IEP, the ligand is not charged which slows the formation of complexes and thus the precipitation of the metal cations ⇒ this pH-value must not be used

5. Gravimetric Analyis

Precipitaion with 8-Hydroxyquinoline (HOx)



3 

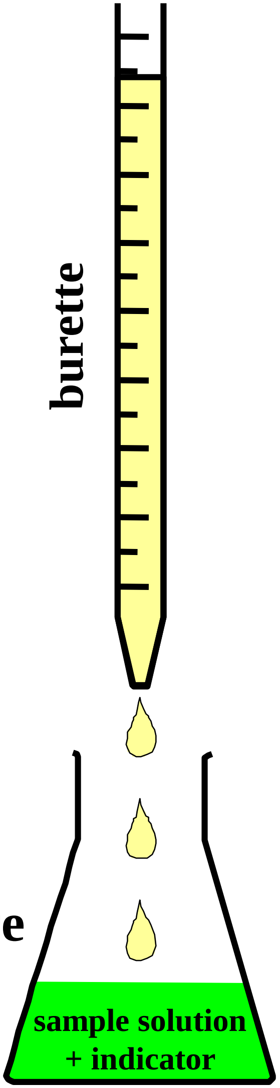
$+ Al^{3+} \rightarrow [Al(Ox)_3]\downarrow + 3\ H^+$

- ⇒ **Formation of highly insoluble $[Al(ox)_3]$ (yellow-green and fluorescent) „AlQ_3“**
- **Beschwerungsefffekt: usage of 5,7-dibromo-8-hydroxyquinoline (higher molar mass)**
- **Selectivity can be tuned via pH-value**

	pH 2 – 6	pH 8 – 10	pH > 10
Al^{3+}, Ga^{3+}	+	+	
Be^{2+}, La^{3+}, Mn^{2+}		+	
Mg^{2+}		+	+

6. Volumetric Analysis

Definition: The Volume of a Sample is Determined



For the successful execution of a volumetric analysis, the following prerequisites must be met:

Course of reaction

- **Stoichiometrically defined**
- **Quantitative**
- **Fast (no oversaturation)**

Equivalence point

- **End of titration visually easy to determine**
- **Measurable, i.e. by an indicator or a physical measurement procedure (conductivity)**

6. Volumetric Analysis

Advantages and Disadvantages in Comparison to Gravimetric Analysis

Advantages

- Less lab work
- Faster
- Can be automated

Disadvantages

- Poor accuracy
- Exactly defined standard solution needed

Standard solution: In principle, every solution where the effective concentration of the reactive species is known precisely

nominal concentration*titer factor (T or F) = effective concentration

Titer factor: The standard solution is titrated with a primary standard

6. Volumetric Analysis

Standard Titrimetric Substances

A standard titrimetric substance is a substance which is infinitely storable, not hygroscopic, readily soluble in H_2O, which can be weight easily and which can be used to set up standard solutions of exactly known concentrations. These standard solutions can then be used for the determination of the solutions used in volumetric analysis.

Standard substance	standard solution to be defined
Na_2CO_3, $NaHCO_3$	HCl, H_2SO_4, HNO_3
NaCl	$AgNO_3$
KIO_3 (potassium iodate)	$Na_2S_2O_3$
Zn	EDTA (Titriplex III)
C_6H_5COOH (benzoic acid)	NaOH, KOH
$Na_2C_2O_4$ (sodium oxalate)	$KMnO_4$

6. Volumetric Analysis

Acid-Base-Titrations

Foundation of acid-base-titrations is the neutralisation reaction

$H_2O \rightleftharpoons H^+ + OH^-$ or $2\,H_2O \rightleftharpoons H_3O^+ + OH^-$

$$\boxed{K = \frac{c(H^+)\cdot c(OH^-)}{c(H_2O)}}$$

Since the concentration of H_2O is constant, it can be included into the constant

$$\boxed{K_W = c(H^+)\cdot c(OH^-)}$$

$-\log K_W = -\log c(H^+) - \log c(OH^-)$ **$p = -\log_{10} c$ (p is just a mathematical operator)**

$pK_W = pH + pOH$

6. Volumetric Analysis

Acids and Bases

S. Arrhenius

W. Ostwald

1. Definition according to Arrhenius and Ostwald (1884)

Acids dissociate in aqueous solution and release H^+-ions

- $HCl \rightarrow H^+ + Cl^-$
- $H_2SO_4 \rightarrow 2\ H^+ + SO_4^{2-}$

Bases dissociate in aqueous solution and release OH^--ions

- $NaOH \rightarrow Na^+ + OH^-$
- $Ba(OH)_2 \rightarrow Ba^{2+} + 2\ OH^-$

Neutralisation: $H^+ + OH^- \rightarrow H_2O$

$HCl + NaOH \rightarrow H_2O + NaCl$

Disadvantages of this definition

- Limited to aqueous systems
- Ammonia NH_3 is no base, although it reacts as such: $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$

6. Volumetric Analysis

Acids and Bases


J.N. Brœnstedt M. Lowry

2. Definition according to Brønsted and Lowry (1923)

Acids are substances that transfer an H^+ to a reaction partner

$HCl + H_2O \rightarrow H_3O^+ + Cl^-$

Base are substances that "accept" protons from a reaction partner

$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$

Conjugated acid-base-pairs:

Acid	⇌	base	+ proton
HCl	⇌	Cl^-	+ H^+
H_3O^+	⇌	H_2O	+ H^+
NH_4^+	⇌	NH_3	+ H^+
H_2O	⇌	OH^-	+ H^+

⇒ In a proton transfer, always two acid-base-pairs participate

⇒ If a substance behaves as an acid or a base, depends on the reaction partner

6. Volumetric Analysis

According to Brønsted + Lowry, Water can act either as an Acid or a Base

Protolytes that can either release or accept a proton, depending on the reaction partner, are called ampholytes (i.e. they exhibit amphoteric properties)

Further ampholytes are

- HSO_4^-
- $H_2PO_4^-$
- HPO_4^{2-}
- HCO_3^-

If a strong acid (completely protonated), e.g. HCl, is mixed with a strong base, e.g. NaOH, a transfer of protons from H_3O^+-ions to OH^--ions will occur (neutralisation)

Typical for a neutralisation reaction is its high velocity (e.g. both reaction partners 0.1 M $\Rightarrow$ 99.9% conversion after 77 ns) and its highly exothermic character ($\Delta H^0 = -57.4$ kJ/mol)

6. Volumetric Analysis

Auto-Dissociation of Water

Even pure water comprises OH^-- und H_3O^+-ions, resulting in a small but measurable electrical conductivity

$$2\ H_2O \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

$$K_W = c(H_3O^+) \cdot c(OH^-) = 10^{-14}\ mol^2/l^2$$

(ionic product of water at 22 °C)

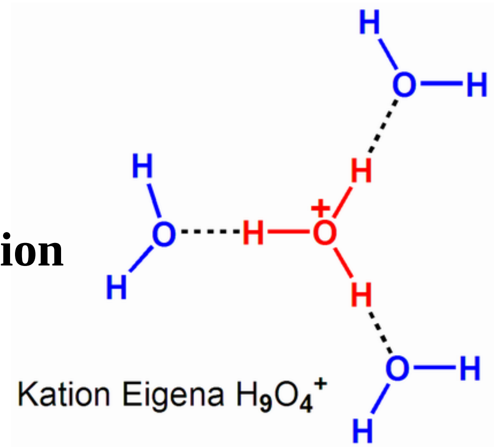
$$\Rightarrow pK_W = 14.00$$

T [°C]	pK_W
0	14.89
22	14.00
50	13.25
100	12.13

In aqueous solution H_3O^+-ions will be hydrated even further:

$$H_3O^+(aq) + 3\ H_2O \rightarrow H_9O_4^+(aq)$$

The total hydration enthalpy of a proton, i.e. the enthalpy of the reaction $H^+(g) + H_2O \rightarrow H_3O^+(aq)$ is $\Delta H^0_{hydr.} = -1091$ kJ/mol



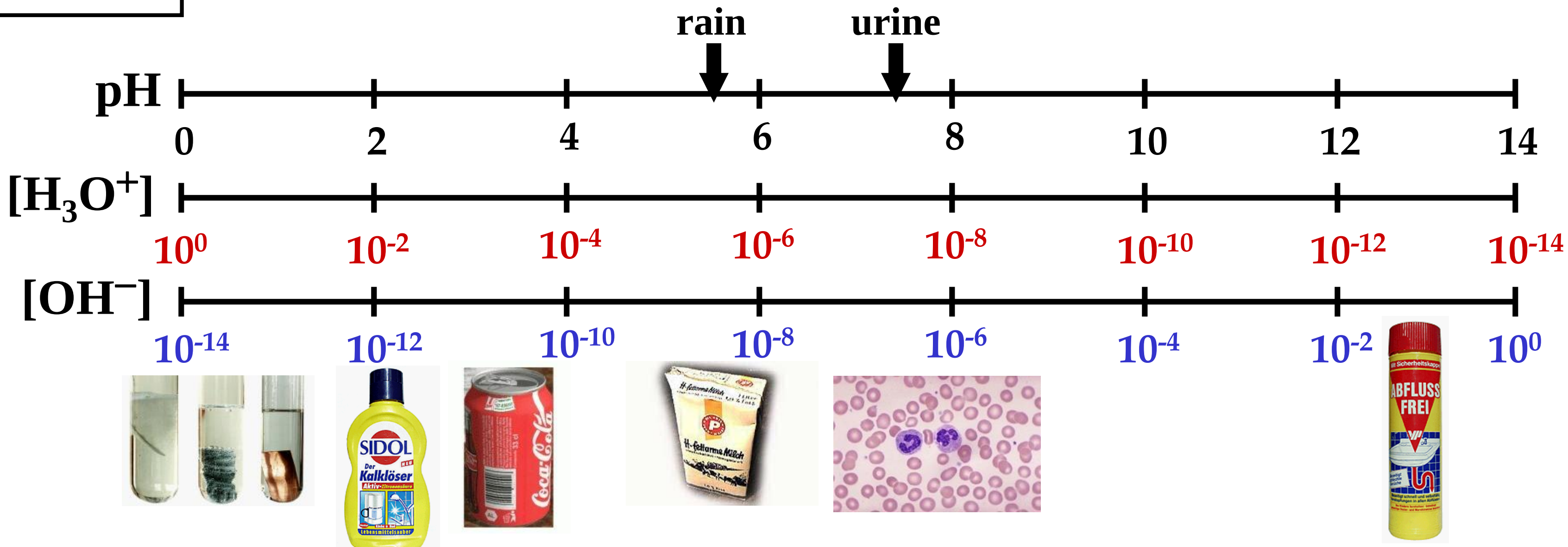
Kation Eigena $H_9O_4^+$

6. Volumetric Analysis

pH-Value (Latin: potentia hydrogenii)

$pH = -\log c(H_3O^+)$ negative decimal logarithm of hydrogen ion concentration

$pOH = -\log c(OH^-)$ negative decimal logarithm of hydroxide ion concentration



- In aqueous solution, the product of the concentrations of H_3O^+ and OH^-–ions is always constant: $pH + pOH = pK_W = 14$ at 22 ° C
- The pH-value can easily outrange the usual scale $pH = -1 \Rightarrow c(H^+) = 10$ mol/l

6. Volumetric Analysis

Strength of Acids and Bases

Extremely strong acids and bases are totally protonated or dissociated in water

Strong acid (HCl)

$HA + H_2O \rightleftharpoons A^- + H_3O^+$

Strong base (KOH)

$B + H_2O \rightleftharpoons HB^+ + OH^-$

The equilibrium constants can be derived from the law of mass action

$$K*[H_2O] = K_s = \frac{[A^-]*[H_3O^+]}{[HA]}$$

$$K*[H_2O] = K_B = \frac{[HB^+]*[OH^-]}{[B]}$$

$pK_S = -\log K_s$

$pK_B = -\log K_B$

K_S = acid constant

K_B = base constant

In water, the strongest acid is the H_3O^+-ion, the strongest base is the OH^--ion!

6. Volumetric Analysis

Strength of Acids and Bases

Strong, intermediate and weak acids and bases are, in contrary to extremely strong acids and bases, only partly dissociated

Example: acetic acid

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

$$\boxed{K_S = \frac{c(H^+)\cdot c(CH_3COO^-)}{c(CH_3COOH)}}$$

$K_s = 1.8\cdot10^{-5}$

$\Rightarrow\ pK_s = 4.75$

Classification according to strength in aqueous solution

Extremely strong acids	$pK_S < pK_S(H_3O^+) = -1.74$
Strong acids	$-1.74 < pK_S < 4.5$
Intermediates	$4.5 < pK_S < 9.5$
Weak acids	$9.5 < pK_S < 15.74$
Extremely weak acids	$pK_S > pK_S(H_2O) = 15.74$

6. Volumetric Analysis

Strength of Acids and Bases

pK_S	Acid ⇌	Base + H^+	pK_B-value	Name	
~ -10	$HClO_4$	ClO_4^-	ca. 24	perchloric acid	extremely strong acids
~ -9	HBr	Br-	ca. 23	hydrobromic acid	
~-6	HCl	Cl^-	ca. 20	hydrochloric acid	
~ -3	H_2SO_4	HSO_4^-	ca. 17	sulphuric acid	
-1.74	H_3O^+	H_2O	15.74	hydronium ion	
-1.32	HNO_3	NO_3^-	15.32	nitric acid	strong acids
1.92	HSO_4-	SO_4^{2-}	12.08	hydrogen sulphate ion	
1.96	H_3PO_4	$H_2PO_4^-$	12.04	phosphoric acid	
4.75	CH_3COOH		9.25	acetic acid	intermediates
6.92	H_2S	HS^-	7.08	hydrogen sulphide	
9.25	NH_4^+	NH_3	4.75	ammonium ion	
10.40	HCO_3-	CO_3^{2-}	3.60	hydrogen carbonate ion	weak acids
12.32	HPO_4^{2-}	PO_4^{3-}	1.68	hydrogen phosphate ion	
12.90	HS-	S^{2-}	1.10	hydrogen sulphide ion	
15.74	H_2O	OH^-	-1.74	water	extremely weak acids
~ 24	OH^-	O^{2-}	ca. -10	hydroxide ion	
~ 40	H_2	H^-	ca. -26	hydrogen	

6. Volumetric Analysis

Extremely Strong Acids (and Bases)

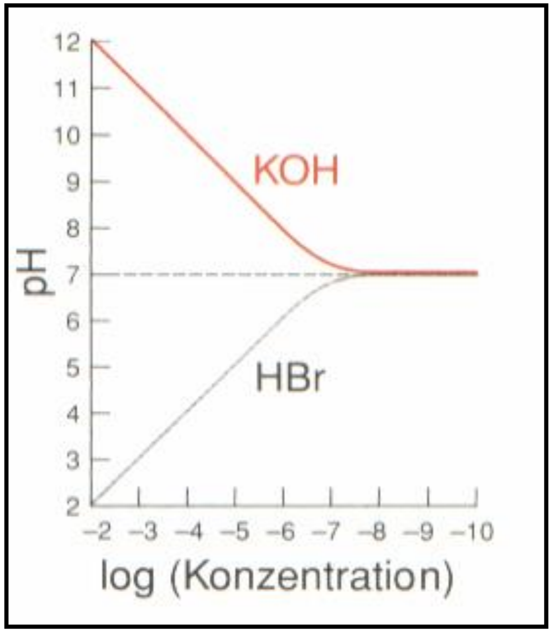
Extremely strong acids are stronger than H_3O^+ and thus completely deprotonated in aqueous solution. That implies that the H_3O^+ concentration equals the acid concentration, i.e. all extremely strong acids show the same pH-value at equal concentrations (levelling effect of water)

$c(H_3O^+) = c(HA)$ is true for $c(HA) < 1$ mol/l

pH of 0.1 M HBr: pH = -log(0.1) = 1

pH of 0.001 M HBr: pH = -log(0.001) = 3

pH of $1 \cdot 10^{-8}$ M HBr: pH = ?



In highly diluted solutions the ionic product of water comes into play again:

$c(H_3O^+) = c(HA) + 10^{-7}$ and $pH = -\log(c(HA) + 10^{-7}) = 6.96$

6. Volumetric Analysis

Strong Acids (and Bases)

In solutions of acids and bases with pK-values > -1.74 the protolysis is incomplete, i.e. apart from the protolysis product some acid/base exists undissociated.

To calculate the pH-value correctly, one must take the concentration of the acid/base and the respective protolysis constants into consideration.

$$\boxed{c(H_3O^+) = -\frac{K_S}{2} + \sqrt{\frac{K_S^{\,2}}{4} + K_S \cdot c_0(HA)}}$$

and

$$\boxed{c(OH^-) = -\frac{K_B}{2} + \sqrt{\frac{K_B^{\,2}}{4} + K_B \cdot c_0(B)}}$$

pH-value of 0.02 M $KHSO_4$ solution?

Multiple proton acids (e.g. H_3PO_4) and bases

⇒ The second and third protolysis constant is normally orders of magnitude smaller than the first, i.e. in most cases it is sufficient to consider only the first one!

pH-value of 0.2 M H_3PO_4 solution?

6. Volumetric Analysis

Weak and extremely weak Acids (and Bases)

For extremely weak protolytes, the auto-dissociation of water cannot be neglected any more

$HA + H_2O \rightleftharpoons A^- + H_3O^+$ and $H_2O + H_2O \rightleftharpoons OH^- + H_3O^+$

$$\Rightarrow \boxed{K_S = \frac{c(H_3O^+) \cdot c(A^-)}{c_0(HA)}} \qquad K_W = c(H_3O^+) \cdot c(OH^-)$$

Prerequisite for

electrical neutrality: $c(H_3O^+) = c(A^-) + c(OH^-) \Rightarrow c(A^-) = c(H_3O^+) - K_W/c(H_3O^+)$

Substitution leads to:

$$\boxed{K_S = \frac{c^2(H_3O^+) - K_W}{c_0(HA)}}$$

Transformation results in: $\boxed{c(H_3O^+) = \sqrt{K_S \cdot c_0(HA) + K_W}}$ $\Rightarrow pH = -1/2 \cdot \log(K_s c_0(HA) + K_W)$

6. Volumetric Analysis

Intermediates

In the case of weak protolytes the following equilibrium is shifted to the left side:

$\mathbf{HA + H_2O \rightleftharpoons A^- + H_3O^+}$

$$\Rightarrow \quad \boxed{K_S = \frac{c(H_3O^+)\cdot c(A^-)}{c_0(HA)}}$$

$\mathbf{c(H_3O^+) = c(A^-) << c(HA)_0}$ **i.e. the concentration of the undissociated acid is way higher than of the deprotonated acid**

$$\Rightarrow \quad \boxed{K_S = \frac{c(H_3O^+)\cdot c(A^-)}{c_0(HA)}}$$

$$\Rightarrow \quad \boxed{c(H_3O^+) = \sqrt{K_S \cdot c_0(HA)}} \qquad \Rightarrow \quad \mathbf{pH = ½(pK_s - \log c_0(HA))}$$

The same applies to bases $\Rightarrow$ $\mathbf{pOH = ½(pK_B - \log c_0(B))}$

6. Volumetric Analysis

Summary of pH-Values for Acids

	$c(H_3O^+)$	pH-Value
Very strong **$pK_S < -1.74$**	$\boxed{c(H_3O^+) = c_0(HA) + 10^{-7}}$	$\boxed{pH = -\log\left(c_0(HA) + 10^{-7}\right)}$
Strong **$-1.74 < pK_S < 4.5$**	$\boxed{c(H_3O^+) = -\frac{K_S}{2} + \sqrt{\frac{K_S{}^2}{4} + K_S \cdot c_0(HA)}}$	$\boxed{pH = -\log\left(-\frac{K_S}{2} + \sqrt{\frac{K_S^2}{4} + K_S \cdot c_0(HA)}\right)}$
Intermediate **$4.5 < pK_S < 9.5$**	$\boxed{c(H_3O^+) = \sqrt{K_S \cdot c_0(HA)}}$	$\boxed{pH = \frac{1}{2}\left(pK_S - \log\left(c_0(HA)\right)\right)}$
(Very) weak **$-pK_S > 9.5$**	$\boxed{c(H_3O^+) = \sqrt{K_S \cdot c_0(HA) + K_W}}$	$\boxed{pH = -\frac{1}{2} \cdot \log\left(K_S \cdot c_0(HA) + K_W\right)}$

6. Volumetric Analysis

Titration of a strong Base (e.g. NaOH) with a strong Acid (e.g. HCl)

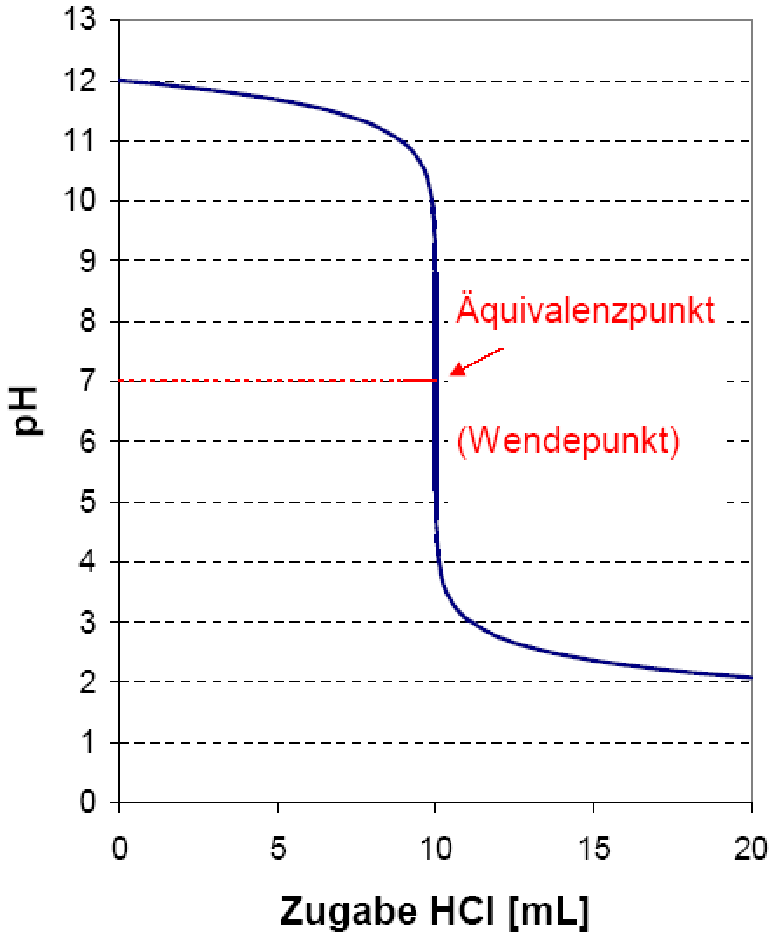
Analyte: 100 ml 0.01 M NaOH
Titrant: x ml 0.1 M HCl are added

NaOH $\rightleftharpoons$ $Na^+ + OH^-$
$OH^- + H_3O^+ \rightleftharpoons 2\ H_2O$

The equivalent point (inflection point) is reached after the addition of 10 ml HCl and is located at the point of neutrality (pH 7) for titrations of strong acids with strong bases and vice versa

Titration ratio T = c(Acid)·V(Acid)/c(Base)·V(Base)

T = 1 at point of neutrality



6. Volumetric Analysis

The Titration Ratio can be derived from the Mass Action Law, if electronic Neutrality, Mass Balance and the ionic Product of Water are taken into account

$$\boxed{T = \frac{10^{pH-14} - 10^{-pH}}{c_0(HA)} + \frac{1}{1+10^{pK_S-pH}}}$$

Simplification for extremely strong acids leads to ($pK_S < -1.74$)

$$\boxed{T = \frac{10^{pH-14} - 10^{-pH}}{c_0(HA)} + 1}$$

Which titration ratio results for pH 1, 7 and 14, if the analyte is 1 M HCl?

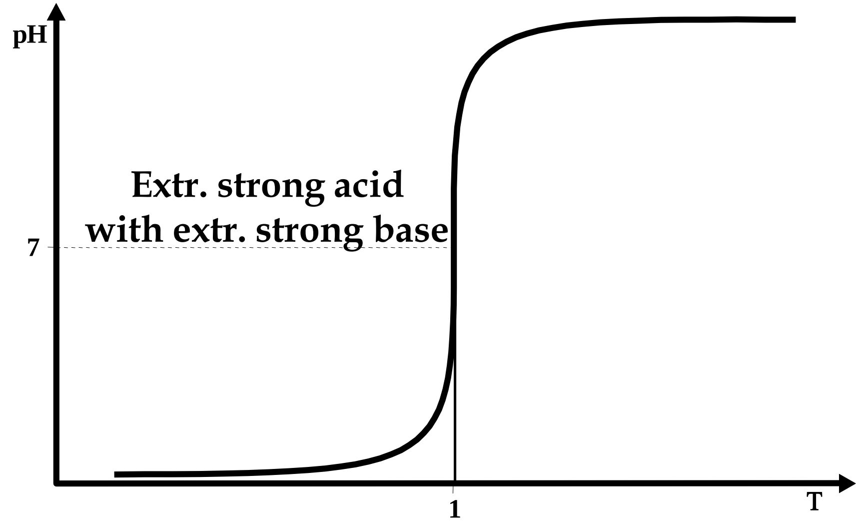
Rearrangement gives:

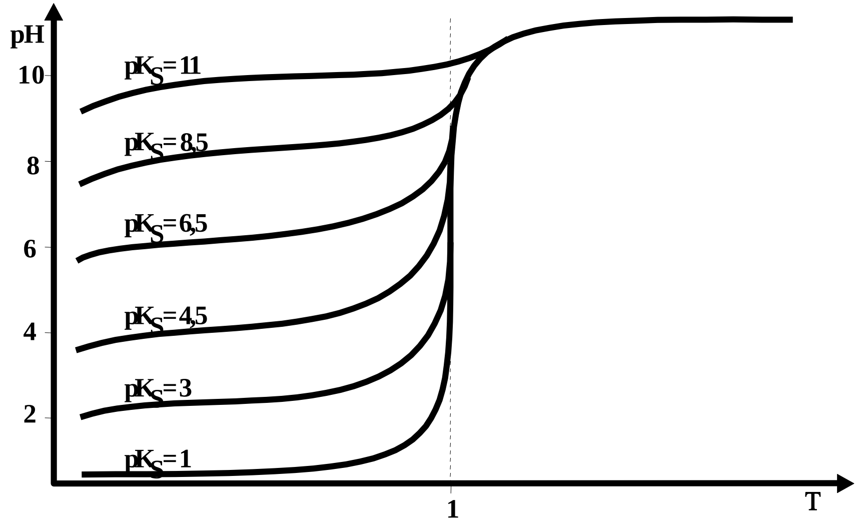
$$\boxed{c(H_3O^+) = \frac{1-T}{2} \cdot c_0(HA) + \sqrt{\frac{(1-T)^2}{4} \cdot c_0(HA) + K_W}}$$

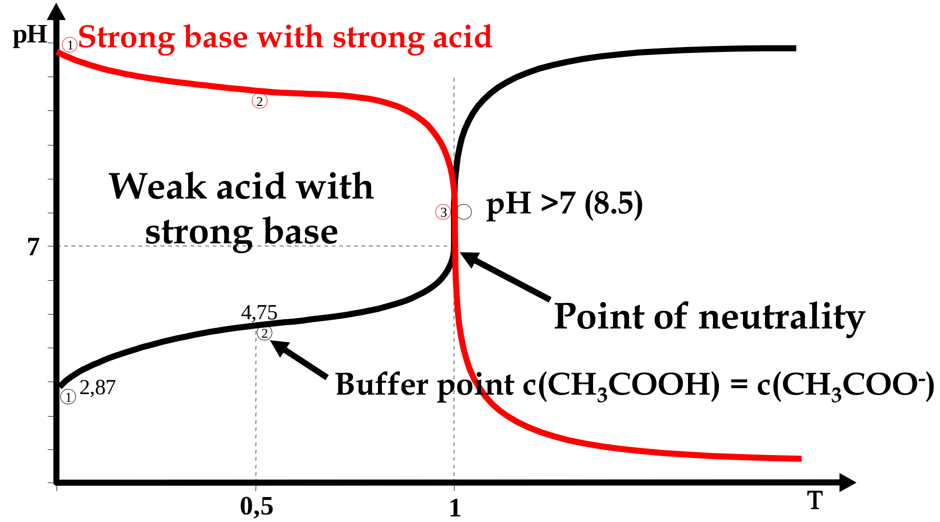
⇒ **for the calculation of titration curves**

6. Volumetric Analysis

Titration Curves for strong and weak Protolytes







Strong to weak acids with strong base

The lower the acidic strength, the more shifted is the equivalent point from the point of neutrality towards the alkaline range
⇒ for extremely weak acids, the equivalent point can be hard to identify!

6. Volumetric Analysis

Titration of a weak Acid with a strong Base

In contrary to the system strong acid/strong base, where the equivalent point is at pH 7, the equivalent point for a system weak acid/strong base is shifted to a pH-value in the alkaline range!

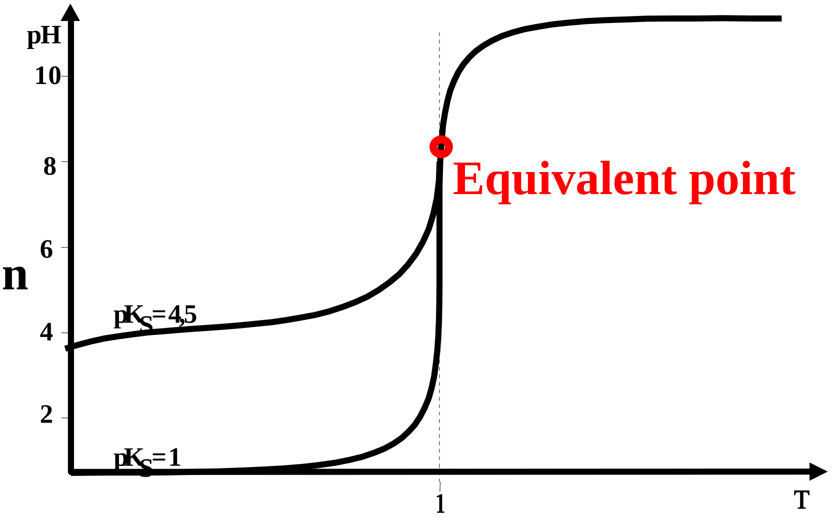
Exp.: Titration of 100 ml 0.1 M acetic acid with 10 M NaOH
Titration ratio T = c(acid)·V(acid)/c(base)·V(base)
T = 1, meaning the neutralisation equivalent
is reached after addition of only 1 ml NaOH

$$H_3O^+ + CH_3COO^- + Na^+ + OH^- \rightleftharpoons 2\,H_2O + CH_3COO^- + Na^+$$

CH_3COO^- is a weak base ($pK_B = 9.25$)
pH-calculation analogous to 0.1 M Na-acetate solution

$$\boxed{c(OH^-) = \sqrt{K_B \cdot c_0(B)}}$$

⇒ pOH = 5.1 and pH = 8.9



Equivalent point

6. Volumetric Analysis

Titration of extremely weak Acids and Bases

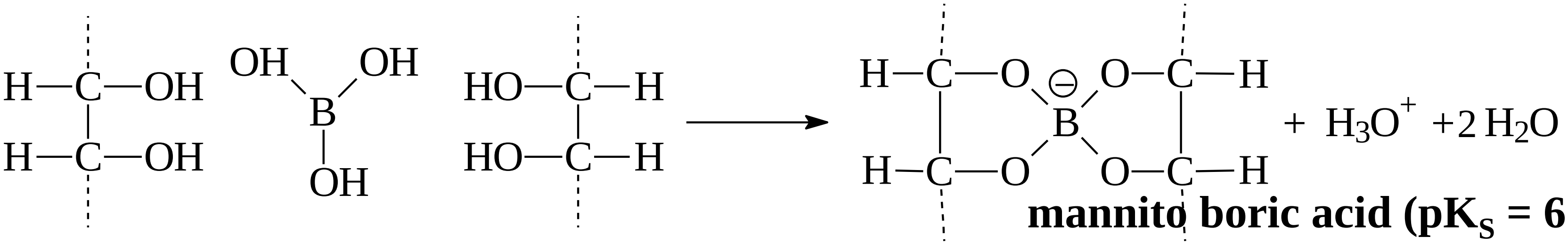
Problems

- **Indication of equivalent point**
- **Titration of indicators (weak acids or bases themselves)**

General rule: The accuracy of a titration is the better, the higher the change of pH is, i.e. the change of the pH-value at the equivalent point (turning point).

Example: Boric acid H_3BO_3 ($pK_S = 9.24$) is an extremely weak acid

On addition of glycerine or mannitol (sugar) a cyclic ester is formed



mannito boric acid ($pK_S = 6.44$)

6. Volumetric Analysis

Acid-Base Indicators (Indicator = Detector)

⇒ must be acids or bases which different states of protonation are coloured differently (reversible protonation)

⇒ organic dyes

Example: Phenolphthalein (lacton)

⇒ cyclic ester with
reversible ring opening

1. Acidic and neutral solution (I)

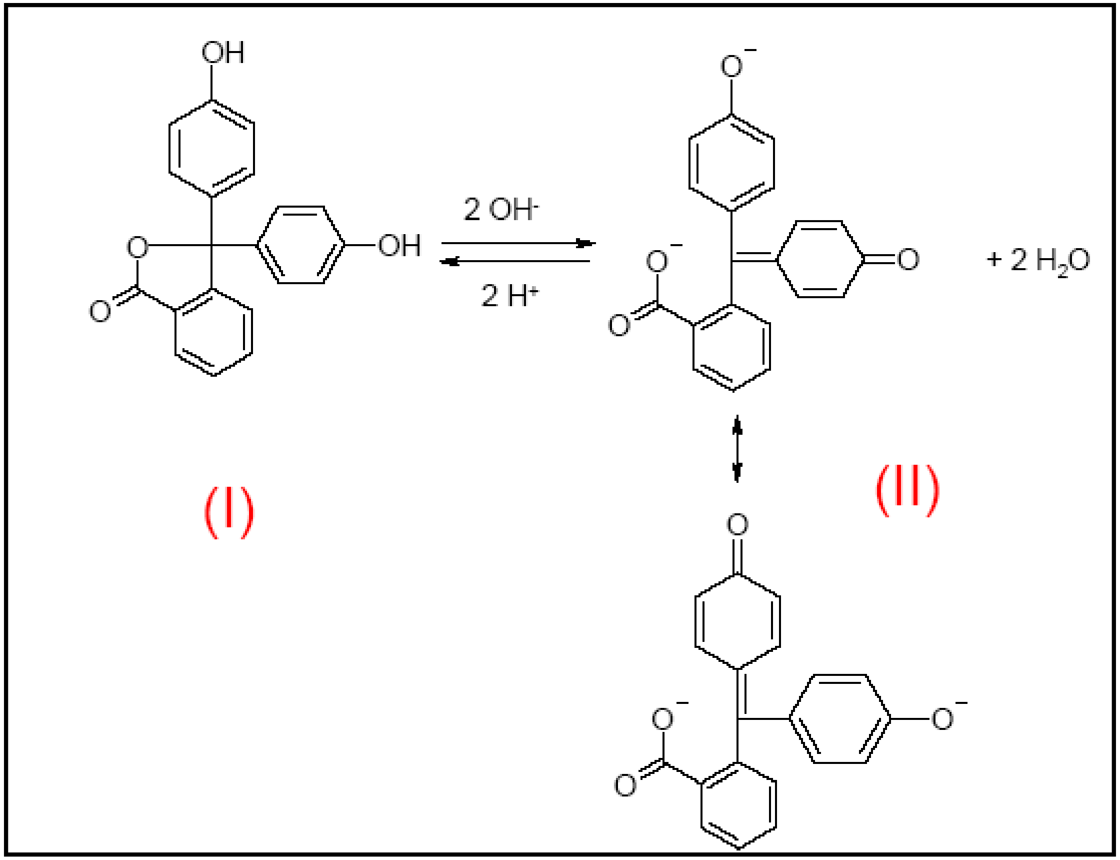
⇒ lactone ring closed

⇒ colourless

2. Alkaline solution (II)

⇒ lactone ring open

⇒ red



6. Volumetric Analysis

Acid-Base Indicators are weak organic Acids or Bases which Solutions change their Colour once the pH-Value is changed

$HInd + H_2O \rightleftharpoons H_3O^+ + Ind^-$ ⇒

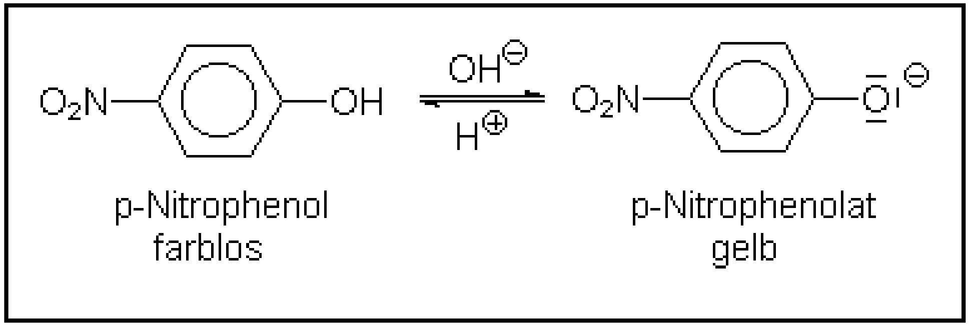
$$K_{Ind} = \frac{c(H_3O^+)\cdot c(Ind^-)}{c(HInd)}$$

Transition range: $pH = pK_{Ind} \pm 1$

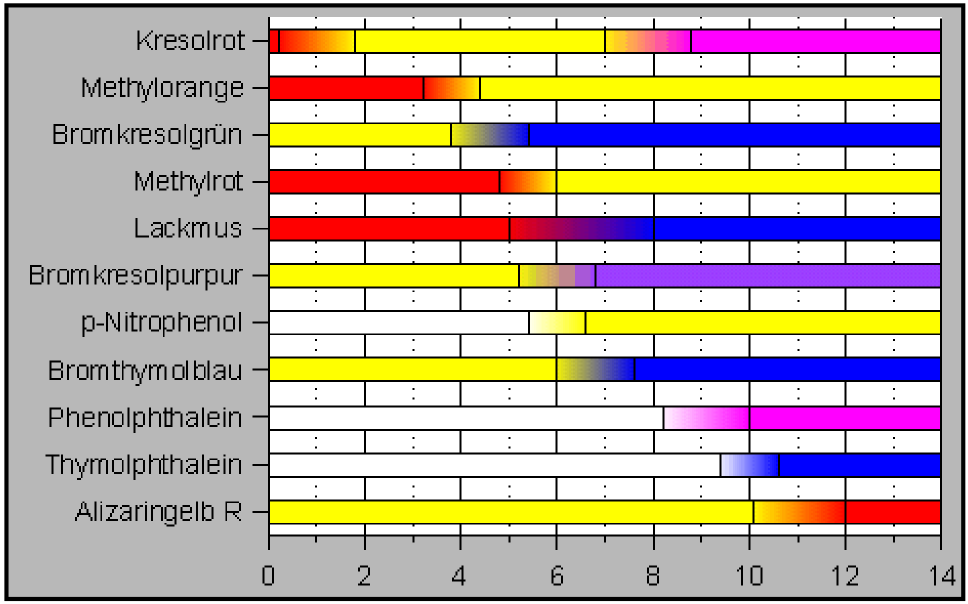
Pure colour 1: $pH = pK_{Ind} - 1$

Pure colour 2: $pH = pK_{Ind} + 1$ ⇒

$$pH = pK_S - \log\frac{c(HInd)}{c(Ind^-)}$$



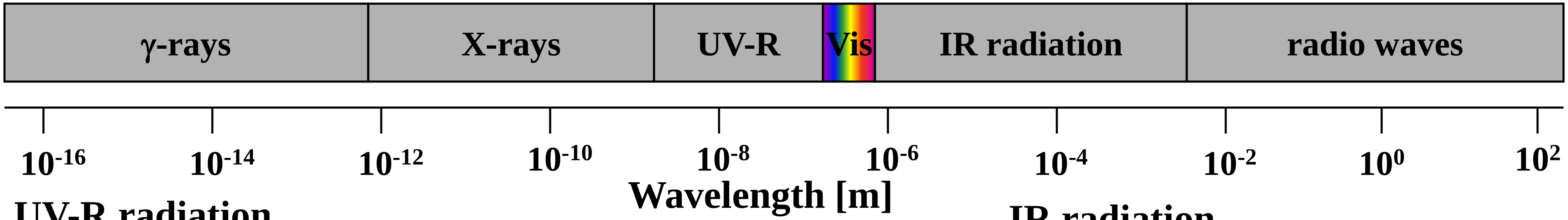
absorbs UV **absorbs blue**



<u>Mixed indicators</u>

Litmus, universal indicator, red cabbage, Tashiro (methyl red + methyl blue)

Excursion: The Electromagnetic Spectrum



UV-R radiation	
EUV	1 - 100 nm (extreme UV)
VUV	100 - 200 nm (vacuum UV)
UV-C	200 - 280 nm
UV-B	280 - 320 nm
UV-A	320 - 400 nm

Visible light	Spectral range	Complementary to
violet	380 - 430 nm	yellow-green
blue	430 - 480 nm	yellow
cyan	480 - 490 nm	orange
cyan-green	490 - 500 nm	red
green	500 - 560 nm	purple
yellow-green	550 - 570 nm	violet
yellow	570 - 590 nm	blue
orange	590 - 610 nm	cyan
red	610 - 780 nm	cyan-green

IR radiation	
IR-A	780 - 1400 nm
IR-B	1.4 - 3 µm
IR-C	3 - 1000 µm

Radio waves	
micro waves	1 - 1000 mm
HF range	1 m - 10 km
LF range	> 10 km

$$\boxed{E = h\cdot\nu = \frac{h\cdot c}{\lambda} = h\cdot c\cdot\tilde{\nu}}$$

6. Volumetric Analysis

Selection of an Indicator

- **Strong acids and bases** can be titrated with all indicators which transition point is located between the pH-range of methyl orange and phenolphthalein

- **Weak acids** can only be titrated by strong bases and indicators that show a change of colour within the weakly alkaline range (e.g. phenolphthalein)

- **Weak bases** can only be titrated by strong acids and indicators that show a change of colour within the weakly acidic range (e.g. methyl orange)

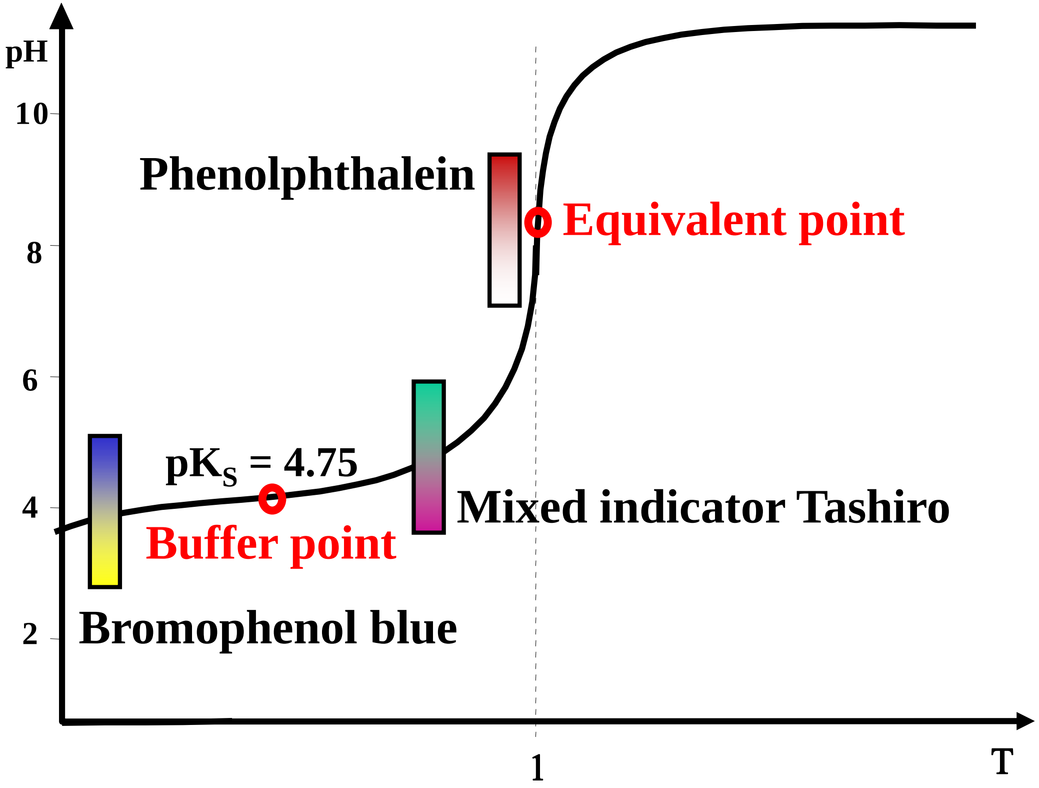
Remember: Titrations of weak bases with weak acids and the other way around lead to inconclusive results, if colorimetric means are used!

⇒ determination of end point via measurement of conductivity (conductometry)

6. Volumetric Analysis

Selection of an appropriate Indicator

Example: Titration of 0.1 M acetic acid with 10 M sodium hydroxide

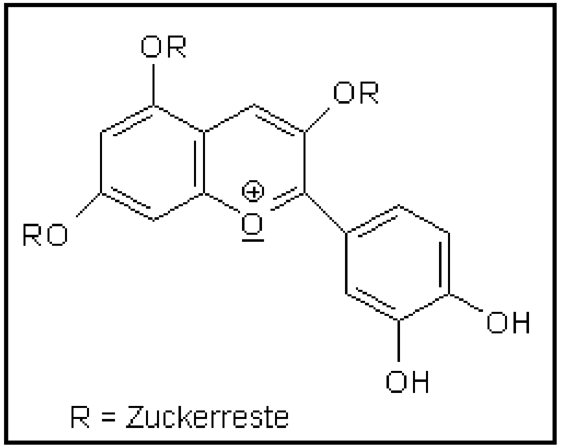


The addition of the indicator must be limited, since indicators are acids or bases themselves and thus have an impact on the protonation equilibrium

6. Volumetric Analysis

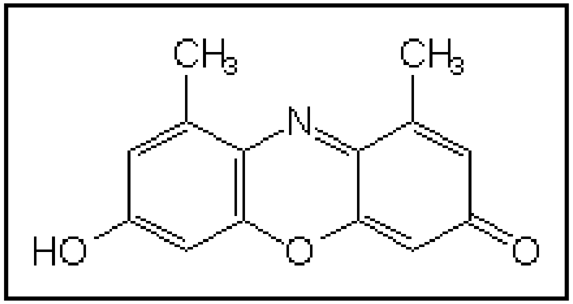
Naturally occurring Indicators

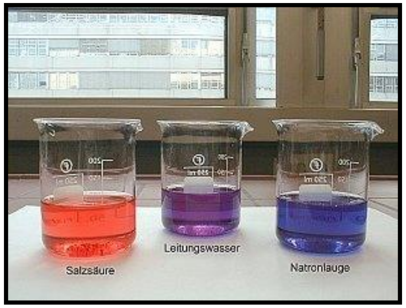
1. Example: cyanidin from red cabbage ⇒ change of colour through stepwise deprotonation



2. Example: Orcein from lichen (rocella tinctoria)

⇒ acid changes the colour of litmus paper/solution from blue to red





6. Volumetric Analysis

Quantitative Nitrogen Determination according to Kjeldahl

⇒ by Acid-base back titration

Course of action

1. Digestion — nitrate $NO_3^- \rightarrow NH_4^+$ — Devarda alloy (50%Cu, 45%Al, 5%Zn)
   amine $R\text{-}NH_2 \rightarrow NH_4^+$ — catalyst: $H_2SO_4/CuSO_4$
   not accessible by digestion: pyridine, $R\text{-}NO_2$, R-N=N-R
2. Distillation — sample: $NH_4^+ + OH^- \rightarrow NH_3 + H_2O$
   receiver: $NH_3 + HCl \rightarrow NH_4Cl$
3. Back titration HCl (residue) + NaOH $\rightarrow$ NaCl + H_2O
4. Calculation

Indicator: Tashiro = methyl orange + methylene blue (contrast dye)

6. Volumetric Analysis

Buffer Systems

⇒ **buffer are able to maintain the pH-value of a solution at a constant level, if acids or bases are added**

$$K_S = \frac{c(H_3O^+)\cdot c(A^-)}{c(HA)}$$

$$\Downarrow$$

$$c(H_3O^+) = K_S \cdot \frac{c(HA)}{c(A^-)}$$

$$\Downarrow$$

$$-\log c(H_3O^+) = -\log K_S + \log\frac{c(A^-)}{c(HA)}$$

$$\Downarrow$$

$$pH = pK_S + \log\frac{c(A^-)}{c(HA)}$$

Buffers are mixtures of

1. **Weak acid HA and its anion A^-**
2. **Weak base B and its cation HB^+**

On case 1)

What happens upon addition of H_3O^+?

$A^- + H_3O^+ \rightarrow HA + H_2O$

What happens upon addition of OH^-?

$HA + OH^- \rightarrow A^- + H_2O$

Entire equation

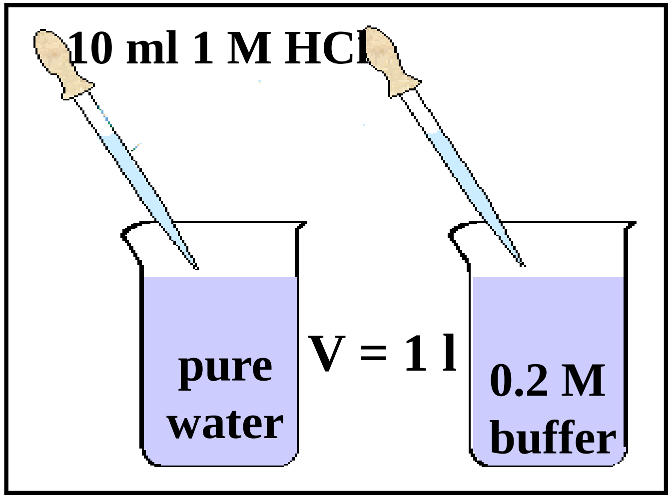
$HA + H_2O \rightleftharpoons A^- + H_3O^+$

Henderson-Hasselbach-Equation

6. Volumetric Analysis

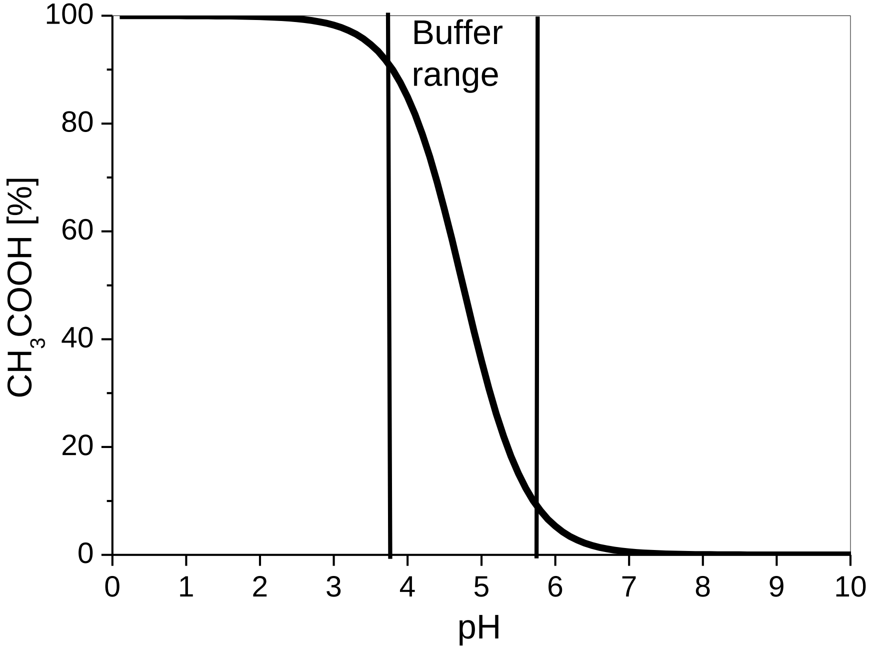
Example: Acetic Acid/Sodium Acetate Buffer

$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$



Start	pH	7.0	4.75
End	pH	2.0	4.71

Dissociation of CH_3COOH as function of the pH-value

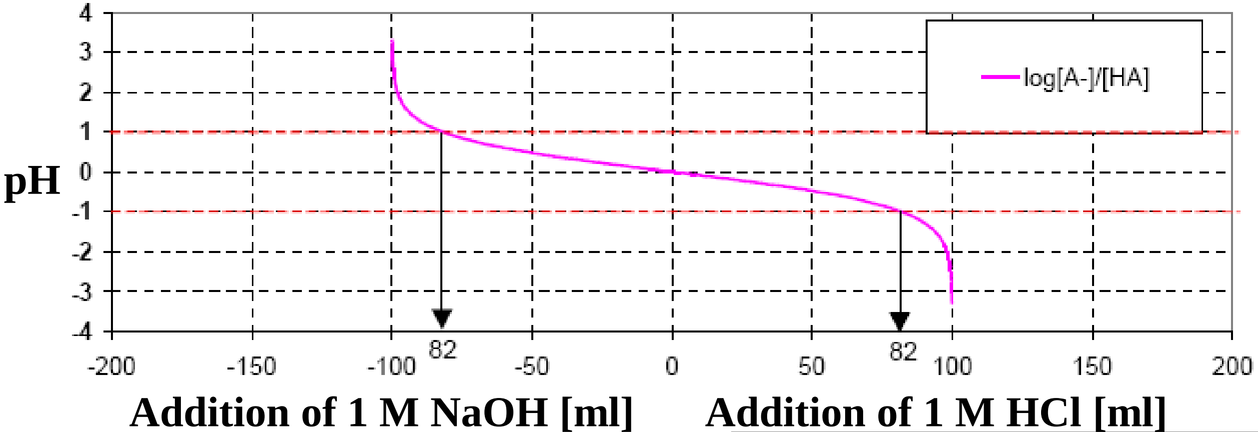


- **The suitable range for a buffer is usually located at $pK_S \pm 1$**
- **For best results, choose the buffer system which pK_S is closest to the desired pH**

6. Volumetric Analysis

Buffer Capacity

Value for the strength of the change in pH, when an acid or a base is added.

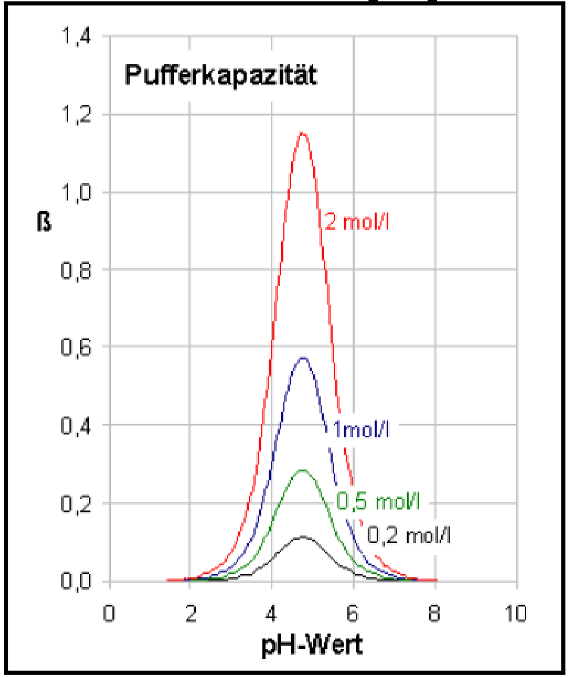


$$\boxed{\beta = \frac{dc(S)}{dpH} = \frac{dc(B)}{dpH}}$$

C(S) and c(B) are the numbers of mols of strong acids or bases that must be added to one litre buffer solution, so that the pH is changed by one unit (fig.: 0.082 mol)

⇒ The maximum of the buffer capacity is reached at $c(HA) = c(A^-)$

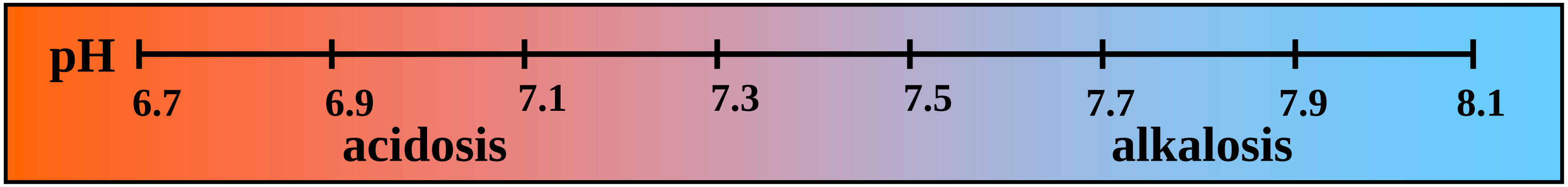
⇒ The buffer capacity can be improved through an increasing buffer concentration



6. Volumetric Analysis

Blood Buffer: Constant Blood pH Value is accomplished by several Buffer Systems

pH of blood plasma (human) $\quad$ **pH = 7.4 ± 0.03**



Buffer system	pK_S	Name	Buffer capacity
$H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^-$	6.1	carbonate	75%
$HbH^+ + H_2O \rightleftharpoons H_3O^+ + Hb$	8.25	hemoglobine	24%
$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-}$	6.8	phosphate	1%

6. Volumetric Analysis

Redox Titration – Theoretical Foundations

A. Lavoisier

A. Lavoisier (1743-1794) understood oxidation as the chemical reaction of a substance with oxygen (lat.: oxygenium) and by reduction (lat.: re-ducere) the re-transformation of the oxidised substance into its original state

Example: $4\ Fe(s) + 3\ O_2(g) \rightleftharpoons 2\ Fe_2O_3(s)$

By now, the definition is as following:

Oxidation – the loss of an electron by a chemical species

Reduction – the uptake of an electron by a chemical species

Example:

$$\begin{aligned} &4\ Fe \rightleftharpoons 4\ Fe^{3+} + 12\ e^- \\ &\underline{12\ e^- + 3\ O_2 \rightleftharpoons 6\ O^{2-}} \\ &4\ Fe + 3\ O_2 \rightleftharpoons 4\ Fe^{3+} + 6\ O^{2-}\ (2\ Fe_2O_3) \end{aligned}$$

Formal correlation to acid-base-concept according to Brœnstedt. In both theories corresponding redox pairs do exist $A_{ox} + z\ e^- \rightleftharpoons A_{red}$

6. Volumetric Analysis

Redox Titration: Oxidation Numbers (Oxidation States)

They are a handy, but fictitious, concept to explain the course of redox reactions!

⇒ the charge an atom or a molecule would possess, if the latter was built up solely by ions (borderline case of ionic bonding)

⇒ the charge an atom would possess, if all electrons from every bond were allocated at the more electronegative bonding partner

Example: Oxidation states of sulphur in its oxo-acids

Formula	*Name*	*Oxidation state*
H_2SO_2	sulphinic acid	+II
H_2SO_3	sulphurous acid	+IV
H_2SO_4	sulphuric acid	+VI
$H_2S_2O_3$	thiosulphuric acid	+II
$H_2S_2O_4$	di-thionous acid	+III
$H_2S_2O_6$	di-thionite acid	+V
$H_2S_2O_7$	di-sulphuric acid	+VI

6. Volumetric Analysis

Redox Reactions: Participation of two Redox Systems ⇒ Separate Description of both Redox Systems

General approach to establish a valid redox reaction

1. Formulate reaction equations of both redox systems
2. Balance electrons by finding the least common multiple (lcm)
3. Balance charge, i.e. establish electrical neutrality
4. Mass balance, i.e. same number of atoms of every type of atom on both sides of the redox equation

Example: $Cu + H_3O^+ + NO_3^- \rightarrow Cu^{2+} + NO$

Redox system 1:	$Cu^{0} \rightarrow Cu^{+II} + 2\,e^-$	x 3
Redox system 2:	$N^{+V}O_3^- + 3\,e^- \rightarrow N^{+II}O$	x 2 ⇒ because lcm is 6
Redox equation:	$3\,Cu + 8\,H_3O^+ + 2\,NO_3^- \rightarrow 3\,Cu^{2+} + 2\,NO + 12\,H_2O$	

6. Volumetric Analysis

Redox Reactions

Reactions in alkaline setting: mass balance to be balanced with OH^- ions

1. Example: **Reaction of hydrogen peroxide with Mn^{2+}**

$$Mn^{2+} + H_2O_2 + OH^- \rightarrow MnO_2 + H_2O$$

Redox system 1:	$Mn^{2+} \rightarrow Mn^{+IV} + 2\ e^-$	x 1
Redox system 2:	$H_2O^{-I}_2 + 2\ e^- \rightarrow 2\ O^{-II}H^-$	x 1
Redox equation:	$Mn^{2+} + H_2O_2 + 4\ OH^- \rightarrow MnO_2 + 2\ H_2O + 2\ OH^-$	
⇒	$Mn^{2+} + H_2O_2 + 2\ OH^- \rightarrow MnO_2 + 2\ H_2O$	

2. Example: **Reaction of hydrogen peroxide with MnO_4^-**

$$MnO_4^- + H_2O_2 + OH^- \rightarrow MnO_2 + O_2 + H_2O$$

Redox system 1:	$Mn^{+VII}O_4^- + 3\ e^- \rightarrow Mn^{+IV}O_2$	x 2
Redox system 2:	$H_2O^{-I}_2 \rightarrow O^0_2 + 2\ e^-$	x 3
Redox equation:	$2\ MnO_4^- + 3\ H_2O_2 \rightarrow 2\ MnO_2 + 3\ O_2 + 2\ H_2O + 2\ OH^-$	

6. Volumetric Analysis

Redox Reactions

Reactions in acidic setting: mass balance to be balanced with H^+

1. Example: **Reaction of dichromate with chloride**

$Cr_2O_7^{2-} + Cl^- + H^+ \rightarrow Cr^{3+} + 3\,Cl_2 + H_2O$

Redox system 1:	$Cr^{+VI}{}_2O_7^{2-} + 6\,e^- \rightarrow 2\,Cr^{3+}$	x 1
Redox system 2:	$2\,Cl^- \rightarrow Cl^0{}_2 + 2\,e^-$	x 3
Redox equation:	$Cr_2O_7^{2-} + 6\,Cl^- + 14\,H^+ \rightarrow 2\,Cr^{3+} + 3\,Cl_2 + 7\,H_2O$	

2. Example: **Reaction of chlorate with iodine**

$ClO_3^- + I_2 + H_2O \rightarrow Cl^- + 3\,IO_3^- + H^+$

Redox system 1:	$Cl^{+V}O_3^- + 6\,e^- \rightarrow Cl^-$	x 5
Redox system 2:	$\frac{1}{2}\,I_2^0 \rightarrow I^{+V}O_3^- + 5\,e^-$	x 6
Redox equation:	$5\,ClO_3^- + 3\,I_2 + 3\,H_2O \rightarrow 5\,Cl^- + 6\,IO_3^- + 6\,H^+$	

6. Volumetric Analysis

Redox Titrations: Manganometry

$MnO_4^- + 8\ H^+ + 5\ e^- \rightarrow Mn^{2+} + 4\ H_2O$ in acidic solution (not HCl!)

$MnO_4^- + 4\ H^+ + 3\ e^- \rightarrow MnO_2 + 2\ H_2O$ in neutral or alkaline solution

⇒ pH-value is set by redox potential of permanganate!

Permanganate is a strong oxidising agent

- Many analytes can be oxidised quantitatively and thus be determined quantitatively (metal ions (e.g. Fe^{2+}), organic substances (e.g. oxalic acid)
- Traces of contaminations (e.g. organic substances) are also oxidised (e.g. when preparing the standard solution, the titer factor must be determined)

Advantages of manganometry

$KMnO_4$ in acidic solution serves as its own indicator (Mn^{2+} is colourless)

Fields of applications for manganometry

1) Titration of Fe^{2+} containing solutions ⇒ direct titration $Fe^{2+} \rightarrow Fe^{3+} + e^-$
2) Determination of oxalate through titration ⇒ direct titration $C_2O_4^{2-} \rightarrow 2\ CO_2 + 2\ e^-$

6. Volumetric Analysis

Redox Titrations: Oxidation with Potassium Dichromate (Chromatometry)

The orange dichromate anion is a strong oxidising agent in acidic solution (e.g. as chromo sulphuric acid):

$Cr_2O_7^{2-} + 14\ H^+ + 6\ e^- \rightarrow 2\ Cr^{3+} + 7\ H_2O \qquad E^0 = +1.33\ V$

Advantages over manganometry

- **Can be used as primary standard**
- **Titration in hydrochloric solution**

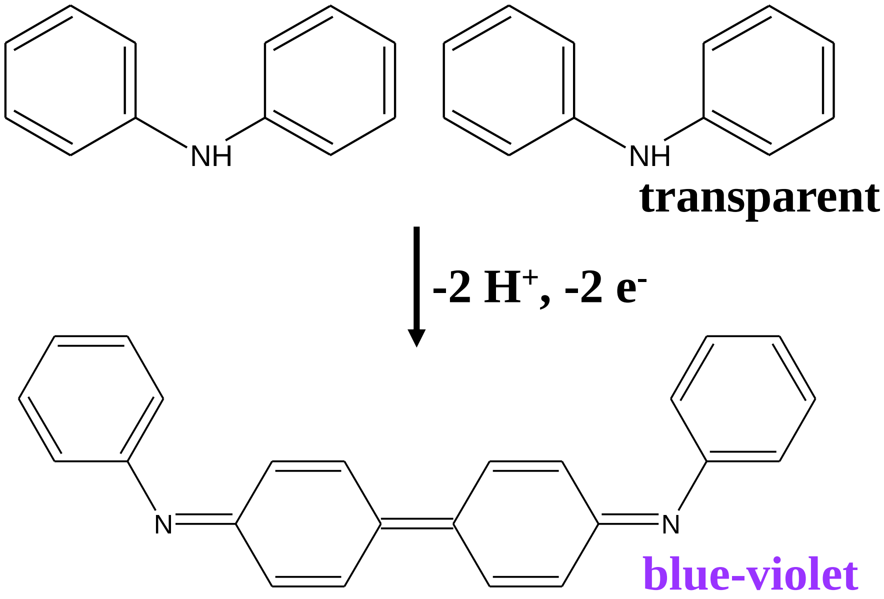
Disadvantages compared to manganometry

- **Difficult to identify end point**

  light orange → light green

  ⇒ use of a redox indicator

  ⇒ diphenylamine



N-[(1*Z*,4*Z*,4'*Z*)-4'-(phenylimino)-1,1'-bi(cyclohexa-2,5-dien-1-yliden)-4-ylidene]aniline

6. Volumetric Analysis

Redox Titrations: Oxidation with Ce^{4+} (Cerimetry)

Possible applications of cerimetry are similar to those of manganometry (but limited to acidic solutions):

$Ce^{4+} + e^- \rightarrow Ce^{3+}$ $E^0 = +1.61\ V$

Advantage compared to manganometry

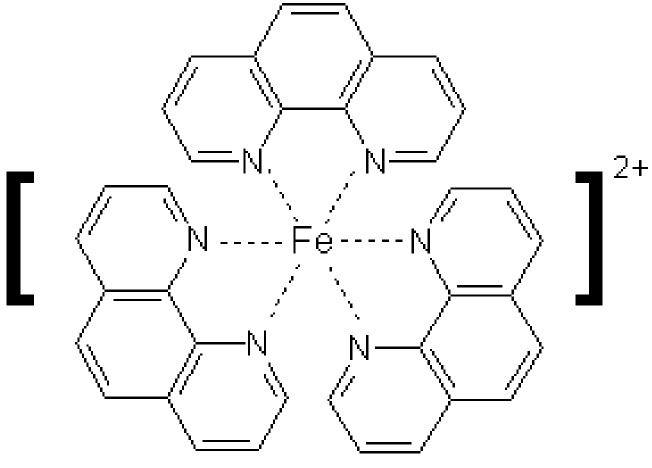
- **Cerium(IV)-sulphate solutions are stabile**

Disadvantages compared to manganometry

- **Ce^{4+} is yellow and Ce^{3+} is colourless**
  - **⇒ use of redox indicator**
  - **⇒ Ferroine**

$[Fe^{II}(phen)_3]^{2+} \rightleftharpoons [Fe^{III}(phen)_3]^{3+} + e^-$

(red) (light blue)



Tri-1,10-phenanthrolin-eisen(II)-Ion (rot)

6. Volumetric Analysis

Redox Titrations: Oxidation with Potassium Bromate $KBrO_3$ (Bromatometry)

Possible applications are again similar to manganometry:

$BrO_3^- + 6\ e^- + 6\ H^+ \rightarrow Br^- + 3\ H_2O$ $E^0 = +1.44$ V

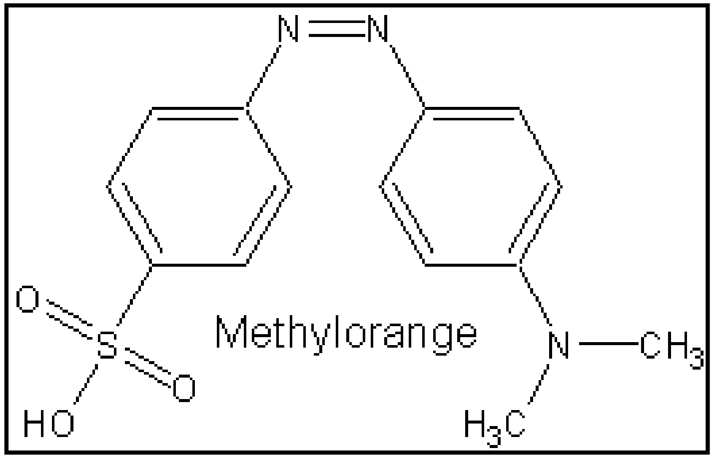
At the end point, residual bromate reacts as following:

$BrO_3^- + 5\ Br^- + 6\ H^+ \rightarrow 3\ Br_2 + 3\ H_2O$

Redox indicator is needed, too:

Methyl orange + $Br_2 \rightarrow$ transparent compound

This reaction is irreversible!



6. Volumetric Analysis

Redox Titrations: Iodometry

Versatile redox titration method, because iodine itself exhibits oxidising properties, whilst iodide solution shows reductive behaviour:

$I_2 + 2\ e^- \rightleftharpoons 2\ I^-$ $E^0 = +0.54$ V reversible

Reductive agents can be titrated directly by iodine solutions. Thereby they are getting oxidised, while the iodine is reduced to iodide:

$S^{2-} + I_2 \rightleftharpoons 2\ I^- + S$

Oxidation agents are reduced with excess acidic potassium iodide solution, whereas the iodide is oxidised to elemental iodine:

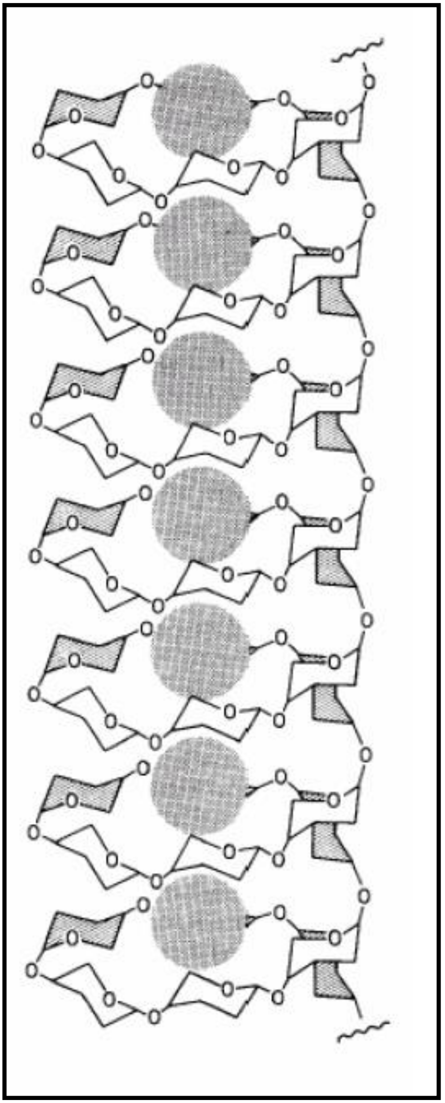
$2\ Fe^{3+} + 2\ I^- \rightleftharpoons I_2 + 2\ Fe^{2+}$

The resulting iodine is subsequently titrated with a standard solution of a suitable reduction agent, e.g. sodium thiosulphate $Na_2S_2O_3$:

$I_2 + 2\ S_2O_3^{2-} \rightarrow 2\ I^- + S_4O_6^{2-}$ (tetrathionate $^-O_3S\text{-}S\text{-}S\text{-}SO_3^-$) „corner connected tetrahedrons“

6. Volumetric Analysis

Redox Titrations: Iodometry – Determination of the End Point



As an indicator starch is used (amylose + amylopectin)

⇒ formation of iodine-starch inclusion compound

The iodine solutions used in iodometry always comprise potassium iodide apart from iodine, and thus the dark brown tri-iodide anion I_3^-

To enhance the recognition of the iodine, some starch solution is still added

Starch forms dark blue compounds with iodine, which allows the determination of iodine concentrations as low as 10^{-5} mol/L.

The colour strength of the blue iodine starch solution exceeds the colour strength of the free ion to a significant extend

⇒ delocalisation of electrons is made easier

6. Volumetric Analysis

Precipitation Titration

Principle: $Me^+ + X^- \rightleftharpoons MeX\downarrow$ $K_L(MeX) < 10^{-9}$ mol²/l²

No determination of:

sulphides, hydroxides, phosphates ⇒ delayed precipitation

Determination of X^-

$Cl^-, Br^-, I^-, OCN^-, SCN^-, CN^-$ ⇒ halides and pseudo-halides with Ag^+

Example: $Ag^+ + X^- \rightleftharpoons AgX\downarrow$

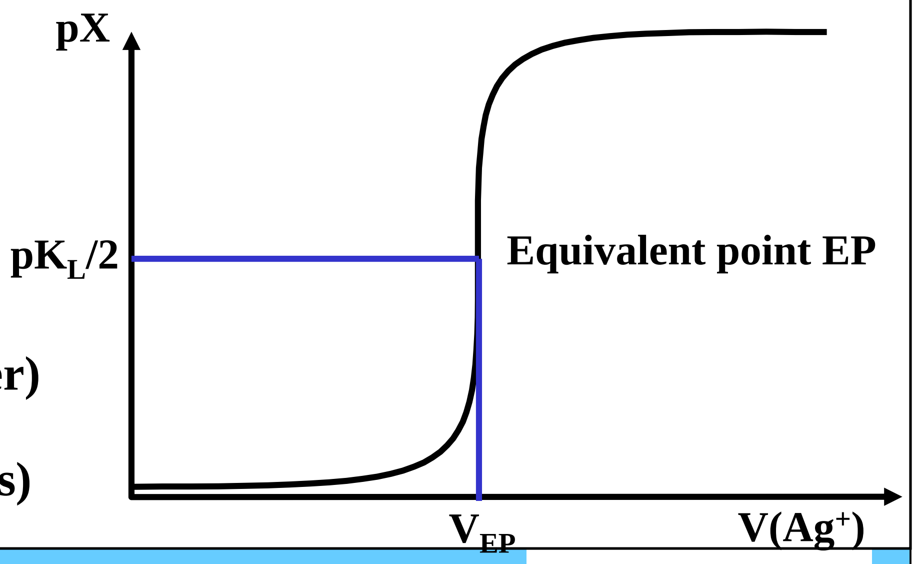
$$K_L(AgX) = c(Ag^+)\cdot c(X^-) = c^2(X^-)$$

$$\Rightarrow \quad c(X^-) = K_L(AgX)^{1/2}$$

$$\Rightarrow \quad pX = pK_L/2$$

Prior to EP: $Ag^+ + X^- \rightleftharpoons \overset{-\,-}{{}^{-}(AgX)^{-}} + X^-$ (receiver)

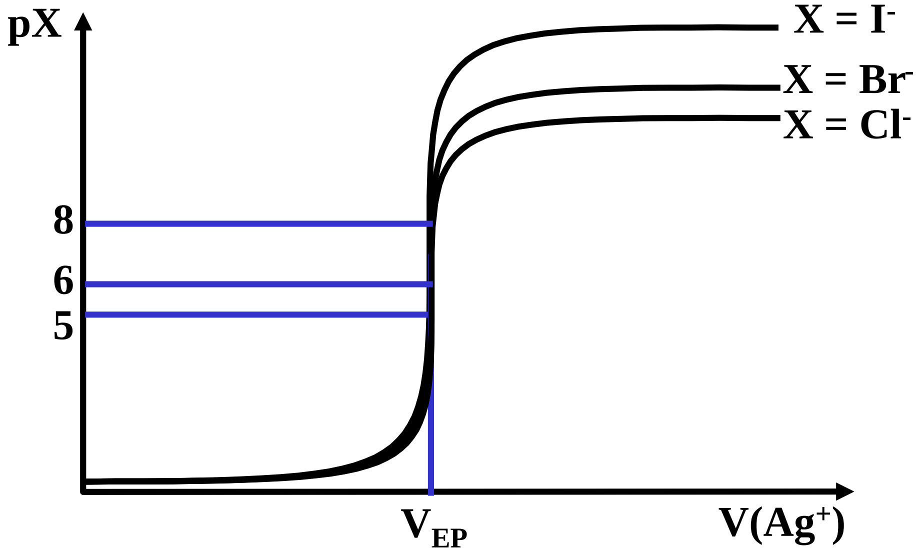
Posterior to EP: $Ag^+ + X^- \rightleftharpoons \overset{+\,+}{{}^{+}(AgX)^{+}} + Ag^+$ (excess)



6. Volumetric Analysis

Precipitation Titration

MeX	K_L(MeX)
AgCl	~10^{-10} mol²/l²
AgBr	~10^{-12} mol²/l²
AgI	~10^{-16} mol²/l²



Problem: a suitable indicator that transforms at the equivalent point must be chosen

1. Approach: titration according to Gay-Lussac (1832)

Prior to EP	$Ag^+ + X^- \rightleftharpoons AgX\downarrow + X^-$ (receiver) → charged particles (colloids)
At EP	$Ag^+ + X^- \rightleftharpoons AgX\downarrow$ → no charged particles ⇒ unobscured point
Posterior to EP:	$Ag^+ + X^- \rightleftharpoons AgX + Ag^+$ (excess) → charged particles (colloids)

6. Volumetric Analysis

Precipitation Titration

2. Approach: titration according to Mohr (1856)

$2\ Ag^+ + CrO_4^{2-} \rightleftharpoons Ag_2CrO_4\downarrow$ $K_L(Ag_2CrO_4) < 4 \cdot 10^{-12}\ mol^3/l^3$

(yellow) (red)

Ag_2CrO_4 is soluble more readily than AgX, i.e. precipitates posterior to the EP of the silver halides and pseudo-halides

Prior to EP $Ag^+ + X^- \rightleftharpoons AgX\downarrow + X^-$ (receiver)

At EP $Ag^+ + X^- \rightleftharpoons AgX\downarrow$

Posterior to EP: $2\ Ag^+ + CrO_4^{2-} \rightleftharpoons Ag_2CrO_4\downarrow$ → precipitation of red Ag_2CrO_4

Caution! Error of titration

When Ag_2CrO_4 precipitates, there is already a small excess of Ag^+ present in the solution

6. Volumetric Analysis

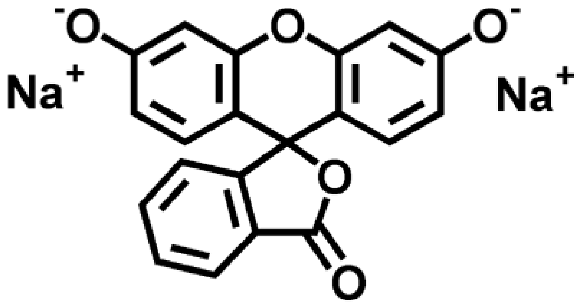
Precipitation Titration

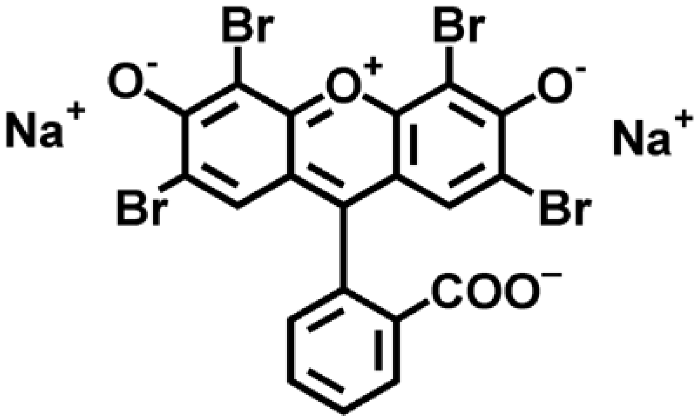
3. Approach: titration according to Fajans (1923)

Principle:

Adsorption indication, i.e. AgCl precipitate adsorbs chloride and, posterior to EP, also silver ions

- ⇒ **that is why the precipitate is charged positively and anionic indicators accumulate at the surface**
- ⇒ **indication of Cl^- with fluorescein, indication of I^-, Br^-, SCN^- with eosin**





6. Volumetric Analysis

Complexometry

Definiton: complexes *(coordination compounds)*

By „complexes“ one understands molecules or ions, where a charged or uncharged central atom Z is surrounded by a number of charged or uncharged ligands L according to its coordination number ⇒ ZL_n

Examples

$Mn^{2+} + 6\ H_2O \rightarrow [Mn(H_2O)_6]^{2+}$	**cationic**
$Ag^{+} + 2\ NH_3 \rightarrow [Ag(NH_3)_2]^{+}$	**cationic**
$Al(OH)_3 + OH^{-} \rightarrow [Al(OH)_4]^{-}$	**anionic**
$Fe^{2+} + 6\ CN^{-} \rightarrow [Fe(CN)_6]^{4-}$	**anionic**
$Ni^{0} + 4\ CO \rightarrow [Ni(CO)_4]^{0}$	**neutral**

⇒ result of Lewis acid-base-reaction $Z + |L \rightarrow Z\text{-}L$

Ligands

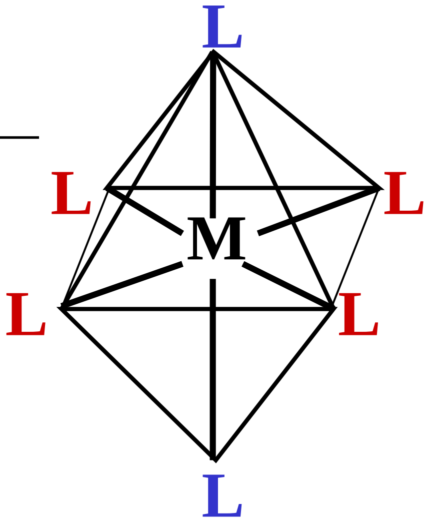
Anions: F^- (fluoro-), Cl^- (chloro-), Br^- (bromo-), I^- (iodo-), OH^- (hydroxo-), CN^- (cyano-)

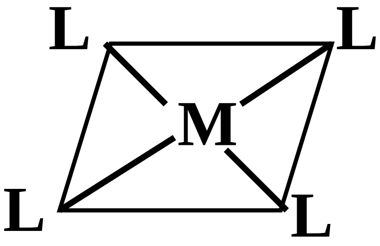
Neutral molecules: NH_3 (ammine-), H_2O (aqua-)

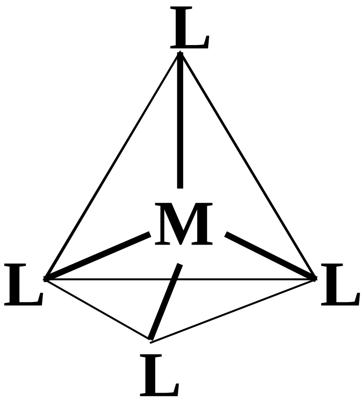
6. Volumetric Analysis

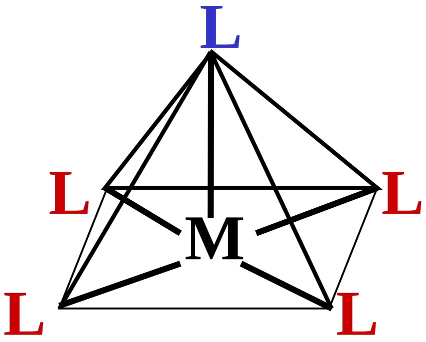
Complexometry

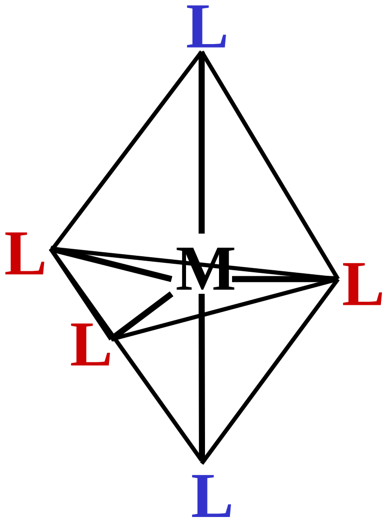
Coordination number	Geometry
2	linear
3	trigonal planar
4	tetrahedral, square planar
5	trigonal bi-pyramidal, square pyramidal
6	octahedral
7	pentagonal bi-pyramidal
8	cubic, dodecahedral









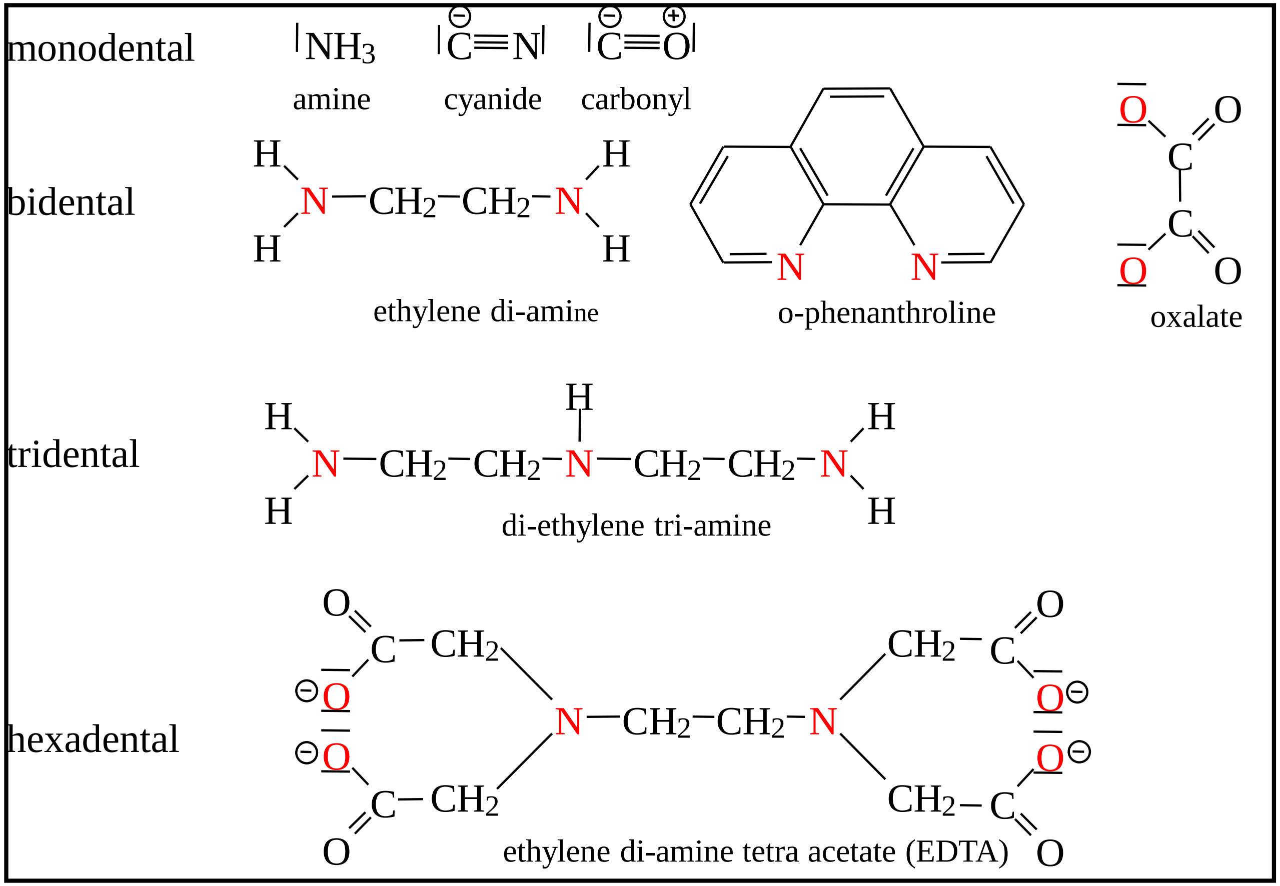


6. Volumetric Analysis

Complexometry

<u>Denticity</u>

Number of electron pairs at the ligand, which are accessible to coordinative bonding to the central atom

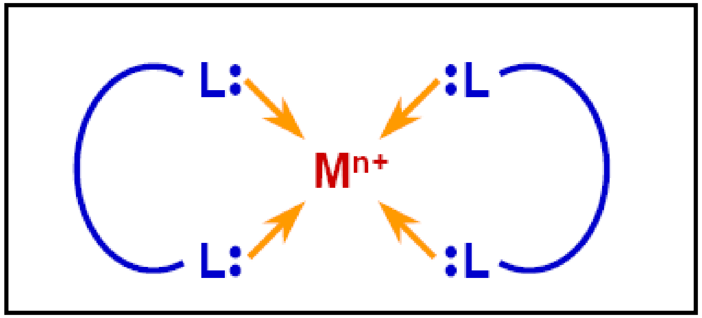


Multidental ligands are also called chelating ligands

Chelating complexes are more stable than complexes with monodental ligands

6. Volumetric Analysis

Complexometry

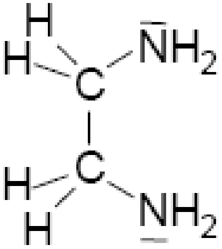


Composition of chelating ligands and complexes

Examples

ethylene di-amine (en)

amino acids NH_2-CHR-COO^-



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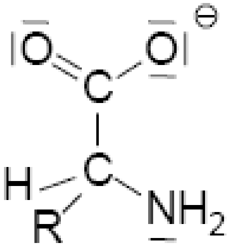


$[Cu(H_2O)_4]^{2+}$ + 2 gly^- ⇌ $[Cu(gly)_2]^0$ + 4 H_2O

„chelate complex“

6. Volumetric Analysis

Complexometry

Chelating effect

Describes the ability of multidental ligands to form more stable complexes with metals than comparable monodental ligands

$$\boxed{K_K = \frac{c([Cd(\text{ethylene di-amine})_2]^{2+})}{c(Cd^{2+}) \cdot c^2(\text{ethylene di-amine})} = 2 \cdot 10^{10}}$$

Example

Cd^{2+} + 2 ethylene di-amine $\rightleftharpoons$ $[Cd(\text{ethylene di-amine})_2]^{2+}$

Cd^{2+} + 4 methyl amine $\rightleftharpoons$ $[Cd(\text{methyl amine})_4]^{2+}$

$$\boxed{K_K = \frac{c([Cd(\text{methyl amine})_4]^{2+})}{c(Cd^{2+}) \cdot c^4(\text{methylamine})} = 2 \cdot 10^{6}}$$

The ethylene di-amine complex is more stable, because the decrease in entropy for this complex formation reaction (relative decrease of particle number) is smaller

6. Volumetric Analysis

Complexometry

Titration with complexes

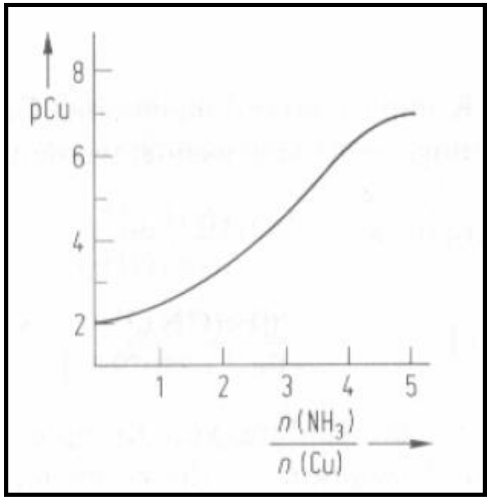
Central atom:	**analyte**
Ligand:	**titration agent, e.g. multidental ligands of the like of EDTA**
Complex formation:	**central atom Z + n ligand $\rightarrow$ complex ZL_n**

A substantial prerequisite for an applicable complex formation reaction in volumetric analysis is a rapid drop in concentration of the analyte close to the equivalent point!

Example: $Cu^{2+} + 4\ NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$ $K_K = 3.9 \cdot 10^{12}$

K_K is relatively high and one could expect a distinct change at EP (but this is not the case!)

Reason: stepwise course of the complex formation reaction



6. Volumetric Analysis

Complexometry

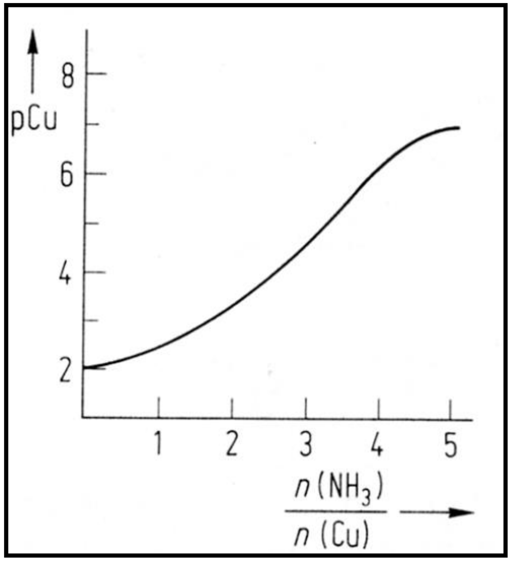
Stepwise complex formation reactions

$Cu^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)]^{2+}$ $K_1 = 1.35 \cdot 10^4$

$[Cu(NH_3)]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_2]^{2+}$ $K_2 = 3.02 \cdot 10^3$

$[Cu(NH_3)_2]^{2}+ + NH_3 \rightleftharpoons [Cu(NH_3)_3]^{2+}$ $K_3 = 7.41 \cdot 10^2$

$[Cu(NH_3)_3]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$ $K_4 = 1.29 \cdot 10^2$

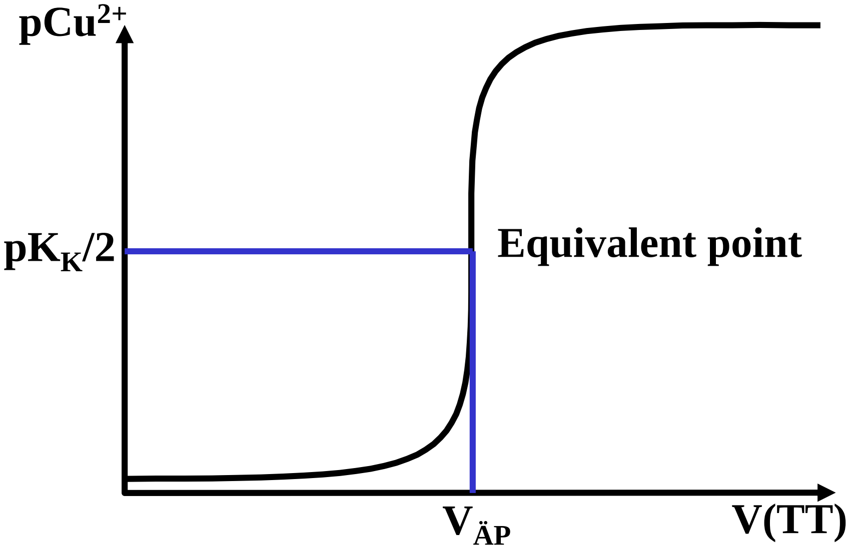


$K_K = K_1 \cdot K_2 \cdot K_3 \cdot K_4$

Immediate complex formation reaction

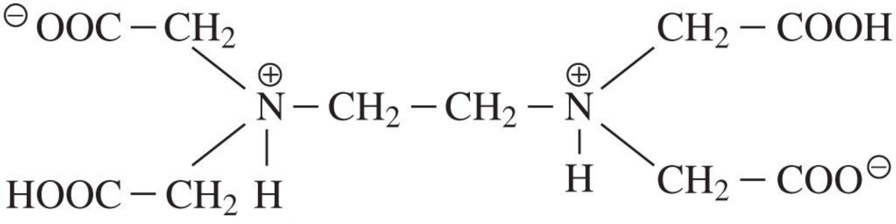
Intermediate states can be avoided through the use of chelating reagents, e.g. Cu^{2+} through use of tri-ethylene tetra amine (TT)

$K_K = 3.16 \cdot 10^{20}$ (chelating effect)



6. Volumetric Analysis

Complexometry



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<u>**Ethylene di-amine tetra acetic acid (EDTA, H_4Y)**</u>

- **Most commonly used chelating reagent in analytical chemistry**
- **Tetra basic acid H_4Y**

$$\xrightarrow[\text{pH-value}]{H_4Y \qquad H_3Y^- \qquad H_2Y^{2-} \qquad HY^{3-} \qquad Y^{4-}}$$

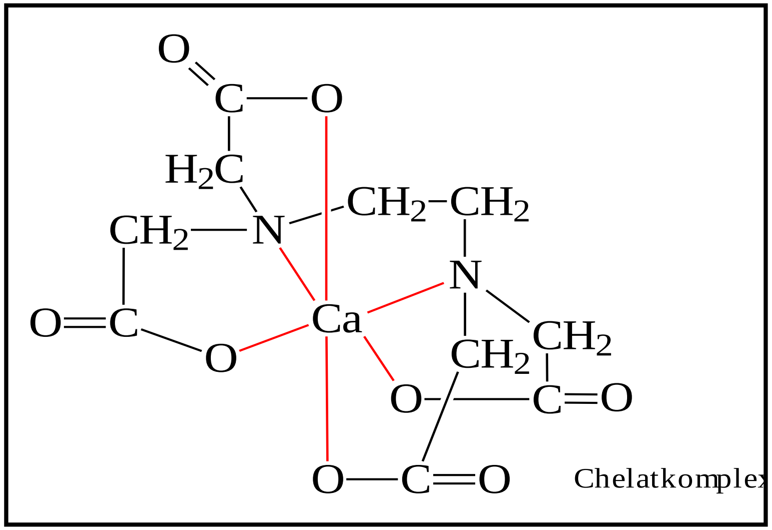
In highly alkaline environments only $[Y]^{4-}$ is present, which is the actual ligand

Example for a complex formation with EDTA

$$[Ca(H_2O)_6]^{2+} + EDTA^{4-} \rightleftharpoons [Ca(EDTA)]^{2-} + 6\ H_2O$$

$$\boxed{K_K = \frac{c([Ca(EDTA)]^{2-})}{c([Ca(H_2O)_6]^{2+}) \cdot c(EDTA^{4-})}}$$

Structure of octahedral $[Ca\text{-}EDTA]^{2-}$-complex



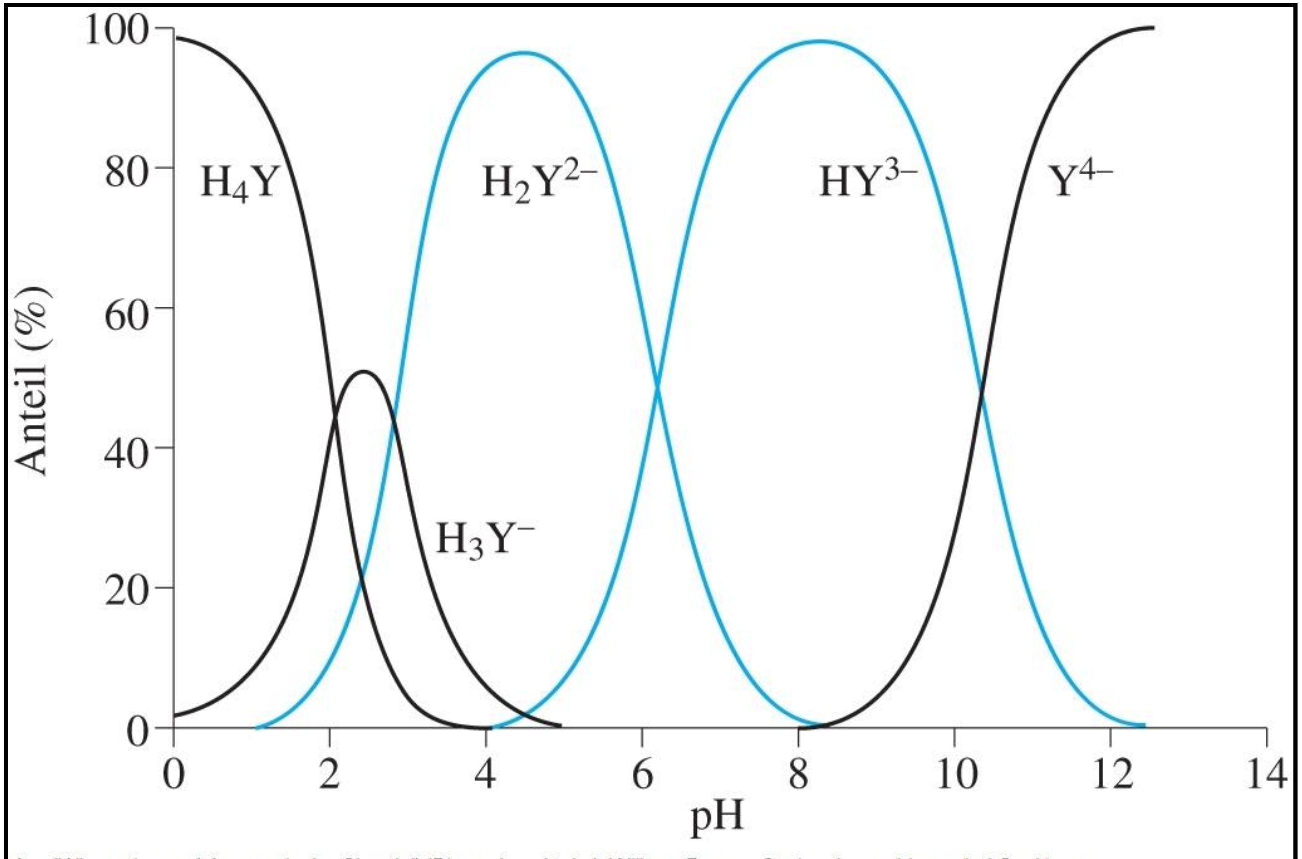
6. Volumetric Analysis

Complexometry

pH-dependance of the reaction with EDTA

At low pH-values EDTA is completely protonated, which is why only a limited number of metals form complexes with it

⇒ Zr^{4+}, Hf^{4+}, Th^{4+}, Bi^{3+}, Fe^{3+}



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6. Volumetric Analysis

Complexometry

pH dependence of the reaction with EDTA

In practice, one cannot work at high pH-values, otherwise the metals would be hydrolysed to their hydroxides!

The concentration/activity of Y^{4-} at the given pH-value must be taken into account (equilibrium activity)

$c(Y^{4-})_H = \alpha_{Y}{}^{4-} \cdot c_0(\mathrm{EDTA})$ **with** $c_0(\mathrm{EDTA}) = c(H_4Y) + c(H_3Y^-) + c(H_2Y^{2-}) + c(HY^{3-}) + c(Y)^{4-}$

$\alpha_{Y}{}^{4-}$ **describes the pH-dependant concentration (activity) of** Y^{4-}

$Me^{2+} + Y^{4-} \rightleftharpoons [MeY]^{2-}$

$$\boxed{K_K = \frac{c([M(Y)]^{2-})}{c(M^{2+}) \cdot c(Y^{4-})} = \frac{c([M(Y)]^{2-})}{c(M^{2+}) \cdot \alpha_{Y^{4-}} c_0(\mathrm{EDTA})}}$$

$\Rightarrow K_{eff} = K_K \cdot \alpha_{Y}{}^{4-}$

(effective stability constant)

6. Volumetric Analysis

Complexometry

pH dependence of the reaction with EDTA

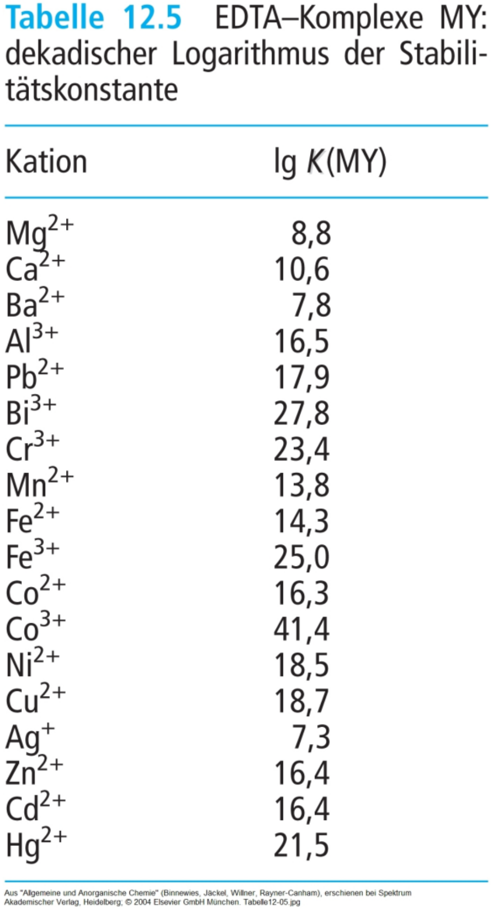

Tabelle 12.5 EDTA–Komplexe MY: dekadischer Logarithmus der Stabilitätskonstante

Kation	lg *K*(MY)
Mg^{2+}	8,8
Ca^{2+}	10,6
Ba^{2+}	7,8
Al^{3+}	16,5
Pb^{2+}	17,9
Bi^{3+}	27,8
Cr^{3+}	23,4
Mn^{2+}	13,8
Fe^{2+}	14,3
Fe^{3+}	25,0
Co^{2+}	16,3
Co^{3+}	41,4
Ni^{2+}	18,5
Cu^{2+}	18,7
Ag^{+}	7,3
Zn^{2+}	16,4
Cd^{2+}	16,4
Hg^{2+}	21,5

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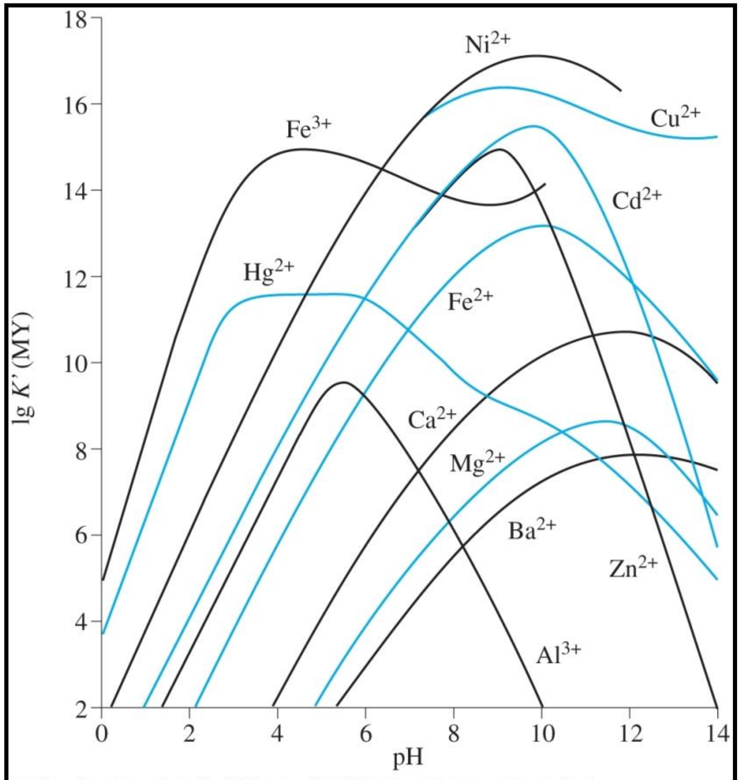
Effective stability constant of EDTA complexes



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7. Methodical Sequence of a Qualitative Analysis

Methodical Sequence of a Qualitative Analysis

1. **Preliminary tests**
   - **Heating in a glow tube**
   - **Flame colourisation**
   - **Phosphoric salt pearl**
   - **Borax pearl**
   - **Specialised preliminary tests**

2. **Detection of anions**
   - **From primary sample**
   - **From soda extraction**

3. **Separation of cations**

4. **Digestion**
   - **Soda-potash digestion**
   - **Acidic digestion**
   - **Oxidative digestion**
   - **Freiberger digestion**
   - **Specialised digestions**

8. Preliminary Tests

Preliminary Tests give a rough Idea about the Composition (or the Presence of Certain Substances) within the Sample

Hints

- **Preliminary tests are carried out prior to the actual analysis**
- **These tests only give hints (no proof!) on the presence or absence of a limited number of certain cat- and anions**
- **Since interference is a common problem, verification via a suitable individual test is mandatory**

Detailed description of primary substance

- **Colour: dependant on the amount of water of crystallisation, degree of decomposition, particle size**
- **Morphology: dust, powder, grains, flakes (fine- or rough)**
- **Hygroscopic properties: „sticks on the walls“**
- **Odour: „like vinegar“ acetates (CH_3COO^-) or „rotten eggs“ sulphides (S^{2-})**
- **Magnetic properties: Fe, Co, Ni, Fe_3O_4**

8. Preliminary Tests

Optical Preliminary Tests

Colour of sample (or how to wing your practical lab exercise...)

Blue	**$CoCl_2$, Cu(II) salts**
Brown	**$CoSO_4$, Ag_2O, CdO, PbO_2, Ag_3AsO_4, SnS, $Fe(OH)_3$, MnO_2, Bi_2S_3, V_2S_5, $Mo(OH)_3$, $PbCr_2O_7$, Ag_2CrO_4**
Crème	**V_2O_5**
Yellow	**As_2S_3, Bi_2O_3, $FeSO_4$, K_2CrO_4, $NiCl_2$, $NiSO_4$, PbO, WO_3, CdS, PbI_2, AgI, $PbCrO_4$, $BaCrO_4$, HgO, Ag_2HPO_4, CdO**
Green	**Cr_2O_3, $FeSO_4$, $Ni(NO_3)_2$, $NiCO_3$, $NiCl_2$, $NiSO_4$, $Cr(OH)_3$**
Orange	**Sb_2S_3, HgO, HgI_2, Hg_2CrO_4**
Pink	**$MnCl_2$, $MnCO_3$, $MnSO_4$, $CoCl_2$**
Red	**Fe_2O_3, HgI_2, HgS, Cu_2O, MnS, $Co(OH)_2$, Fe-thiocyanates, $K_2Cr_2O_7$**
Black	**Co_2O_3, CuO, HgS, Sb_2S_3, PbS, CuS, NiS, CoS, FeS, FeI_2, $Co(OH)_3$, $Cu(SCN)_2$, Ag_2S_3, $Mn(OH)_3$, $MnO(OH)_2$**
Violet	**$CoCO_3$, $KCr(SO_4)_2$, $KMnO_4$**

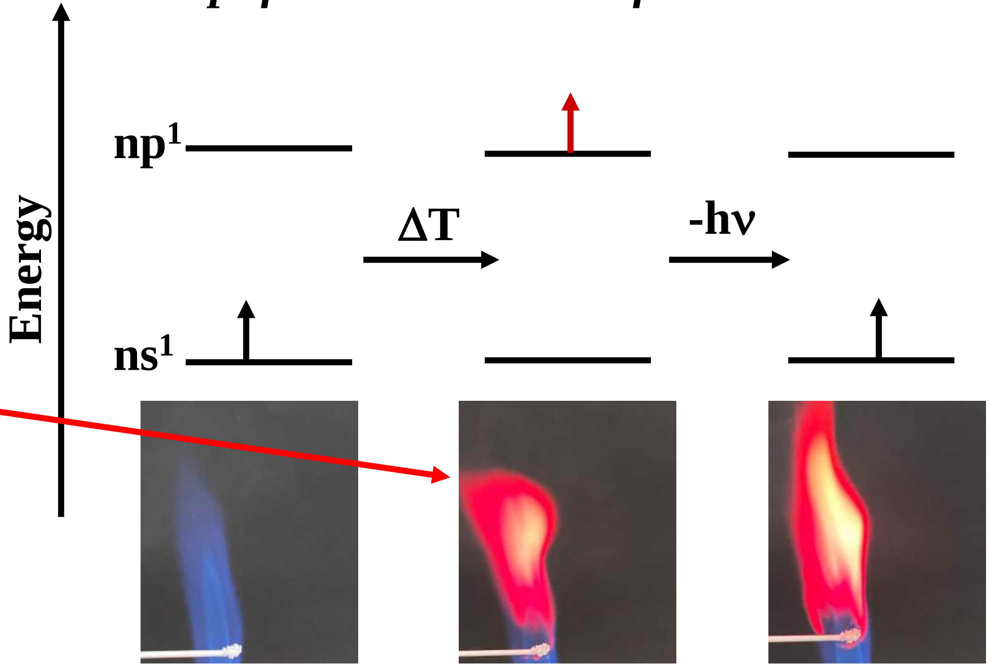
⇒ If there are several distinguishable agglomerates present, it is recommended to separate them and to investigate them individually

8. Preliminary Tests

Flame Colourisation: Thermal Excitation of Electrons can lead to the Emission of Visible Radiation and Colourisation of a Flame

Element	Colour	λ [nm]
Li	*crimson*	*670.8*
Na	*yellow*	*589.3*
K	*pale violet*	*768.2, 404.4*
Rb	*red violet*	*780, 421*
Cs	*blue violet*	*458*
Ca	brick-red	622.0, 553.3
Sr	red	red lines, 604.5
Ba	green	524.2, 513.7
Ga	violet	417.2, 403.3
In	violet	452.1
Tl	green	535.0
Cu	green	
Pb, As, Sb	pale blue	
V	pale green	
Se	bluish	
Te	pale blue	
Mo	pale green	

Simplified term scheme of alkaline metals

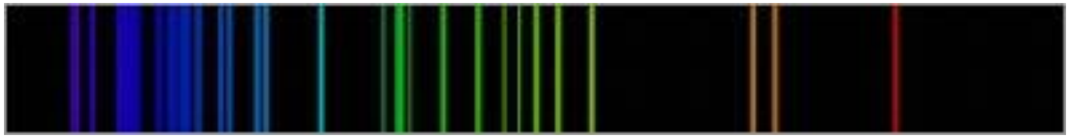


In the case of the alkaline metals, it is always the electron farthest from the core (ns^1) that is thermally excited. On relaxation, a photon with a distinct energy, which corresponds to the energy difference ΔE = hν between the first excited and the ground state, is emitted.

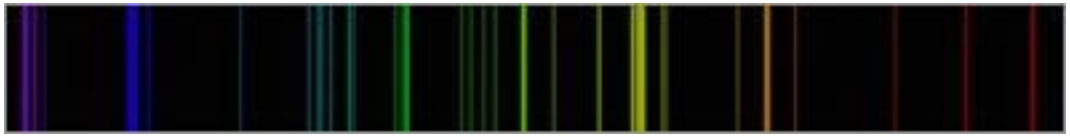
8. Preliminary Tests

The Flame Colourisation is like a Fingerprint for each Element

Emission spectrum of arsenic



Emission spectrum of lead



Emission spectrum of mercury

Every element possesses a unique emission spectrum which is composed of multiple spectral lines. The spectrum is unmistakable and can thus be used as a fingerprint → spectral analysis in analytical chemistry (AAS, ICP-OES) and astrophysics (exoplanets, exobiology, cosmology)

8. Preliminary Tests

Heating in Glow Tube

Execution

A small amount (mg) of the primary substance is added to a tube, which is closed at one side, and heated

Observation ⇒ release of gases

Type of gas	Origin	Colour	Odour
O_2	peroxides, chlorates, bromates	colourless	none
CO_2	carbonates, organic compounds	colourless	none
CO	oxalates, organic compounds	colourless	none (toxic)
$(CN)_2$	cyanides	colourless	bitter almonds (toxic)
SO_2	sulphides in air, sulphites, thiosulphates	colourless	piercing (corrosive)
HCl	chlorides	colourless	piercing (corrosive)
Cl_2	chlorides + oxidising substances (PbO_2)	light green	piercing
Br_2	bromides + oxidising substances	brown	piercing
I_2	iodides + oxidising substances	violet	piercing
NH_3	ammonium salts	colourless	piercing
NO_2	nitrates, nitrites	brown	piercing

8. Preliminary Tests

Borax and Phosphor Salt Pearl

Principle

If one melts borax ($Na_2B_4O_7$) or a phosphor salt (e.g. $NaNH_4HPO_4$) and adds a heavy metal salt, characteristic colourisations can occur (depends if the melting takes place in an oxidative or a reductive flame) through the formation of heavy metal borates or phosphates

Phosphor salt pearl ($NaNH_4HPO_4$)

Upon heating, $NaNH_4HPO_4$ transforms into meta- or polyphosphate $(NaPO_3)_x$ (x = 3 - 12)

$$NaNH_4HPO_4 \rightarrow NaPO_3 + NH_3\uparrow + H_2O\uparrow$$

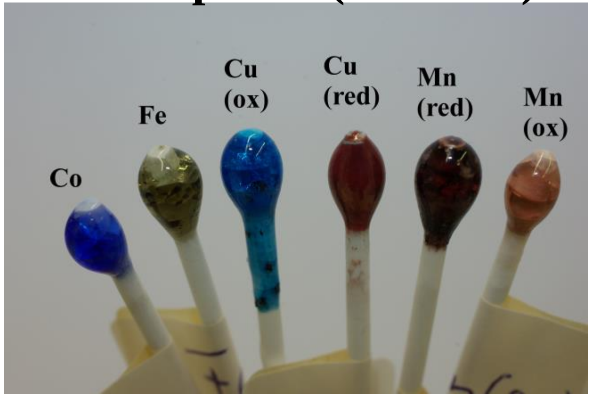
In the heat, meta phosphate is able to dissolve oxides and to drive out volatile acids from their respective salts

$$NaPO_3 + CoSO_4 \rightarrow NaCoPO_4 + SO_3\uparrow$$

Borax pearl ($Na_2B_4O_7$)

$$Na_2B_4O_7 + CoSO_4 \rightarrow 2\ NaBO_2 + Co(BO_2)_2 + SO_3\uparrow$$

Borax pearls (selection)



8. Preliminary Tests

Borax and Phosphor Salt Pearl

Course of action

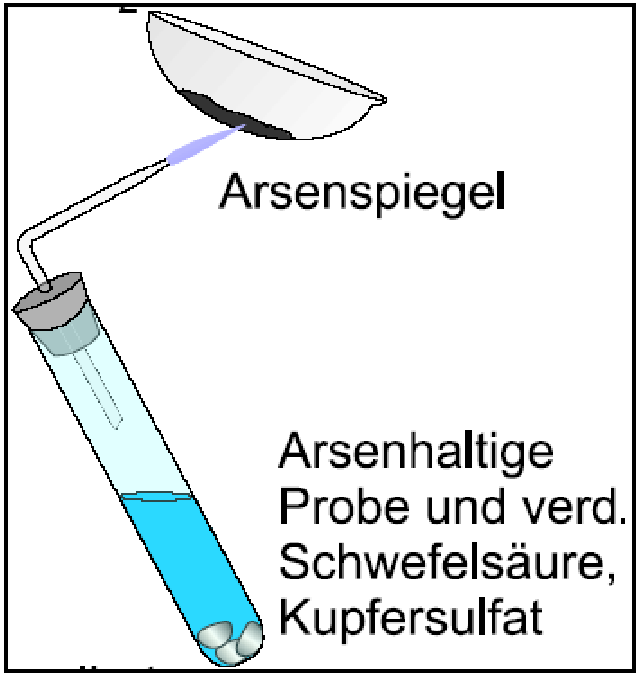
1. On spot plates, add some HCl (diluted) + phosphor salt/borax + primary substance
2. Magnesia rods in HCl (diluted) + phosphor salt/borax
3. Melt in hottest spot of the flame, until one gets a transparent melt (important: low amount of analyte & constant rotation of rod during melting)
4. Immerse pearl in HCl + AS (not too much!)
5. Hold in Bunsen burner flame (oxidative or reductive zone)

Cation	Oxidative flame	Reductive flame
Fe	yellow	light green
Mn	violet	colourless
Co	blue	blue
Ni	yellow-red	brown
Cr	emerald green	emerald green

Caution: this test is only valid for Co^{2+} (blue) and Cr^{3+} (green)

8. Preliminary Tests

Specialised Preliminary Tests



Marsh‘s test (detection of As and Sb)

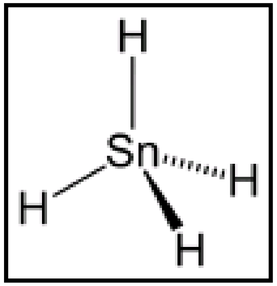
$As_2O_3 + 6\ Zn + 12\ H^+ \rightarrow 2\ AsH_3\uparrow + 6\ Zn^{2+} + 3\ H_2O$

$4\ AsH_3 + 3\ O_2 \rightarrow 4\ As + 6\ H_2O$ (oxidation)

$2\ AsH_3 \rightleftharpoons 2\ As + 3\ H_2$ (thermal decomposition)

Discrimination of antimony and arsenic: arsenic is soluble in freshly prepared ammoniacal hydrogen peroxide solution or in sodium hypochlorite solution

$2\ As + 5\ H_2O_2 + 6\ NH_3 \rightarrow 2\ AsO_4^{3-} + 6\ NH_4^+ + 2\ H_2O$



Glow test (detection of Sn through luminescence)

$Sn^{4+} + Zn \rightarrow Sn^{2+} + Zn^{2+}$

$Sn^{2+} + 6\ H$ (nascent hydrogen) $\rightarrow 2\ H^+ + SnH_4 \xrightarrow{3/2\ O_2} Sn^{2+} + 3\ H_2O$

$Sn^{2+} + 2\ Cl^- \rightarrow SnCl_2\uparrow$

$SnCl_2 + \Delta T \rightarrow SnCl_2^* \rightarrow SnCl_2 + h\nu$ (blue)

8. Preliminary Tests

Specialised Preliminary Tests

Molybdenum blue (detection of Mo)

If a small amount of a sample, which includes molybdenum of some sort, is combusted together with some drops of concentrated H_2SO_4 and subsequently solidified again, an intensive blue colouring will occur

$Mo^{VI}O_3$	→	$MoO_{3-x}(OH)_x$ (x = 0...2)	→	$Mo^{IV}O(OH)_2$
(white)		(blue)		(dark green)

Interferences

- **Tungsten forms a sky –blue oxide (tungsten blue) of the approximate composition $WO_{3-x}(OH)_x$ (x = 0...2)**
- **Vanadium causes a change of colour from light blue (VO^{2+}) to green (V^{3+})**

Sequence

- **Primary substance + some $SnCl_2$ + 20 ml conc. H_2SO_4 in an open pod, heated upon dryness, let it cool down ⇒ blue colour**

8. Preliminary Tests

Specialised Preliminary Tests

Detection of titanium

A small amount of primary substance is refluxed with conc. H_2SO_4 in a test tube and then brought to reaction with H_2O_2

$$\underset{\text{(white)}}{TiO_2(s)} \rightarrow \underset{\text{(colourless)}}{[Ti(OH)_2(H_2O)_4]^{2+}} \xrightarrow[-\,2\,H_2O]{+\,H_2O_2} \underset{\text{(yellow to yellow-orange)}}{[Ti(O_2)(H_2O)_4]^{2+}(aq)}$$

“Ligand-to-Metal CT”

Disturbances

- Titanium forms colourless $[TiF_6]^{2-}$ with fluoride

Sequence

- Primary substance + 5 ml conc. H_2SO_4 in test tube refluxed for ca. 5 minutes
- After cooling, 2 – 3 drops of 3 % H_2O_2-solution is added ⇒ yellow-/orange colour

9. Detection of Anions

Tests for Solubility

General course of action

- 1/4 tip of a spatula of the analyte in large test tube
- Fill test tube till half of the height with solvent
- Check solubility at rt and at elevated temperatures (caution: boiling retardation!)

Sequence of solvents

1. H_2O ⇒ measure pH-value
2. HCl (dil.)
3. HCl (conc.)
4. HNO_3 (dil.)
5. HNO_3 (conc.)
6. Aqua regia (1 fraction HNO_3 (conc.) + 3 fractions HCl (conc.))
7. H_2SO_4 (conc.)

Potential observations

- Change of colour and release of gases
- Substance is soluble = no residue or clouding of solution
- Poorly soluble residue ⇒ separation ⇒ washing ⇒ digestion

9. Detection of Anions

The Detection of Anions can partially be carried out on the Primary Sample, on the Soda Extraction and sometimes even on the Residual of the Soda Extraction

From primary sample: CO_3^{2-}, CH_3COO^-, S^{2-}, BO_3^{3-}, F^-, SiO_4^{4-}, PO_4^{3-}

From soda extraction: $S_2O_3^{2-}$, SO_3^{2-}, SO_4^{2-}, SCN^-, NO_3^-, NO_2^-, Cl^-, Br^-, I^-, ClO_3^-, BrO_3^-, IO_3^-

Purpose of soda extraction

- Cations are transformed into poorly soluble carbonates (exceptions are alkaline metals) in order to eliminate interferences during the detection of anions
- Transformation of anions into dissolved state (prerequisite for detection)

Course of action

- Re-slurry a mixture of 1 g primary substance + 3-5 times as much water-free soda (Na_2CO_3) in 50-100 ml of water (demineralised) and let it boil for at least 10 minutes
- Separate residue
- Acidify the filtrate and check for anions

9. Detection of Anions

Soda Extraction

Reaction

In general	$MA_2 + Na_2CO_3 \rightarrow MCO_3\downarrow + 2\,Na^+ + 2\,A^-$ (M = metal cation)
Example	$BaCl_2(aq) + Na_2CO_3(aq) \rightarrow BaCO_3(s)\downarrow + 2\,Na^+(aq) + 2\,Cl^-(aq)$

Filtrate

is highly alkaline at first

must be clear but not necessarily colourless

• yellow	chromate (CrO_4^{2-})
• violet	permanganate (MnO_4^-)
• blue	Cu^{2+}
• pink	$[Co(H_2O)_6]^{2+}$
• green	$[Cr(H_2O)_6]^{3+}$

⇒ soda extract still contains amphoteric metals: $[Al(OH)_4]^-$, $[Zn(OH)_4]^{2-}$, $[Sn(OH)_4]^{2-}$

⇒ they precipitate upon acidifying: $Al(OH)_3\downarrow$, $Zn(OH)_2\downarrow$, $Sn(OH)_2\downarrow$

9. Detection of Anions

Soda Extraction

Salt	K_L [mol²/l²]
AgCl	$1 \cdot 10^{-10}$
AgCN	$4 \cdot 10^{-12}$
AgSCN	$1 \cdot 10^{-12}$
AgBr	$4 \cdot 10^{-13}$
AgI	$1 \cdot 10^{-16}$

Treatment with $AgNO_3$

- Acidify filtrate of soda extraction with HNO_3 until pH ≅ 0
- Dropwise addition of $AgNO_3$ solution

Colour of precipitate	caused by
white	Cl^-, ClO_3^-, BrO_3^-, IO_3^-, CN^-, SCN^-, SO_3^{2-}
light yellow	Br^-
yellow	I^-
orange to red	CrO_4^{2-}
black	S^{2-}

AgX	Colour	Absorption of	Photo sensitivity of silver halides
AgCl	white	UV	
AgBr	light yellow	violet	↓
AgI	yellow	blue	

⇒ photographic pigments
⇒ sluggish decomposition
⇒ formation of Ag^0

9. Detection of Anions

Soda Extraction

Addition of $AgNO_3$

- The obtained precipitate must be filtered off and washed
- Subsequently treat with NH_3

$Ag^+ + 2\ NH_3 \rightleftharpoons [Ag^I(NH_3)_2]^+$ with $K_K = 1.67 \cdot 10^{-7}\ l^2/mol^2$

⇒ in solution: AgCl, AgBr, $AgBrO_3$, $AgIO_3$ and Ag_2SO_3

⇒ in residue: AgI, Ag_2S

- Treatment with cyanide

$Ag^+ + 2\ CN^- \rightleftharpoons [Ag^I(CN)_2]^-$ with $K_K = 1.0 \cdot 10^{-21}\ l^2/mol^2$ $[NC\text{-}Ag\text{-}CN]^-$ linear

⇒ even AgI is dissolved

Principle: the amount of free Ag^+ is decreased by complexation, which allows the more readily soluble precipitates to dissolve

9. Detection of Anions

Soda Extraction

Addition of $AgNO_3$

- Acidify filtrate of soda extraction with HNO_3 until pH ≅ 0
- Dropwise addition of Na_2SO_3 solution

$BrO_3^- + SO_3^{2-} + 2\ H^+ \rightarrow Br_2 + 5\ SO_4^{2-} + H_2O$

$Br_2 + SO_3^{2-} + 2\ H_2O \rightarrow 2\ Br^- + SO_4^{2-} + 2\ H_3O^+$

⇒ reduction of $Br^{+V}O_3^-$ (bromate) to Br^- (bromide)

- Dropwise addition of $AgNO_3$

$Br^- + Ag^+ \rightarrow AgBr\downarrow$

⇒ light yellow precipitate

9. Detection of Anions

Soda Extraction

Treatment with $CaCl_2$

- Acidify filtrate of soda extraction with acetic acid until pH ≅ 5
- Dropwise addition of $CaCl_2$ solution

⇒ observation of white precipitate

Precipitate consists of

MoO_4^{2-} (molybdate), WO_4^{2-} (tungstate), PO_4^{3-} (phosphate), $P_2O_7^{4-}$ (di-phosphate), VO_4^{3-} (vanadate), F^- (fluoride), $C_2O_4^{2-}$, (oxalate), $C_4H_4O_6^{2-}$ (tartrate)

- In high concentrations: SO_4^{2-}
- At elevated temperatures: SO_3^{2-}

Note: do not use too much acetic acid, otherwise the dilution will be to high!

9. Detection of Anions

Soda Extraction

Treatment with $KMnO_4$ (test on reducing substances)

- Acidify filtrate of soda extraction with diluted H_2SO_4 until pH ≅ 0
- Dropwise addition of $KMnO_4$ solution

⇒ if the $KMnO_4$ solution decolours, there are reducing anions present in the soda extraction

At room temperature

Br^-(bromide), I^- (iodide), SCN^- (thiocyanate), S^{2-} (sulphide), SO_3^{2-} (sulphite) , $S_2O_3^{2-}$ (thiosulphate), $C_2O_4^{2-}$ (oxalate), NO_2^- (nitrite), AsO_3^{3-} (arsenide)

At elevated temperatures

$S_2O_8^{2-}$ (peroxo di-sulphate), $C_4H_4O_6^{2-}$ (tartrate)

Note: no precipitation but redox reaction!

9. Detection of Anions

Soda Extraction

Treatment with I_2/starch (test on reducing substances)

- **Acidify filtrate of soda extraction with HCl until pH ≅ 0**
- **Dropwise addition of I_2/starch solution (blue)**

⇒ If the I_2/starch solution decolours, there are reducing anions present in the soda extraction

$$2\ S_2O_3^{2-} + I_2 \rightarrow 2\ I^- + S_4O_6^{2-}$$

Reduction of: I^0 to I^-

Oxidation of: S^{+II} to $S^{+2.5}$

Note: Cl_2 and Br_2 will be reduced by $S_2O_3^{2-}$, too
thereby $S_2O_3^{2-}$ is oxidised to SO_4^{2-}

9. Detection of Anions

Soda Extraction

Treatment with KI/starch (test on oxidising substances)

- Acidify filtrate of soda extraction with HCl until pH ≅ 0
- Dropwise addition of KI/starch solution

⇒ blue colour occurs, if oxidising anions are present in the soda extraction

I^- is oxidised to I_2, which forms a blue inclusion compound with starch (amylose)

example: $Cl^{V}O_3^- + 6\,I^- + 6\,H^+ \rightarrow 3\,I_2 + Cl^- + 3\,H_2O$

Oxidation of iodide to iodine through:

- ClO^- (hypochlorite), CrO_4^{2-}, NO_2^-, $S_2O_8^{2-}$, ClO_3^-, BrO_3^-, IO_3^-, MnO_4^-, NO_3^-, Cu^{2+}, Fe^{3+}
- Weak reaction for: AsO_4^{3-} (arsenate)

Note: no precipitation but redox reaction!

9. Detection of Anions

Detection of individual Anions (from Soda Extraction)

Sulphate SO_4^{2-}

- Acidify soda extraction with diluted HCl until pH ≅ 0
- Dropwise addition of $BaCl_2$ solution (10%)

$Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4\downarrow$ (white)

Barium sulphate is poorly soluble in diluted mineral acids and concentrated HCl, but it readily dissolves in hot concentrated H_2SO_4 under formation of a complex

Peroxo di-sulphate $S_2O_8^{2-}$

- Acidify soda extraction and reflux

$S_2O_8^{2-} + H_2O \rightarrow SO_4^{2-} + HSO_5^{-} + H^+$

$HSO_5^{-} + H_2O \rightarrow HSO_4^{-} + H_2O_2$

- Dropwise addition of $BaCl_2$ solution (10%)

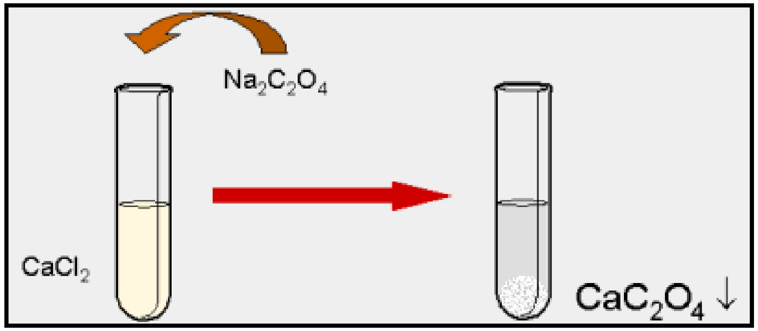
$Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4\downarrow$ (white) → white standard in spectroscopy

9. Detection of Anions

Detection of individual Anions (from Soda Extraction)

Oxalate $C_2O_4^{2-}$

- Acidify filtrate of soda extraction with acetic acid until pH ≅ 5
- Dropwise addition of $CaCl_2$ solution



$Ca^{2+} + C_2O_4^{2-} \rightarrow CaC_2O_4\downarrow$ (white)

(forms kidney stone in kidney or bladder)

Additional probing for oxalate

1. With concentrated H_2SO_4

$C_2O_4^{2-} + 2\ H^+ \rightarrow CO_2\uparrow + CO\uparrow + H_2O \Rightarrow$ disproportionation

2. With $KMnO_4$

$5\ H_2C_2O_4 + 2\ MnO_4^- + 6\ H^+ \rightarrow 2\ Mn^{2+} + 10\ CO_2\uparrow + 8\ H_2O$

9. Detection of Anions

Detection of individual Anions (from Soda Extraction)

Thiocyanate SCN^-

- Acidify filtrate of soda extraction with diluted HNO_3 until pH ≅ 0
- Dropwise addition of $FeCl_3$ solution (freshly made!)

$Fe^{3+} + 3\ SCN^- \rightarrow Fe(SCN)_3\downarrow$ (crimson)

Additional tests for thiocyanate

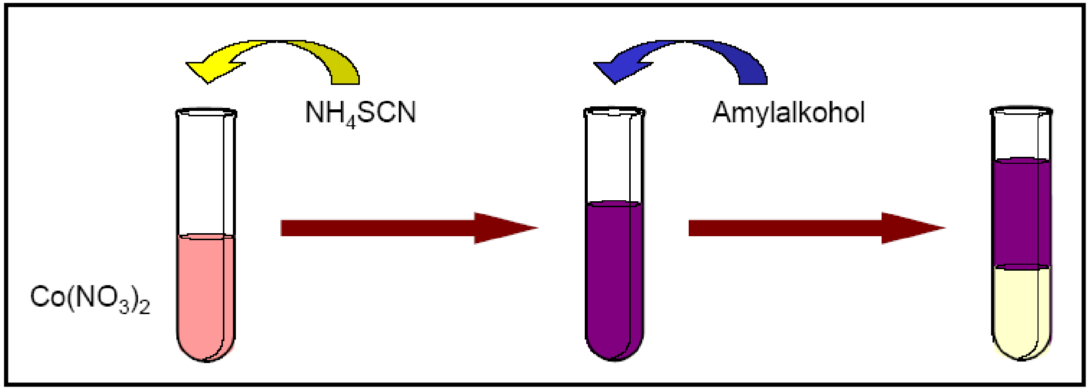
1. With $CuSO_4$

$2\ SCN^- + Cu^{2+} \rightarrow Cu^{II}(SCN)_2\downarrow$ (black)

2. With $Co(NO_3)_2$

$Co^{2+} + 2\ SCN^- \rightleftharpoons Co(SCN)_2\downarrow$ (blue)

$Co(SCN)_2 + 2\ SCN^- \rightleftharpoons [Co^{II}(SCN)_4]^{2-}$ (blue)



$Co(SCN)_2$ is neutral and soluble in amyl alcohol (amyl alcohol = 1-pentanol $C_5H_{11}OH$)

9. Detection of Anions

Detection of individual Anions (from Soda Extraction)

Nitrite NO_2^- and nitrate NO_3^-

Since nitrite disturbs the detection of nitrate (ring test or Lunge's reagent), it must be removed prior to detection:

- $HNO_2 + NH_3 \rightarrow N_2 + 2\ H_2O$
- $HNO_2 + HN_3 \rightarrow N_2 + N_2O + H_2O$
- $2\ HNO_2 + (NH_2)_2CO \rightarrow N_2 + CO_2 + 3\ H_2O$

1. Ring test

- **Acidify filtrate of soda extraction with diluted H_2SO_4**
- **Add some $FeSO_4$**
- **Add a sub-layer of concentrated H_2SO_4 underneath the solution**

⇒ formation of brown ring, if NO_3^- is present

$NO_3^- + 3\ Fe^{2+} + 4\ H^+ \rightarrow 3\ Fe^{3+} + NO + 2\ H_2O$

$NO + [Fe^{II}(H_2O)_6]^{2+} \rightarrow H_2O + [Fe^{II}(NO)(H_2O)_5]^{2+}$ **(brown)**

9. Detection of Anions

Detection of individual Anions (from Soda Extraction)

Nitrite NO_2^- and nitrate NO_3^-

2. Lunge's reagent

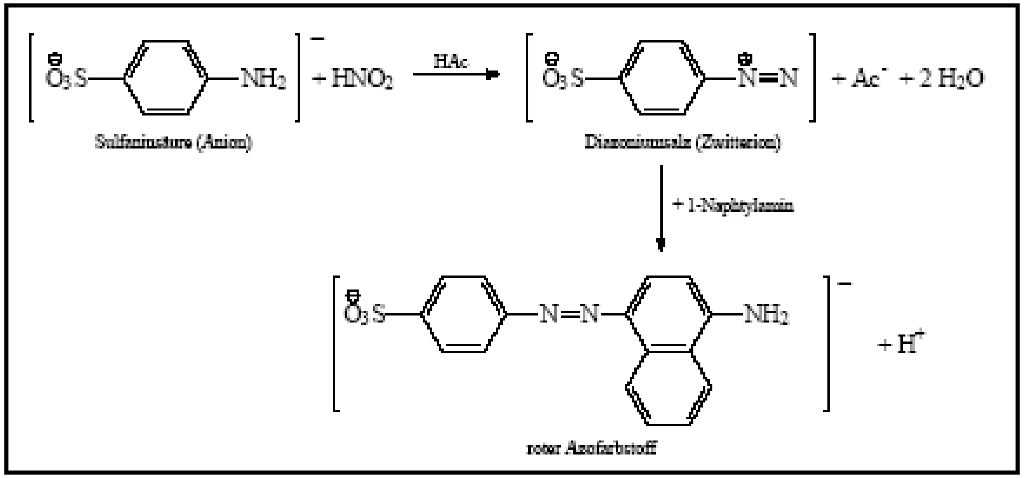
- Acidify filtrate of soda extraction with diluted acetic acid
- Add sulphanilic acid and α-naphthylamine solution
- Add a Zn granule (for NO_3^- detection only!)

⇒ formation of red colour upon presence of NO_2^-/NO_3^-

$NO_3^- + Zn + 2\,H^+ \rightarrow NO_2^- + Zn^{2+} + H_2O$

$NO_2^- + H^+ \rightarrow HNO_2$

$Ph\text{-}NH_2 + HNO_2 + H^+ \rightarrow Ph\text{-}N{\equiv}N^+ + 2\,H_2O$



9. Detection of Anions

Detection of individual Anions (from Soda Extraction)

Chloride Cl^-

- Acidify filtrate of soda extraction with diluted nitric acid
- Dropwise addition of $AgNO_3$ solution

⇒ precipitation of white to yellow solid, if Cl^- is present

$Ag^+ + X^- \rightarrow AgX\downarrow$ (white to yellow) problem: bromide and iodide precipitate, too!

- Wash with $(NH_4)_2CO_3$ solution
- Addition of NaBr or KBr solution

⇒ solely AgCl reacts to the di-amine complex and Ag^+ precipitates upon addition of Br!

$AgCl + 2\ NH_3 \rightarrow [Ag^I(NH_3)_2]^+ + Cl^-$

$[Ag^I(NH_3)_2]^+ + Br^- \rightarrow AgBr\downarrow + 2\ NH_3$

9. Detection of Anions

Detection of individual Anions (from Soda Extraction)

Bromide Br^- next to iodide I^-

- Acidify filtrate of soda extraction with diluted sulphuric acid and add a sub-layer of CCl_4 (carbon tetrachloride) or $CHCl_3$ (chloroform) underneath solution
- Slow dropwise addition of Cl_2 water

⇒ colouring of organic phase, if Br^- or I^- are present

$2\ I^- + Cl_2 \rightarrow 2\ Cl^- + I_2$ (violet)

$2\ Br^- + Cl_2 \rightarrow 2\ Cl^- + Br_2$ (brown)

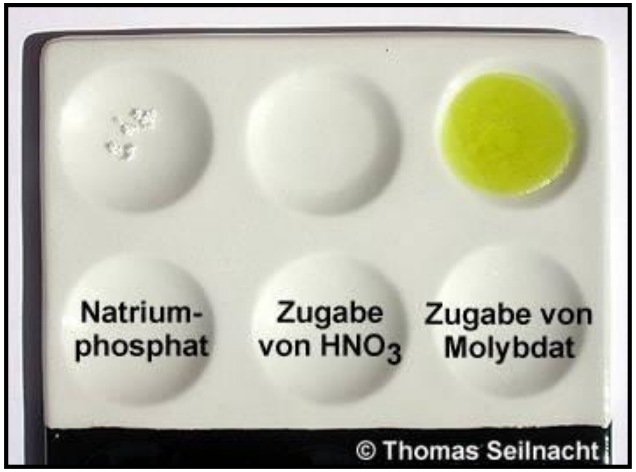
- Further addition of Cl_2 water ⇒ decolouring

$I_2 + 5\ Cl_2 + 6\ H_2O \rightarrow 2\ HIO_3 + 10\ HCl$ (colourless)

$Br_2 + Cl_2 \rightarrow 2\ BrCl$ (pale yellow, like white wine)

9. Detection of Anions

Detection of individual Anions (from Soda Extraction)



Phosphate PO_4^{3-}

- Acidify filtrate of soda extraction with diluted nitric acid
- Add saturated ammonium molybdate solution
- Add some drops of concentrated NH_3 solution

⇒ yellow precipitate, if PO_4^{3-} is present

$$HPO_4^{2-} + 23\ H^+ + 3\ NH_4^+ + 12\ MoO_4^{2-} \rightarrow (NH_4)_3[P(Mo_3O_{10})_4]\downarrow + 12\ H_2O$$

$[P(Mo_3O_{10})_4]^{3-}$ is the anion of the hetero-polyacid

Remember: phosphates interfere with the separation of the cations, because they might form poorly soluble salts with Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+} and Li^+

⇒ must be removed prior to separation of cations

9. Detection of Anions

Detection of individual Anions (from Primary Substance)

Acetate CH_3COO^-

- 0.1 - 0.2 g of primary substance are ground together with $KHSO_4$

⇒ piercing smell (of vinegar), if acetate anions are present

$$2\ CH_3COONa + 2\ KHSO_4 \rightleftharpoons K_2SO_4 + Na_2SO_4 + 2\ CH_3COOH\uparrow$$

Ponal (wood glue) = polyvinyl acetate in aqueous suspension

Complementary tests for acetate

- Addition of a Fe(III)-salt-solution to primary substance

⇒ crimson/red colour of sample, if acetate anion is present

$$3\ Fe^{3+} + 9\ CH_3COO^- + 2\ H_2O \rightarrow [Fe^{III}{}_3(OH)_2(CH_3COO)_6]^+ + CH_3COO^- + 2\ CH_3COOH$$

9. Detection of Anions

Detection of individual Anions (from Primary Substance)

Borate BO_3^{3-}

- In a test tube, 0.1 - 0.2 g of primary substance are added to 1-2 ml of methanol
- Addition of some drops of concentrated sulphuric acid
- Following the reaction, the mixture is heated and the fumes ignited

⇒ green colouring of flames, if borate is present

$BO_3^{3-} + 3\ H^+ \rightarrow H_3BO_3$

$H_3BO_3 + 3\ CH_3OH \rightarrow B(OCH_3)_3 + 3\ H_2O$ (acid catalysed esterification)

⇒ boric acid tri-methyl ester burns with green flame

The experiment can be performed in a porcelain crucible!

9. Detection of Anions

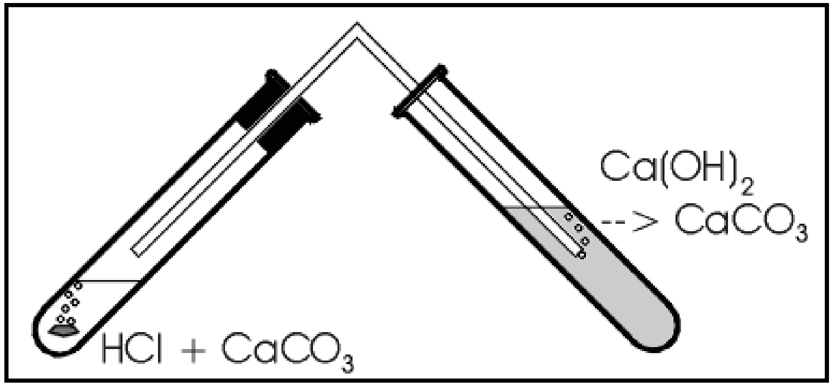
Detection of individual Anions (from Primary Substance)

Carbonate CO_3^{2-}

- In a test tube, 0.1 - 0.2 g of primary substance are added to 1-2 ml of 10% HCl
- The test tube is sealed with a fermentation tube, filled with baryte or lime water i.e. $Ba(OH)_2$ or $Ca(OH)_2$ dissolved in H_2O
- Subsequent heating drives formed CO_2 through the baryte or lime water

⇒ white clouding of solution, if carbonate is present in primary substance

$$CO_3^{2-} + 2\,H^+ \rightleftharpoons H_2CO_3 \rightarrow H_2O + CO_2\uparrow$$



Reactions in fermentation tube:

$$CO_2\uparrow + 2\,OH^- \rightleftharpoons CO_3^{2-} + H_2O$$

$$CO_3^{2-} + Me^{2+} \rightarrow MeCO_3\downarrow$$

$$MeCO_3 + H_2O + CO_2 \rightleftharpoons Me(HCO_3)_2$$

(→ formation of dripstone caves)

upon CO_2 excess, carbonates dissolve as hydrogen carbonates

9. Detection of Anions

Detection of individual Anions (from Primary Substance)

Fluoride F^-

- In a lead or platinum crucible, 0.1 – 0.2 g of primary substance are combined with concentrated sulphuric acid
- The crucible is covered by a watch glass and heated cautiously

⇒ the watch glass will be etched slightly, if the sample contains fluorides (etching test)

$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2\ HF\uparrow$

$SiO_2\ (glass) + 4\ HF \rightarrow SiF_4\uparrow + 2\ H_2O$

Creep test

- Some mg of primary substance are heated in a dried test tube together with a small amount of concentrated H_2SO_4
- Originating HF etches the inner wall of the test tube, so that H_2SO_4 can not wet the glass wall any more

⇒ if the test tube is then turned upside down, the H_2SO_4 drips off the test tube wall

9. Detection of Anions

Detection of individual Anions (from Primary Substance)

Silicate SiO_3^{2-}

- In a lead crucible, 0.1 – 0.2 g of primary substance are mixed with calcium fluoride in a 1:1 ratio
- Then, concentrated H_2SO_4 is added until a mushy texture is reached
- The crucible is covered by a black and moist filter paper and heated cautiously in a water bath

⇒ white spots will form on the filter paper, if the sample contains silicates

$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2\ HF\uparrow$

$SiO_3^{2-} + 4\ HF + 2\ H^+ \rightarrow SiF_4\uparrow + 3\ H_2O$

SiF_4 is hydrolysed on moist filter paper:

$3\ SiF_4 + 3\ H_2O \rightarrow H_2SiO_3$ (white gel) $+ 2\ H_2SiF_6$

$H_2SiO_3 \rightarrow H_2O + SiO_2$

9. Detection of Anions

Detection of individual Anions (from Primary Substance)

Sulphide S^{2-}

- 0.1 – 0.2 g of primary substance are acidified by diluted HCl in a test tube

⇒ stink of rotten eggs, if sulphides are present

$S^{2-} + 2\ HCl \rightarrow 2\ Cl^- + H_2S\uparrow$

Small amounts of hydrogen sulphide can be detected with moist lead acetate paper:

$Pb(CH_3COO)_2 + H_2S \rightarrow PbS\downarrow$ (black) $+ 2\ CH_3COOH$

Complementary tests

- Addition of $Cd(CH_3COO)_2$ solution to soda extraction

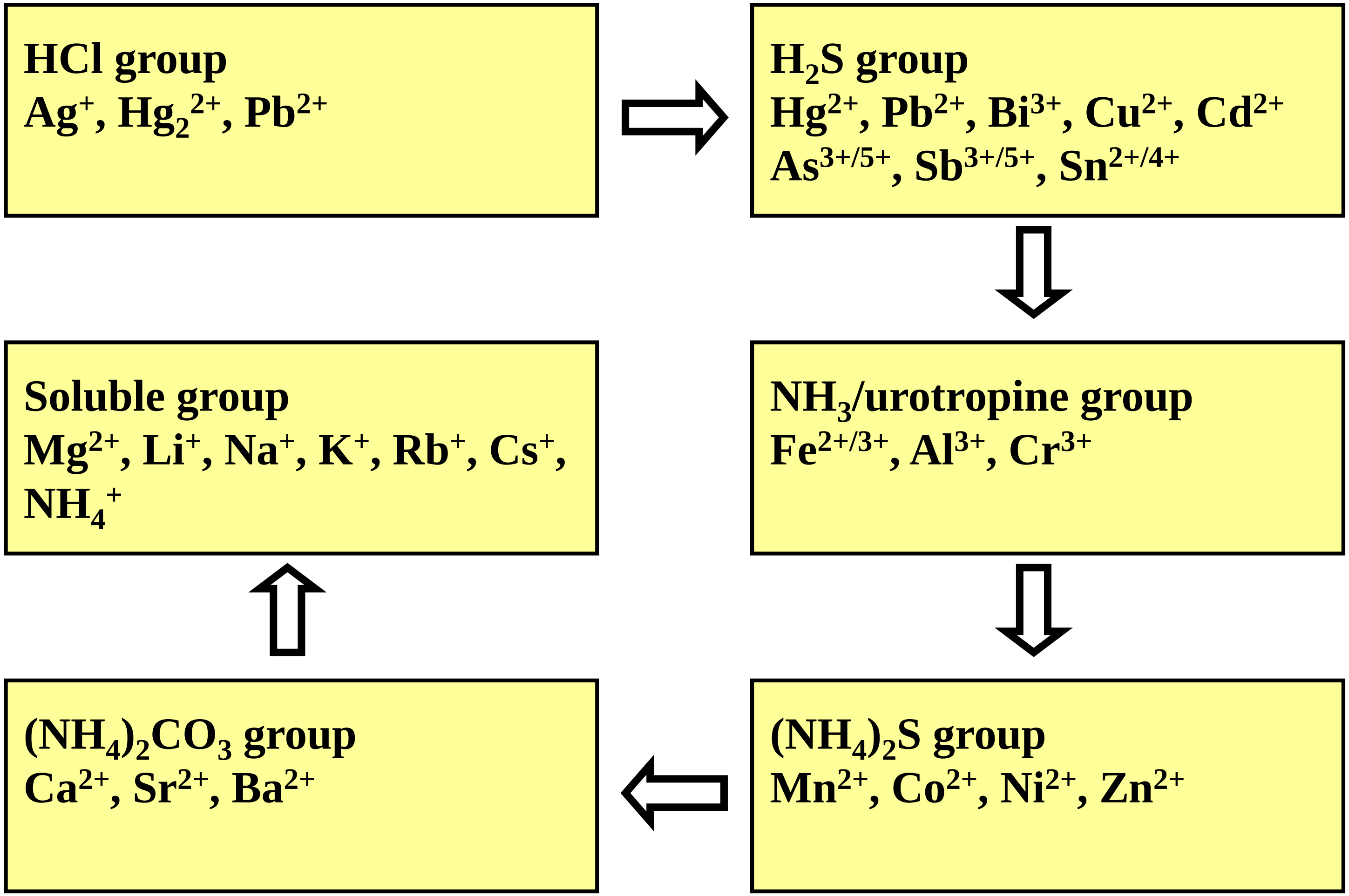
$Cd(CH_3COO)_2 + H_2S \rightarrow CdS\downarrow$ (yellow) $+ 2\ CH_3COOH$

10. Separation Process for Cations

Overview of the Separation Process for Cations

Groups

1. HCl
2. H_2S
3. NH_3/urotropine
4. $(NH_4)_2S$
5. $(NH_4)_2CO_3$
6. Soluble group



HCl group
Ag^+, Hg_2^{2+}, Pb^{2+}

H_2S group
Hg^{2+}, Pb^{2+}, Bi^{3+}, Cu^{2+}, Cd^{2+}
$As^{3+/5+}$, $Sb^{3+/5+}$, $Sn^{2+/4+}$

NH_3/urotropine group
$Fe^{2+/3+}$, Al^{3+}, Cr^{3+}

$(NH_4)_2S$ group
Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}

$(NH_4)_2CO_3$ group
Ca^{2+}, Sr^{2+}, Ba^{2+}

Soluble group
Mg^{2+}, Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+

10. Separation Process for Cations

Solubility of Salts

⇒ determined by lattice and hydration enthalpy

Lattice enthalpy

Energy, which is released, when a crystalline compound is formed from its gaseous components (atoms, molecules or ions). The unit is stated in kJ/mol.

Order of magnitude depends on: ionic charge, ionic radius, ratio of ionic radii, covalency

Hydration enthalpy

Energy, which is released, when a (gaseous) ion is hydrated. The unit is stated in kJ/mol, too.

Order of magnitude depends on: ionic charge, ionic radius, polarity of solvent, i.e. strength of interaction between ions and solvent molecules

10. Separation Process for Cations

HCl Group

Ag^+, Pb^{2+}, Hg_2^{2+} ⇒ precipitation as chlorides

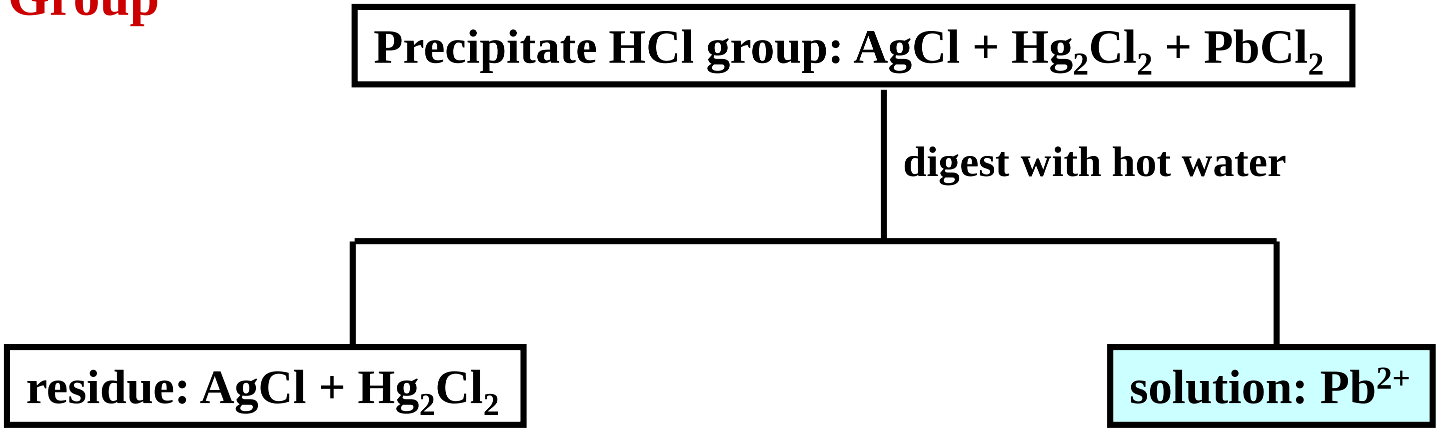
Reaction	pK_L	
$Hg_2^{2+} + 2\,Cl^- \rightarrow Hg_2Cl_2\downarrow$	17.9	
$Ag^+ + Cl^- \rightarrow AgCl\downarrow$	9.7	
$Pb^{2+} + 2\,Cl^- \rightarrow PbCl_2\downarrow$	4.8	incomplete precipitation!

Work instructions

- The nitric or hydrochloric suspension from the solubility test has to be refluxed, cooled down and filtrated
- Acidify the solution with HNO_3 and HCl
- Centrifugate or filtrate
  - Precipitate: HCl group
  - Centrifugate / filtrate: further groups (H_2S group)

10. Separation Process for Cations

HCl Group



Precipitate HCl group: $AgCl + Hg_2Cl_2 + PbCl_2$

digest with hot water

residue: $AgCl + Hg_2Cl_2$

solution: Pb^{2+}

Solubility increases with increasing temperature

$Pb^{2+} + 2\ Cl^- \rightarrow PbCl_2$ $\qquad K_L(20\ ^\circ C) = 9.4 \cdot 10^{-6}$

$K_L(90\ ^\circ C) = 3.0 \cdot 10^{-5}$

Problems

- $PbCl_2$ re-precipitates from concentrated solutions
- $PbCl_2$ is soluble in hot HCl, and can thus be easily dragged into the H_2S group

10. Separation Process for Cations

HCl Group

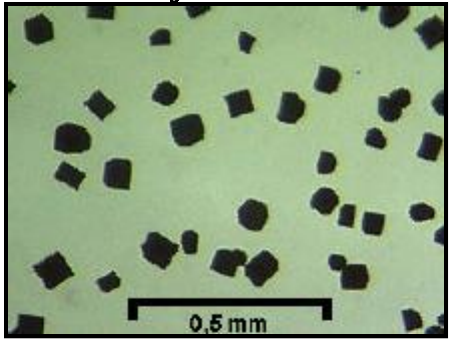
Solution: Pb^{2+}

concentrate solution + cool down → **$PbCl_2$** – transparent needles

dropwise addition of 2n H_2SO_4 → **$PbSO_4$** – white solid

add K_2CrO_4 to solution + acidify with CH_3COOH (pH 5) → **$PbCrO_4$** – yellow solid

add a mixture of glacial acetic acid, NH_4CH_3COO, (Cu acetate) + KNO_2 → **$K_2CuPb(NO_2)_6$** – black crystals



Problems

- $PbSO_4$ dissolves in concentrated H_2SO_4 and forms the complex acid $H_2[Pb(SO_4)_2]$
- Lead chromate is poorly soluble, but lead di-chromate is not

  $Pb^{2+} + CrO_4^{2-} \rightarrow PbCrO_4$ $K_L = 3.2\cdot10^{-11}$

  poorly soluble in CH_3COOH, NH_3

  soluble in NaOH, HNO_3

  $2\ CrO_4^{2-} + 2\ H_3O^+ \rightleftharpoons Cr_2O_7^{2-} + 3\ H_2O$ $K = 3.5\cdot10^{14}$

10. Separation Process for Cations

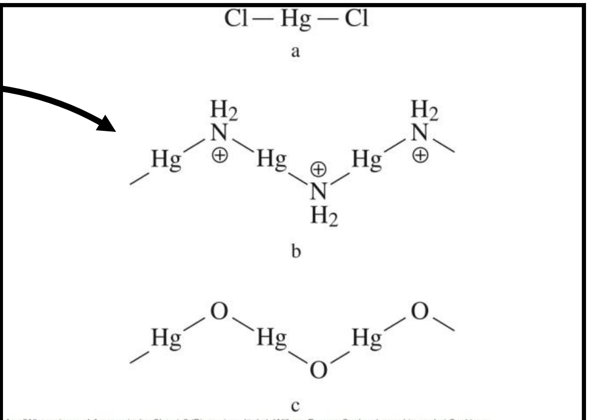
HCl Group

Residue: $AgCl + Hg_2Cl_2$

**pour a mixture of NH_4OH
and H_2O (1:1) over the residue**

solution: $[Ag(NH_3)_2]^+$

$Hg + [Hg(NH_2)]Cl$



Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung24-49.jpg

1. **Formation of poorly soluble silver di-amine complex $[Ag(NH_3)_2]^+$**

   $AgCl + 2\ NH_3 \rightarrow [Ag^{I}(NH_3)_2]^+ + Cl^-$

2. **Blackening of white residue due to formation of metallic Hg^0**

   $Hg_2^{2+} + 2Cl^- + 2\ NH_3 \rightarrow [Hg^{II}(NH_3)_2]Cl_2 + Hg^0$

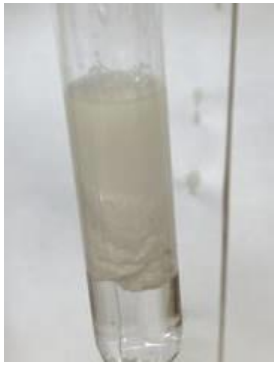
   $[Hg^{II}(NH_3)_2]Cl_2 \rightarrow [Hg^{II}(NH_2)]Cl + NH_4^+ + Cl^-$

   Combination of black metallic mercury and white mercury(II)-amide chloride = calomel („pleasant black“)

10. Separation Process for Cations

HCl Group

Solution: $[Ag(NH_3)_2]^+$



acidify with 2n HCl

AgCl

heat upon dryness

$[Ag(NH_3)_2]Cl$

decomposition of $[Ag(NH_3)_2]^+$ leads to precipitation of white AgCl

$AgCl + 2\ NH_4^+ + OH^- \rightleftharpoons [Ag^{I}(NH_3)_2]^+ + Cl^- + H_2O$

acidification decreases concentration of OH^-

⇒ shifting the equilibrium to the left side

octahedral, transparent to black crystals

$[Ag^{I}(NH_3)_2]Cl + h\nu$

$\rightarrow Ag^{0} + \frac{1}{2}\ Cl_2 + 2\ NH_3$

10. Separation Process for Cations

H_2S Group

Filtrate/centrifugate of HCl group: Hg^{2+}, Pb^{2+}, Bi^{3+}, Cu^{2+}, Cd^{2+}, $As^{3+/5+}$, $Sb^{3+/5+}$, $Sn^{2+/4+}$

pass H_2S through the hydrochloric solution (pH 0-2)

add thio-acetic amide CH_3CSNH_2 + hydrolyse:
$CH_3CSNH_2 + 2\,H_2O \rightarrow CH_3COO^- + NH_4^+ + H_2S$

precipitate: HgS, PbS, Bi_2S_3, CuS, CdS, As_2S_3, As_2S_5, Sb_2S_3, Sb_2S_5, SnS, SnS_2

The concentration of sulphide depends on pH-value ⇒ stepwise precipitation possible!

Problems

- **If nitrates are present (e.g. from aqua regia), one must add concentrated HCl and heat until no brown fumes originate any more:**

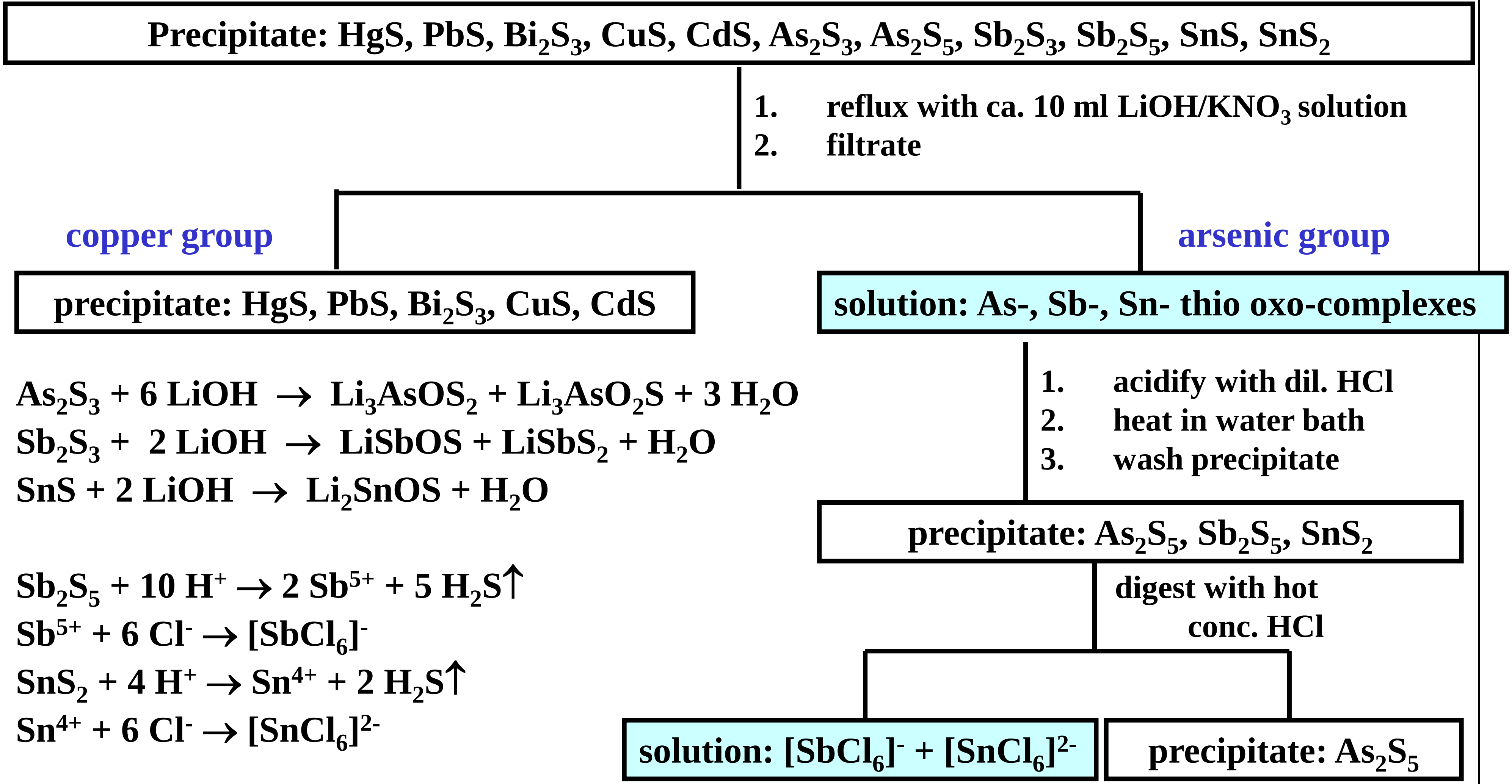
  $HCl \rightarrow H^+ + Cl^-$ $\quad pK_S = -7.0$ $\qquad HNO_3 \rightarrow H^+ + NO_3^-$ $\quad pK_S = -1.37$

  $4\,NO_3^- + 4\,H^+ \rightarrow 2\,H_2O + 2\,N_2O_4\uparrow + O_2\uparrow$

  otherwise sulphides will be oxidised to sulphur (this also happens, if H_2O_2 is present)
- **Solution can be yellow (CrO_4^{2-}) or violet (MnO_4^-). In order to reduce these coloured anions, ethanol should be added dropwise to the refluxing solution, until the solution becomes transparent or pale green/blue-green.**

10. Separation Process for Cations

H_2S Group



Precipitate: HgS, PbS, Bi_2S_3, CuS, CdS, As_2S_3, As_2S_5, Sb_2S_3, Sb_2S_5, SnS, SnS_2

1. reflux with ca. 10 ml LiOH/KNO_3 solution
2. filtrate

copper group

precipitate: HgS, PbS, Bi_2S_3, CuS, CdS

arsenic group

solution: As-, Sb-, Sn- thio oxo-complexes

1. acidify with dil. HCl
2. heat in water bath
3. wash precipitate

precipitate: As_2S_5, Sb_2S_5, SnS_2

digest with hot conc. HCl

solution: $[SbCl_6]^- + [SnCl_6]^{2-}$

precipitate: As_2S_5

$As_2S_3 + 6\ LiOH \rightarrow Li_3AsOS_2 + Li_3AsO_2S + 3\ H_2O$

$Sb_2S_3 + 2\ LiOH \rightarrow LiSbOS + LiSbS_2 + H_2O$

$SnS + 2\ LiOH \rightarrow Li_2SnOS + H_2O$

$Sb_2S_5 + 10\ H^+ \rightarrow 2\ Sb^{5+} + 5\ H_2S\uparrow$

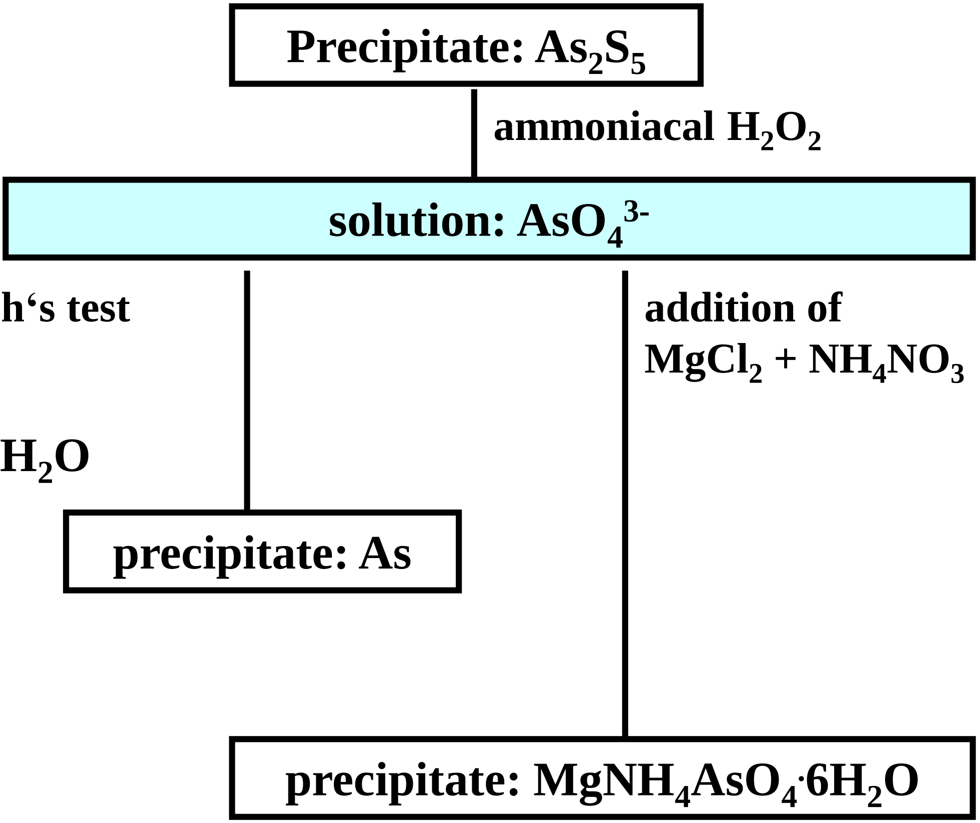
$Sb^{5+} + 6\ Cl^- \rightarrow [SbCl_6]^-$

$SnS_2 + 4\ H^+ \rightarrow Sn^{4+} + 2\ H_2S\uparrow$

$Sn^{4+} + 6\ Cl^- \rightarrow [SnCl_6]^{2-}$

10. Separation Process for Cations

H_2S Group



Precipitate: As_2S_5

ammoniacal H_2O_2

solution: AsO_4^{3-}

Marsh‘s test

addition of $MgCl_2 + NH_4NO_3$

precipitate: As

precipitate: $MgNH_4AsO_4 \cdot 6H_2O$

Oxidation of sulphides

$As_2S_5 + 16\ OH^- \rightarrow 2\ AsO_4^{3-} + 5\ S^{2-} + 8\ H_2O$

$S^{2-} + 4\ HO_2^- \rightarrow SO_4^{2-} + 4\ OH^-$

Marsh‘s test

$AsO_4^{3-} + 4\ Zn + 11\ H^+ \rightarrow AsH_3\uparrow + 4\ Zn^{2+} + 4\ H_2O$

$4\ AsH_3 + 3\ O_2 \rightarrow 4\ As\downarrow + 6\ H_2O$

As-mirror, soluble in ammoniacal H_2O_2

solution:

$2\ As + 5\ H_2O_2 + 6\ OH^- \rightarrow 2\ AsO_4^{3-} + 8\ H_2O$

Precipitation as magnesium ammonium arsenate

$AsO_4^{3-} + NH_4^+ + Mg^{2+} + 6\ H_2O \rightarrow MgNH_4AsO_4 \cdot 6H_2O$

10. Separation Process for Cations

H_2S Group

Reduction of Sn^{4+}

$Sn^{4+} + Fe \rightarrow Sn^{2+} + Fe^{2+}$

Reduction of Sb^{5+}

$2\ H[SbCl_6] + 5\ H_2O \rightarrow Sb_2O_5 + 12\ HCl$

$Sb_2O_5 + 10\ H^+ + 5\ Fe \rightarrow 2\ Sb^0 + 5\ H_2O + 5\ Fe^{2+}$

Oxidation of Sb

$Sb + NO_3^- + 2\ H^+ \rightarrow NO\uparrow + SbO^+ + H_2O$

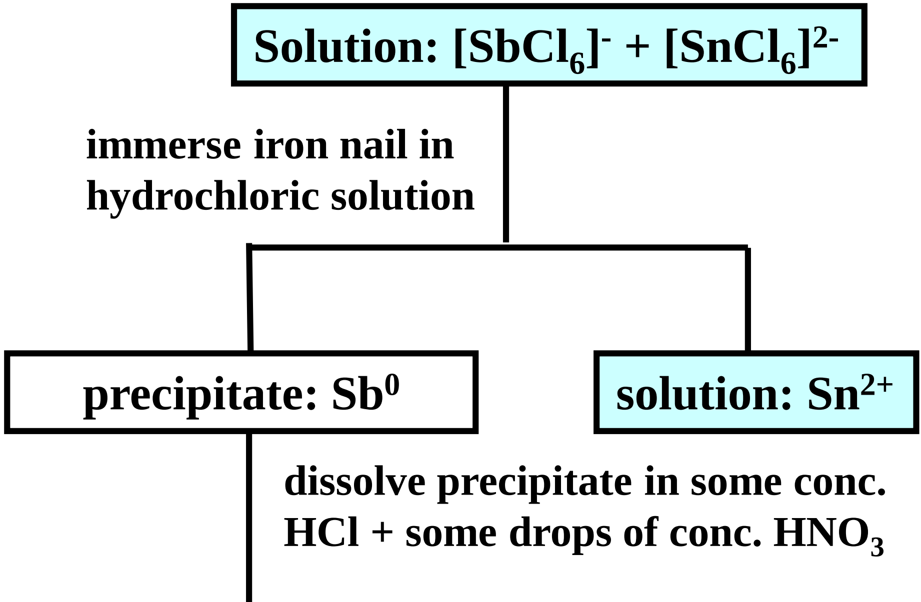
Precipitation of Sb^{3+} as sulphide

$2\ SbO^+ + 3\ S^{2-} + 4\ H^+ \rightarrow Sb_2S_3\downarrow + 2\ H_2O$

Problem

If too much HNO_3 was used:

$NO_3^- + S^{2-} + 2\ H^+ \rightarrow 1/8\ S_8\downarrow + NO_2^- + H_2O$



Solution: $[SbCl_6]^- + [SnCl_6]^{2-}$

immerse iron nail in hydrochloric solution

precipitate: Sb^0

solution: Sn^{2+}

dissolve precipitate in some conc. HCl + some drops of conc. HNO_3

solution: Sb^{3+}

addition of H_2S water

precipitate: Sb_2S_3

10. Separation Process for Cations

H_2S Group

Solution: Sn^{2+}

immerse a test tube, filled with water, first into the solution and then into the flame of a Bunsen burner

add ammonium molybdate and di-sodium hydrogenphosphate to the solution

gas phase: $SnCl_2\uparrow$

solution: Sn^{4+} + „$Mo^{VI}O_3 \cdot Mo^{V}{}_2O_5$"

Glow tests

$$Sn^{2+} + 2\,Cl^- \rightarrow SnCl_2(s) \rightarrow SnCl_2(g)\uparrow$$

$$SnCl_2(g) + \Delta T \rightarrow SnCl_2(g)^* \rightarrow SnCl_2(g) + h\nu \text{ (blue)}$$

"s^2-luminescence" Sn^{2+}: $[Kr]4d^{10}5s^2$

Sn^{2+*}: $[Kr]4d^{10}5s^15p^1$

Detection through formation of molybdenum blue

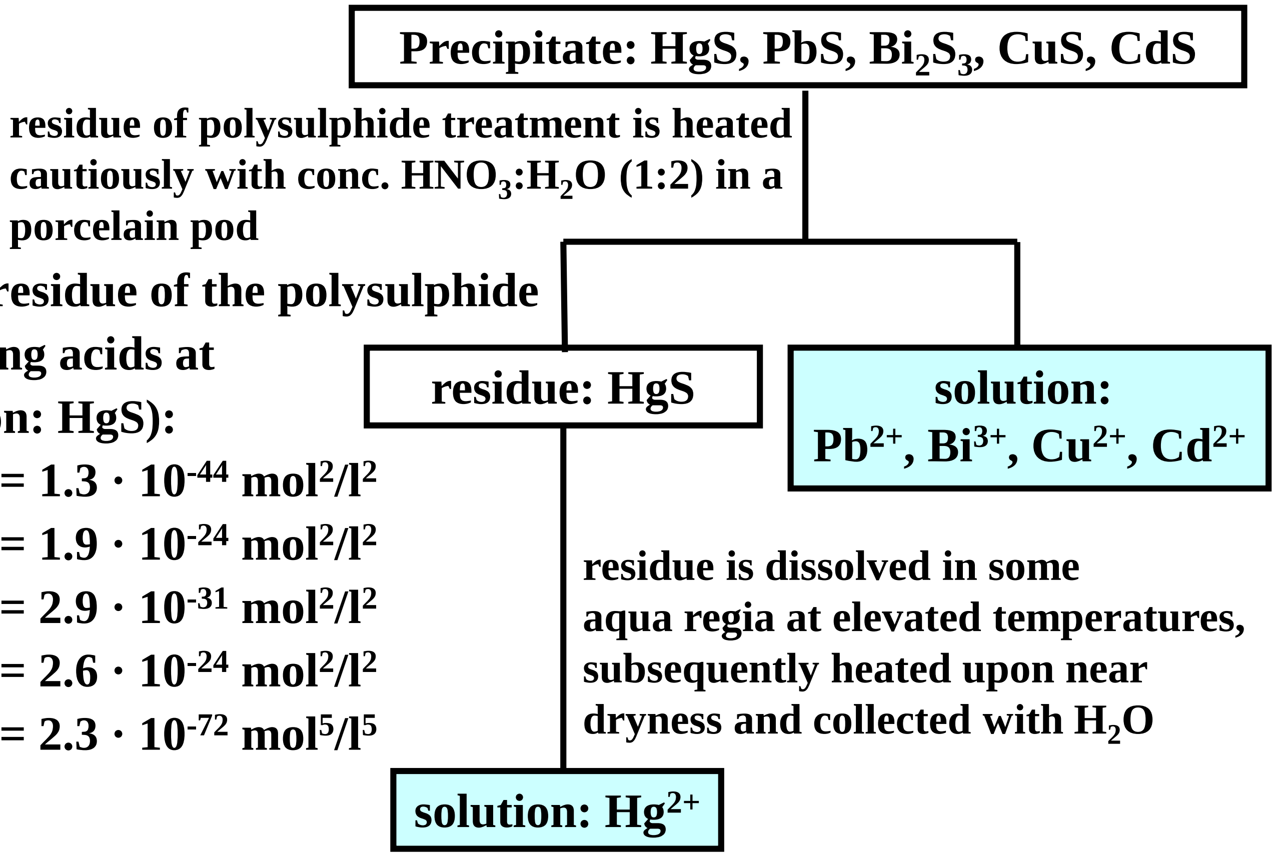
$$(NH_4)_3[P(Mo_3O_{10})_4] + 12\,H_2O \rightleftharpoons HPO_4^{2-} + 12\,MoO_4^{2-} + 3\,NH_4^+ + 23\,H^+$$

$$12\,Mo^{VI}O_4^{2-} + 4\,Sn^{2+} + 32\,H^+ \rightarrow 4\,Sn^{4+} + „4\,Mo^{VI}O_3 \cdot Mo^{V}{}_2O_5" + 16\,H_2O$$

(molybdenum blue)

10. Separation Process for Cations

H_2S Group



Precipitate: HgS, PbS, Bi_2S_3, CuS, CdS

residue of polysulphide treatment is heated cautiously with conc. HNO_3:H_2O (1:2) in a porcelain pod

residue: HgS

solution: Pb^{2+}, Bi^{3+}, Cu^{2+}, Cd^{2+}

residue is dissolved in some aqua regia at elevated temperatures, subsequently heated upon near dryness and collected with H_2O

solution: Hg^{2+}

The sulphides contained in the residue of the polysulphide treatment are all soluble in strong acids at elevated temperatures (exception: HgS):

- $Hg^{2+} + S^{2-} \rightleftharpoons HgS$ $K_L = 1.3 \cdot 10^{-44}$ mol²/l²
- $Pb^{2+} + S^{2-} \rightleftharpoons PbS$ $K_L = 1.9 \cdot 10^{-24}$ mol²/l²
- $Cu^{2+} + S^{2-} \rightleftharpoons CuS$ $K_L = 2.9 \cdot 10^{-31}$ mol²/l²
- $Cd^{2+} + S^{2-} \rightleftharpoons CdS$ $K_L = 2.6 \cdot 10^{-24}$ mol²/l²
- $2\,Bi^{3+} + 3\,S^{2-} \rightleftharpoons Bi_2S_3$ $K_L = 2.3 \cdot 10^{-72}$ mol⁵/l⁵

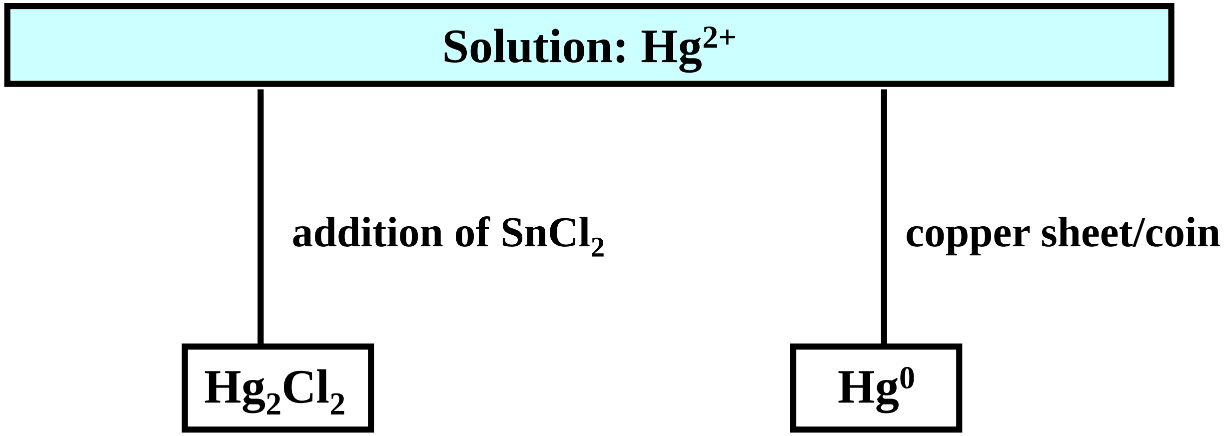
(all values for T = 90 ° C)

HgS dissolves in aqua regia, because the sulphide is oxidised to elemental sulphur:

$HNO_3 + 3\,HCl \rightarrow NOCl + 2\,Cl^{\cdot} + 2\,H_2O$ and $S^{2-} + 2\,Cl^{\cdot} \rightarrow 1/8\,S_8 + 2\,Cl^{-}$

10. Separation Process for Cations

H_2S Group



Solution: Hg^{2+}

addition of $SnCl_2$

copper sheet/coin

Hg_2Cl_2

Hg^0

Reduction and subsequent precipitation as chloride

$2\ Hg^{2+} + Sn^{2+} \rightarrow Hg_2^{2+} + Sn^{4+}$

$Hg_2^{2+} + 2\ Cl^- \rightarrow Hg_2Cl_2 \qquad K_L = 8.5 \cdot 10^{-19}\ mol^3/l^3$

Reduction to elemental Hg

Hg is more noble than Cu

$Hg^{2+} + Cu^0 \rightarrow Cu^{2+} + Hg^0$

The segregated metallic Hg forms a shiny silver alloy together with Cu (amalgam)

10. Separation Process for Cations

H_2S Group

Precipitation of $PbSO_4$

$Pb^{2+} + SO_4^{2-} \rightleftharpoons PbSO_4 \qquad K_L = 1.7 \cdot 10^{-8}$

$PbSO_4 + H_2SO_4 \rightleftharpoons H_2[Pb^{II}(SO_4)_2]$

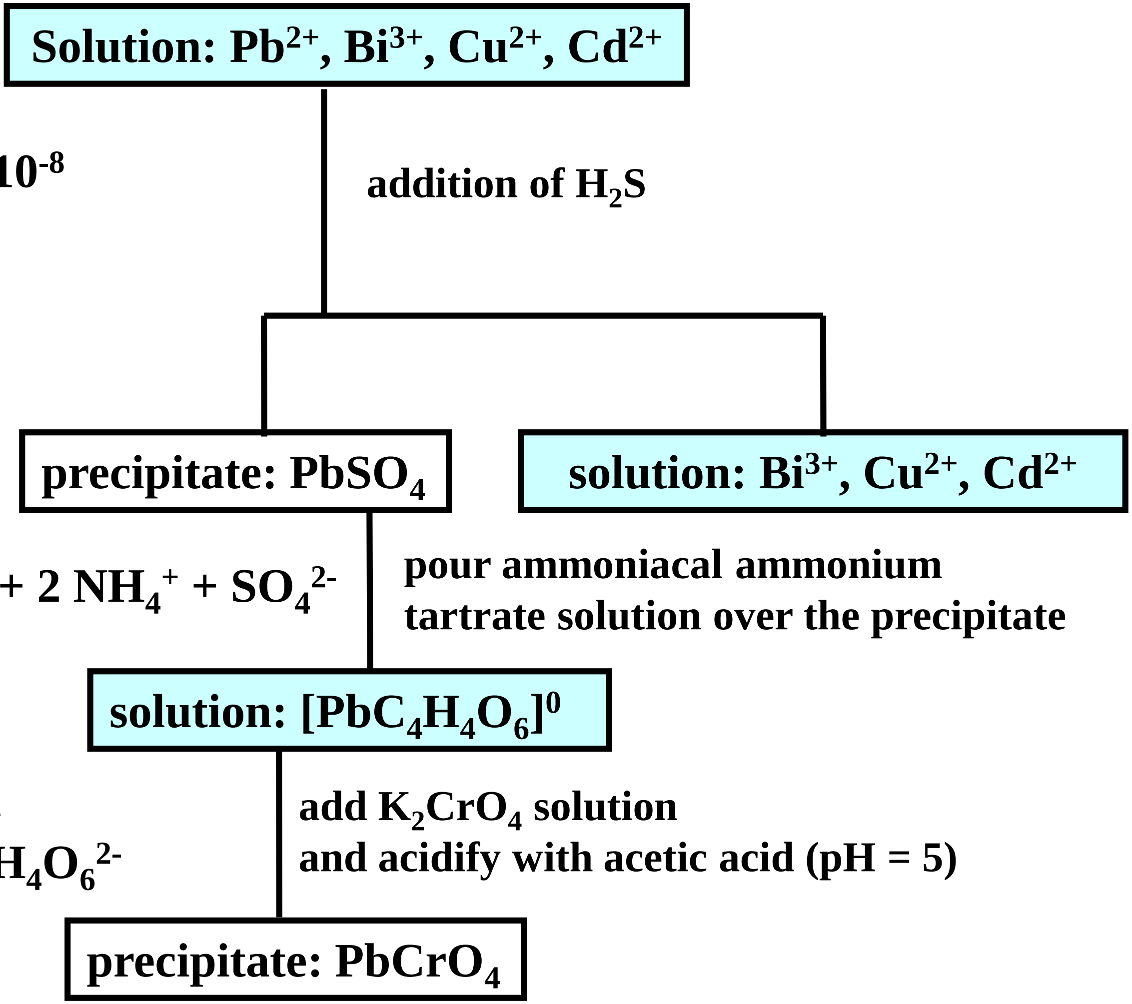
Dissolution with ammonium tartrate

$PbSO_4 + (NH_4)_2C_4H_4O_6 \rightleftharpoons PbC_4H_4O_6 + 2\ NH_4^+ + SO_4^{2-}$

Precipitation with potassium chromate

$PbC_4H_4O_6 + CrO_4^{2-} \rightleftharpoons PbCrO_4\downarrow + C_4H_4O_6^{2-}$

$K_L = 3.2 \cdot 10^{-11}$ (yellow)



Solution: Pb^{2+}, Bi^{3+}, Cu^{2+}, Cd^{2+}

addition of H_2S

precipitate: $PbSO_4$

solution: Bi^{3+}, Cu^{2+}, Cd^{2+}

pour ammoniacal ammonium tartrate solution over the precipitate

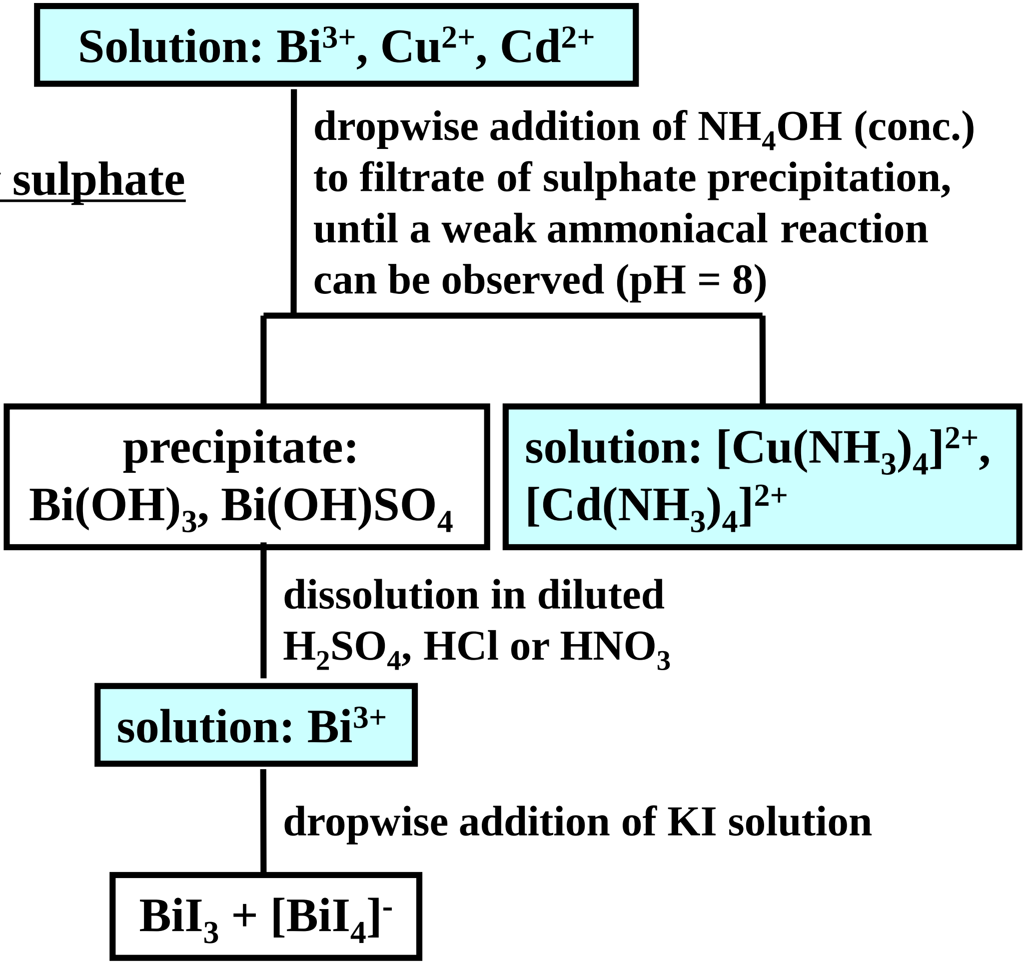
solution: $[PbC_4H_4O_6]^0$

add K_2CrO_4 solution and acidify with acetic acid (pH = 5)

precipitate: $PbCrO_4$

10. Separation Process for Cations

H_2S Group



Solution: Bi^{3+}, Cu^{2+}, Cd^{2+}

dropwise addition of NH_4OH (conc.) to filtrate of sulphate precipitation, until a weak ammoniacal reaction can be observed (pH = 8)

precipitate: $Bi(OH)_3$, $Bi(OH)SO_4$

solution: $[Cu(NH_3)_4]^{2+}$, $[Cd(NH_3)_4]^{2+}$

dissolution in diluted H_2SO_4, HCl or HNO_3

solution: Bi^{3+}

dropwise addition of KI solution

$BiI_3 + [BiI_4]^-$

Precipitation of bismuth hydroxide/hydroxy sulphate

$Bi^{3+} + 3\,OH^- \rightleftharpoons Bi(OH)_3\downarrow$

$Bi^{3+} + OH^- + SO_4^{2-} \rightleftharpoons Bi(OH)SO_4\downarrow$

Dissolution in HCl

$Bi(OH)_3 + 3\,HCl \rightarrow Bi^{3+} + 3\,H_2O + 3\,Cl^-$

Reaction with iodide

$Bi^{3+} + 3\,I^- \rightleftharpoons BiI_3\downarrow \qquad K_L = 4 \cdot 10^{-7}$

$BiI_3 + I^- \rightleftharpoons [Bi^{III}I_4]^- (aq) \qquad K_K = 9.7 \cdot 10^{-18}$

(yellow-orange solution)

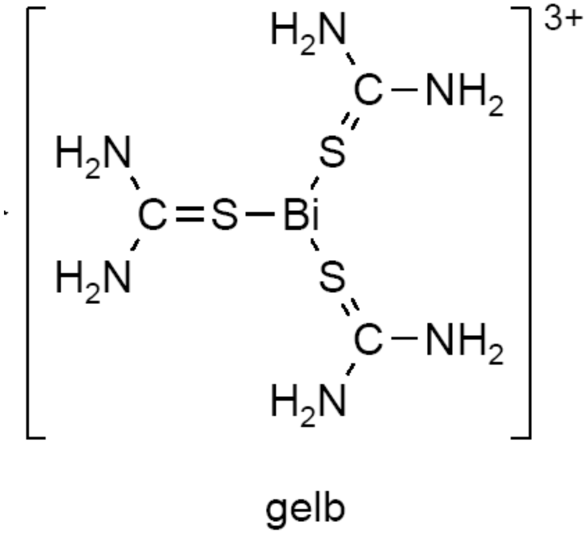
10. Separation Process for Cations

H_2S Group

Complementary tests for Bi^{3+}

1. Through reduction to the metal

$2\ Bi(OH)_3 + 3\ [Sn(OH)_4]^{2-} \rightarrow 2\ Bi\downarrow + 3\ [Sn(OH)_6]^{2-}$

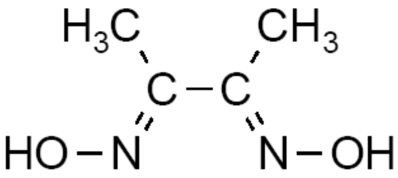

gelb

2. Via reaction with thio-urea $H_2N\text{-}CS\text{-}NH_2$

$Bi^{3+} + 3\ H_2N\text{-}CS\text{-}NH_2 \rightarrow [Bi(S{=}C(NH_2)_2)_3]^{3+}$

3. Through reaction with di-methyl glyoxime

$2\ Bi^{3+} + HO\text{-}N{=}C(CH_3)\text{-}C(CH_3){=}N\text{-}OH + 2\ H_2O \rightarrow O{=}Bi\text{-}O\text{-}N{=}C(CH_3)\text{-}C(CH_3){=}N\text{-}O\text{-}Bi{=}O + 6\ H^+$



10. Separation Process for Cations

H_2S Group

Masking of copper

$2\ Cu^{2+} + 6\ CN^- \rightarrow 2\ [Cu(CN)_2]^- + (CN)_2\uparrow$

$[Cu(CN)_2]^- + 2\ CN^- \rightarrow [Cu(CN)_4]^{3-}$ (no colour)

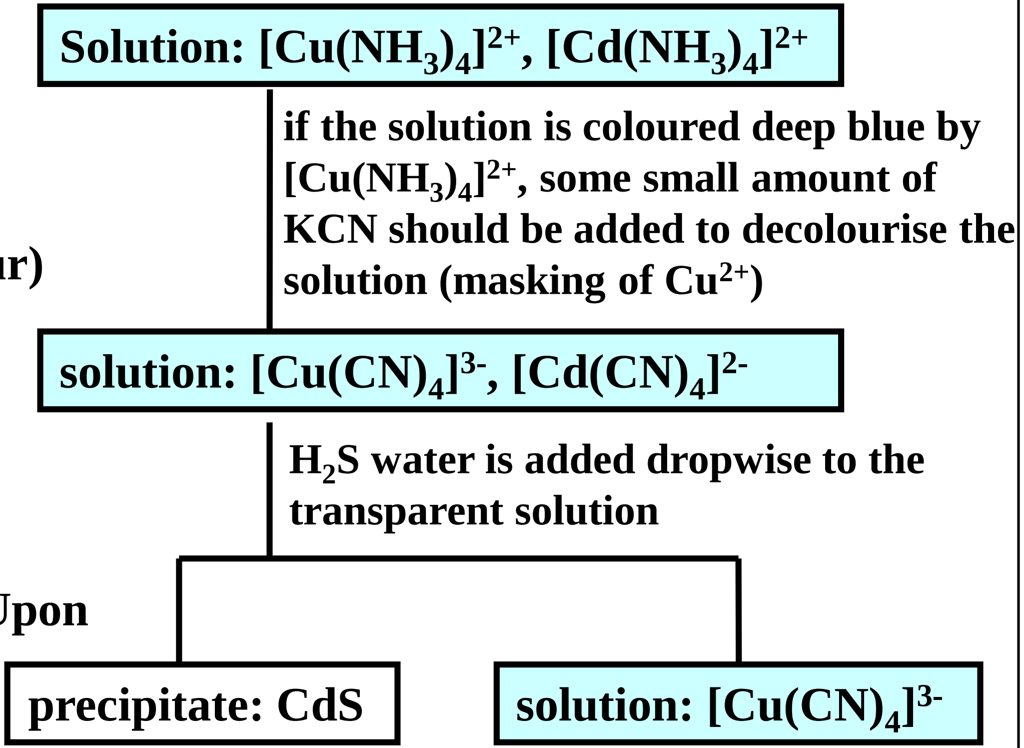
$Cu^+ + 4\ CN^- \rightleftharpoons [Cu(CN)_4]^{3-}\quad K_K = 7.9 \cdot 10^{27}$

$Cd^{2+} + 4\ CN^- \rightleftharpoons [Cd(CN)_4]^{2-}\quad K_K = 3.5 \cdot 10^{18}$

The copper cyanide complex is more stable than the corresponding cadmium complex. Upon introduction of H_2S, the solubility product of copper sulphide is not reached, in contrast to that of CdS

⇒ yellow cadmium sulphide precipitates:

$Cd^{2+} + S^{2-} \rightleftharpoons CdS\downarrow \quad K_L = 6.5 \cdot 10^{-28}\ mol^2/l^2$



Solution: $[Cu(NH_3)_4]^{2+}$, $[Cd(NH_3)_4]^{2+}$

if the solution is coloured deep blue by $[Cu(NH_3)_4]^{2+}$, some small amount of KCN should be added to decolourise the solution (masking of Cu^{2+})

solution: $[Cu(CN)_4]^{3-}$, $[Cd(CN)_4]^{2-}$

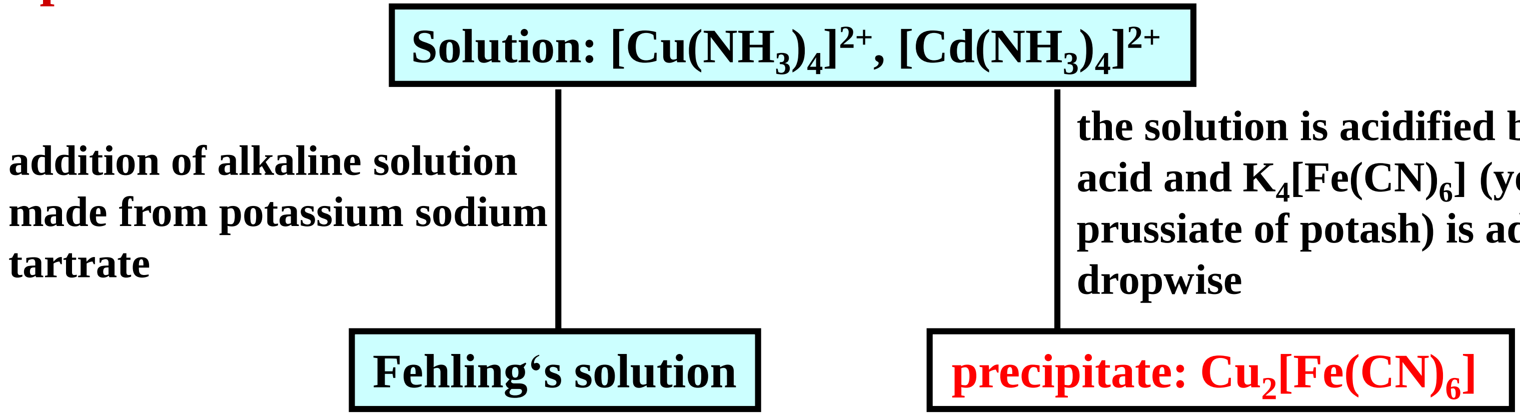
H_2S water is added dropwise to the transparent solution

precipitate: CdS

solution: $[Cu(CN)_4]^{3-}$

10. Separation Process for Cations

H_2S Group



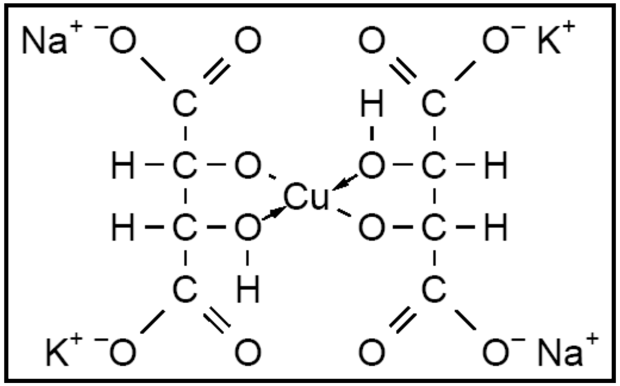
Solution: $[Cu(NH_3)_4]^{2+}$, $[Cd(NH_3)_4]^{2+}$

addition of alkaline solution made from potassium sodium tartrate

Fehling‘s solution

the solution is acidified by acetic acid and $K_4[Fe(CN)_6]$ (yellow prussiate of potash) is added dropwise

precipitate: $Cu_2[Fe(CN)_6]$



Formation of Fehling‘s solution

$$[Cu(NH_3)_4]^{2+} + 2\ OH^- \rightarrow Cu(OH)_2 + 4\ NH_3$$

$$2\ C_4H_4O_6^{2-} + Cu(OH)_2 \rightarrow [Cu^{II}(C_4H_3O_6)_2]^{4-} + 2\ H_2O$$

Fehling‘s solution is reduced by sugar/aldehyde ⇒ formation of yellow-red Cu_2O

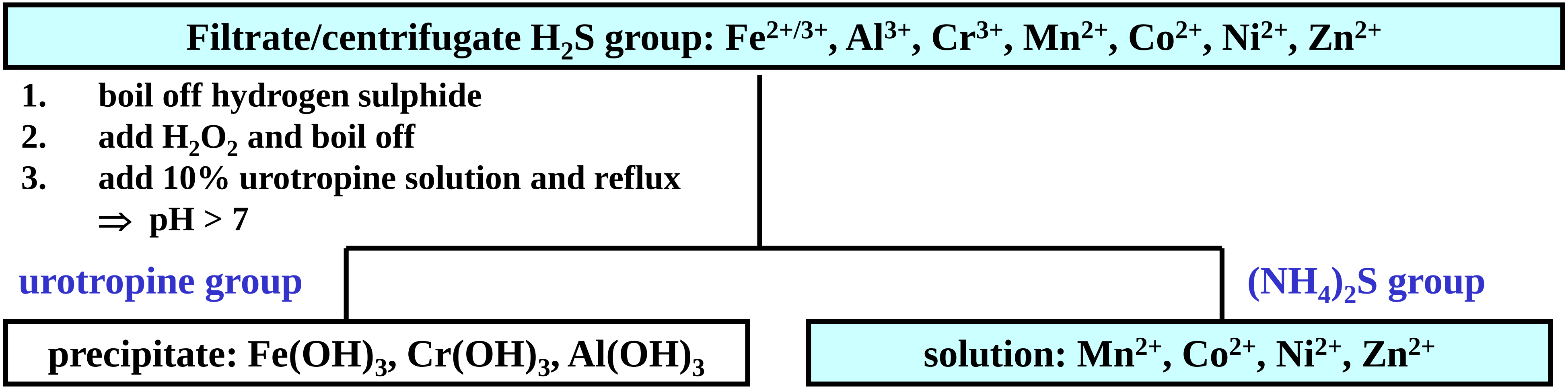
$$R\text{-}CH{=}O + 2\ Cu^{2+} + 2\ H_2O \rightarrow R\text{-}COOH + Cu_2O + 4\ H^+$$

(sugar)

10. Separation Process for Cations

Urotropine and $(NH_4)_2S$ Group

Members of this group are cations which form poorly soluble hydroxides in ammoniacal solution or which form poorly soluble sulphides in alkaline solutions



Filtrate/centrifugate H_2S group: $Fe^{2+/3+}$, Al^{3+}, Cr^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}

1. boil off hydrogen sulphide
2. add H_2O_2 and boil off
3. add 10% urotropine solution and reflux
   ⇒ pH > 7

urotropine group

precipitate: $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$

$(NH_4)_2S$ group

solution: Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}

The more alkaline, doubly charged, cations remain in solution as amine complexes:

$Ni^{2+} \rightarrow [Ni(NH_3)_6]^{2+}$

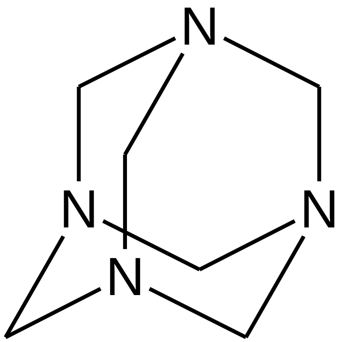
$Co^{2+} \rightarrow$ oxidises in air in presence of NH_3 to $Co^{3+} \rightarrow [Co(NH_3)_6]^{3+}$

$Mn^{2+} \rightarrow [Mn(NH_3)_6]^{2+}$

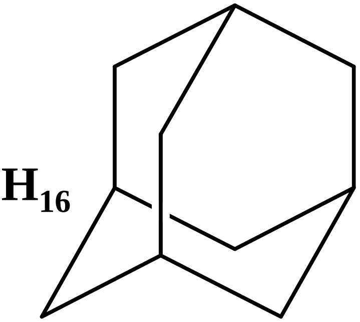
$Zn^{2+} \rightarrow [Zn(NH_3)_4]^{2+}$

10. Separation Process for Cations

Urotropine (hexamethylenetetramine)



adamantane structure → adamantane $C_{10}H_{16}$



Hydrolysis of urotropine

$N_4(CH_2)_6 + 6\ H_2O \rightarrow 4\ NH_3 + 6\ CH_2O$

formaldehyde prevents the oxidation of Mn^{2+}/Cr^{3+} through its reductive properties

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

Hydrolysis of acidic aqua complexes

$[M(H_2O)_6]^{3+} + OH^- \rightleftharpoons [M(OH)(H_2O)_5]^{2+} + H_2O$

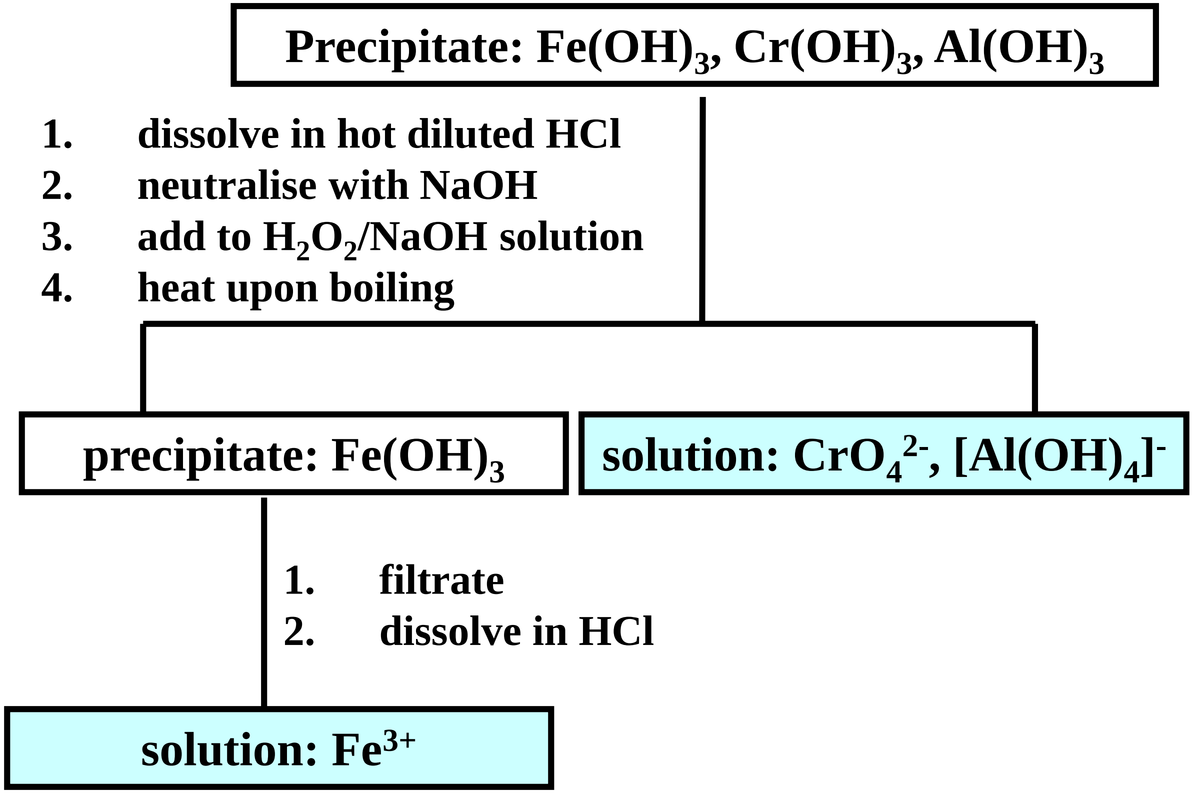
$[M(OH)(H_2O)_5]^{2+} + OH^- \rightleftharpoons [M(OH)_2(H_2O)_4]^{+} + H_2O$

$[M(OH)_2(H_2O)_4]^{+} + OH^- \rightleftharpoons [M(OH)_3(H_2O)_3]^{0} \rightarrow M(OH)_3\downarrow + 4\ H_2O$

10. Separation Process for Cations

Urotropine Group

$M(OH)_3 + 3\ H^+ \rightarrow M^{3+} + 3\ H_2O$



Precipitate: $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$

1. dissolve in hot diluted HCl
2. neutralise with NaOH
3. add to H_2O_2/NaOH solution
4. heat upon boiling

precipitate: $Fe(OH)_3$

solution: CrO_4^{2-}, $[Al(OH)_4]^-$

1. filtrate
2. dissolve in HCl

solution: Fe^{3+}

<u>**Alkaline precipitation**</u>

$Fe^{3+} + 3\ OH^- \rightarrow Fe(OH)_3\downarrow$

$Al^{3+} + 4\ OH^- \rightarrow [Al(OH)_4]^-$

$2\ Cr^{3+} + 3\ H_2O_2 + 10\ OH^- \rightarrow$
$2\ CrO_4^{2-} + 8\ H_2O$

$\Rightarrow$ the solution is coloured yellow, if Cr^{3+} is present (chromate/di-chromate)

10. Separation Process for Cations

Urotropine Group

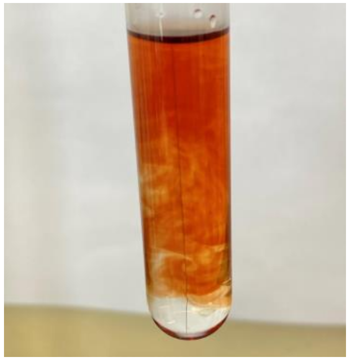
Solution: Fe^{3+}

dilute solution with H_2O and add KSCN

$[Fe(NCS)(H_2O)_5]^{2+}$

dilute with H_2O and add $K_4[Fe(CN)_6]$ (*yellow prussiate of potash*)

$KFe[Fe(CN)_6]$



Verification as penta aqua thiocyanato(III)-ions

$$[Fe^{III}(H_2O)_6]^{3+}(aq) + SCN^-(aq) \rightarrow [Fe^{III}(NCS)(H_2O)_5]^{2+}(aq) + H_2O$$

Detection as Prussian blue

$$[Fe^{III}(H_2O)_6]^{3+}(aq) + [Fe^{II}(CN)_6]^{4-}(aq) + K^+(aq) \rightarrow KFe^{II/III}[Fe^{II/III}(CN)_6](s) + 6\ H_2O$$

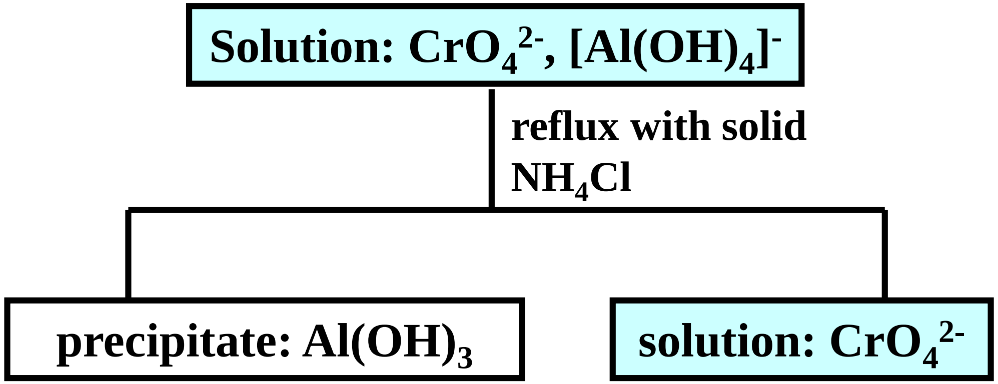
⇒ charge-transfer absorption in the yellow range of the spectrum

10. Separation Process for Cations

Urotropine Group

$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

$[Al(OH)_4]^- + H_3O^+ \rightarrow Al(OH)_3\downarrow + 2\ H_2O$



Solution: CrO_4^{2-}, $[Al(OH)_4]^-$

reflux with solid NH_4Cl

precipitate: $Al(OH)_3$

solution: CrO_4^{2-}

Detection of Al^{3+} as cobalt blue on magnesia gutter

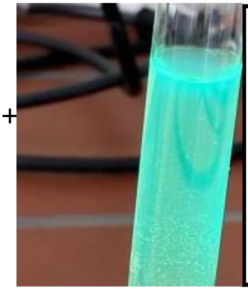
$2\ Al(OH)_3 \rightarrow Al_2O_3 + 3\ H_2O$

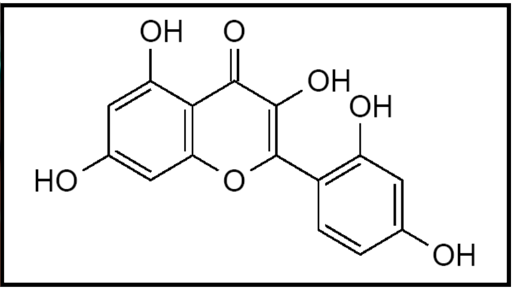
$2\ Al_2O_3 + 2\ Co(NO_3)_2 \rightarrow 2\ CoAl_2O_4 + 4\ NO_2\uparrow + O_2\uparrow$

Detection of Al^{3+} with morine (fluorescent dye)

$Al(OH)_3 + 3\ H_3O^+ \rightarrow Al^{3+} + 3\ H_2O$ in acetic solution

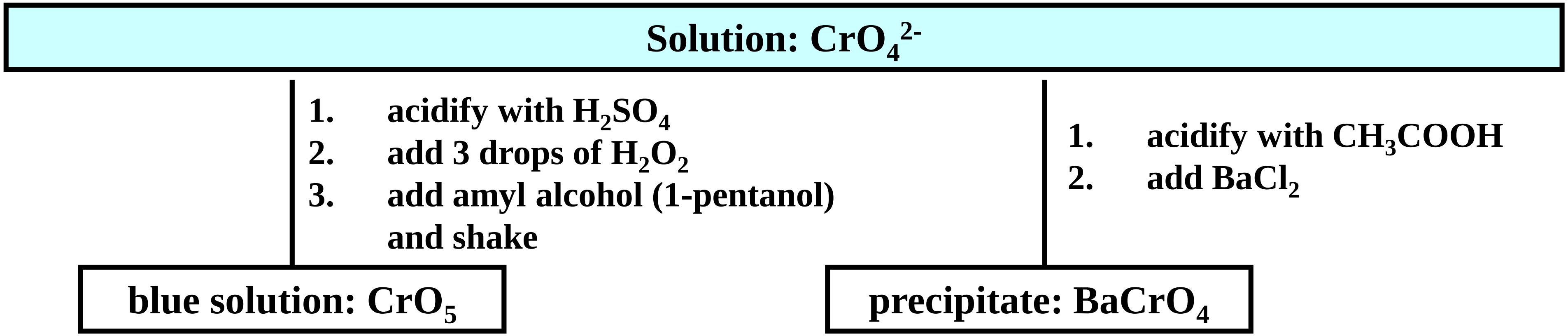
$Al^{3+}(aq) + 3$ morine-H $\rightarrow [Al^{III}(morine)_3]$(colloidal) $+ 3\ H^+$





10. Separation Process for Cations

Urotropine Group



Solution: CrO_4^{2-}

1. acidify with H_2SO_4
2. add 3 drops of H_2O_2
3. add amyl alcohol (1-pentanol) and shake

blue solution: CrO_5

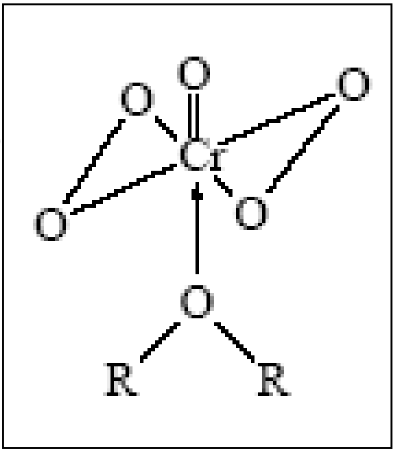
1. acidify with CH_3COOH
2. add $BaCl_2$

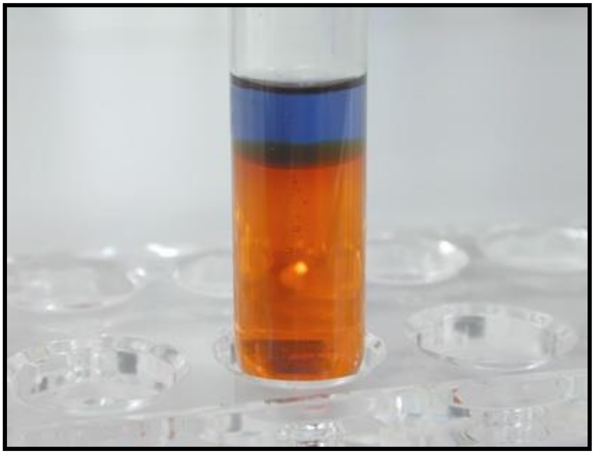
precipitate: $BaCrO_4$

Detection as CrO_5

$$2\ CrO_4^{2-} + 2\ H_3O^+ \rightleftharpoons Cr_2O_7^{2-} + 3\ H_2O$$

$$Cr_2O_7^{2-} + 4\ H_2O_2 + 2\ H^+ \rightleftharpoons 2\ Cr^{VI}O_5 + 5\ H_2O$$





Detection as barium chromate

$$CrO_4^{2-} + Ba^{2+} \rightleftharpoons BaCrO_4$$

10. Separation Process for Cations

$(NH_4)_2S$ Group

Solution: Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}

1. make solution alkaline (pH 8-9)
2. heat and introduce H_2S

precipitate: MnS, CoS, NiS, ZnS

$$H_2S + 2\ NH_3 \rightarrow (NH_4)_2S$$
$$(NH_4)_2S \rightleftharpoons 2\ NH_4^+ + S^{2-}$$

Precipitation of sulphides

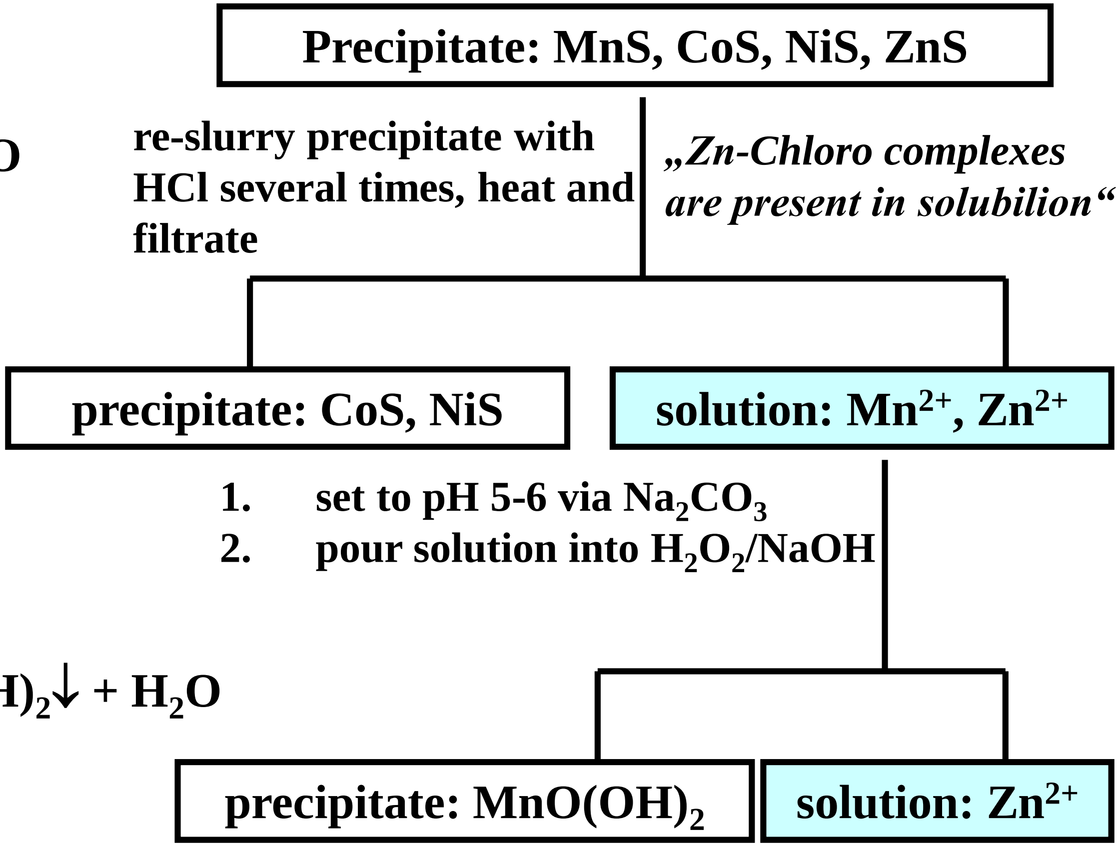
- $Mn^{2+} + S^{2-} \rightleftharpoons MnS$ $\quad K_L = 1.0 \cdot 10^{-15}\ mol^2/l^2$
- $Co^{2+} + S^{2-} \rightleftharpoons CoS$ $\quad K_L = 6.1 \cdot 10^{-21}\ mol^2/l^2$
- $Ni^{2+} + S^{2-} \rightleftharpoons NiS$ $\quad K_L = 4.9 \cdot 10^{-24}\ mol^2/l^2$
- $Zn^{2+} + S^{2-} \rightleftharpoons ZnS$ $\quad K_L = 8.9 \cdot 10^{-25}\ mol^2/l^2$

10. Separation Process for Cations

$(NH_4)_2S$ Group

$ZnS + 2\ H_3O^+ \rightarrow H_2S\uparrow + Zn^{2+} + 2\ H_2O$

$MnS + 2\ H_3O^+ \rightarrow H_2S\uparrow + Mn^{2+} + 2\ H_2O$



Precipitate: MnS, CoS, NiS, ZnS

re-slurry precipitate with HCl several times, heat and filtrate

„Zn-Chloro complexes are present in solubilion“

precipitate: CoS, NiS

solution: Mn^{2+}, Zn^{2+}

1. set to pH 5-6 via Na_2CO_3
2. pour solution into H_2O_2/NaOH

precipitate: $MnO(OH)_2$

solution: Zn^{2+}

<u>Separation of zinc and manganese</u>

- $Mn^{2+} + H_2O_2 + 2\ OH^- \rightarrow MnO(OH)_2\downarrow + H_2O$

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

  (tetra hydroxozincate)

10. Separation Process for Cations

$(NH_4)_2S$ Group

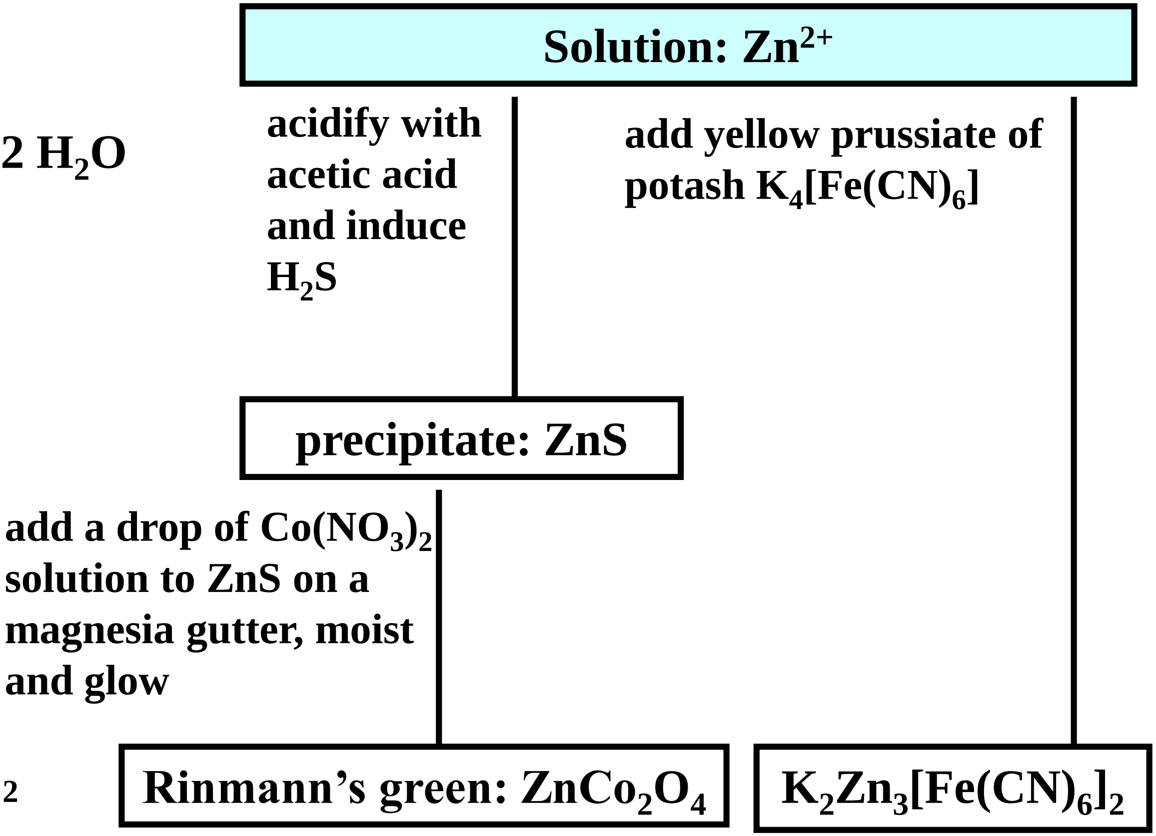
$[Zn(OH)_4]^{2-} + 2\ H^+ \rightarrow Zn(OH)_2\downarrow + 2\ H_2O$

(white)

$Zn(OH)_2 + 2\ H^+ \rightarrow Zn^{2+} + 2\ H_2O$

$Zn^{2+} + H_2S \rightarrow ZnS\downarrow + 2\ H^+$

(white)



Solution: Zn^{2+}

acidify with acetic acid and induce H_2S

precipitate: ZnS

add a drop of $Co(NO_3)_2$ solution to ZnS on a magnesia gutter, moist and glow

Rinnmann’s green: $ZnCo_2O_4$

add yellow prussiate of potash $K_4[Fe(CN)_6]$

$K_2Zn_3[Fe(CN)_6]_2$

<u>Detection of Rinmann’s green</u>

$4\ Co(NO_3)_2 \rightarrow 2\ Co_2O_3 + 8\ NO + 5\ O_2$

$ZnO + Co_2O_3 \rightarrow ZnCo_2O_4$

<u>Detection as stained-white potassium zinc hexacyanoferrate</u>

$3\ Zn^{2+} + 2\ K_4[Fe^{II}(CN)_6] \rightarrow K_2Zn_3[Fe^{II}(CN)_6]_2\downarrow + 6\ K^+$

10. Separation Process for Cations

$(NH_4)_2S$ Group

$MnO(OH)_2 + 4\ H^+ + 2\ Cl^- \rightarrow\ Mn^{2+} + Cl_2 + 3\ H_2O$

Precipitate: $MnO(OH)_2$

wash precipitate with some conc. HCl

solution: Mn^{2+}

acidify with conc. HNO_3, add PbO_2 and reflux

acidify with conc. H_2SO_4, add $(NH_4)_2S_2O_8$ and reflux

solution: MnO_4^-

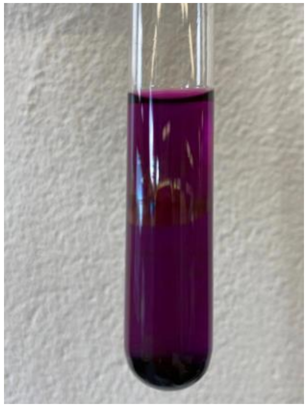
<u>Detection as permanganate</u>

1. Oxidation with lead oxide

$2\ Mn^{2+} + 5\ PbO_2\ + 4\ H^+ \rightarrow\ 5\ Pb^{2+} + 2\ MnO_4^- + 2\ H_2O$

2. Oxidation with ammonium peroxo-di-sulphate

$2\ Mn^{2+} + 5\ (NH_4)_2S_2O_8 + 8\ H_2O\ \rightarrow\ 10\ NH_4^+ + 2\ MnO_4^- + 10\ SO_4^{2-} + 16\ H^+$



10. Separation Process for Cations

$(NH_4)_2S$ Group

$CoS + H_2O_2 + 2\ H^+ \rightarrow Co^{2+} + S\downarrow + 2\ H_2O$

$NiS + H_2O_2 + 2\ H^+ \rightarrow Ni^{2+} + S\downarrow + 2\ H_2O$

Precipitate: CoS, NiS

dissolve precipitate in mixture of acetic acid and 30% H_2O_2 (1:1)

solution: Co^{2+}, Ni^{2+}

1. add some NH_4SCN
2. add a sub-layer of amyl alcohol

precipitate: $Co(SCN)_2$

make solution alkaline and add di-methyl glyoxime

precipitate: $[Ni(Hdmg)_2]$

Detection of cobalt with thiocyanate

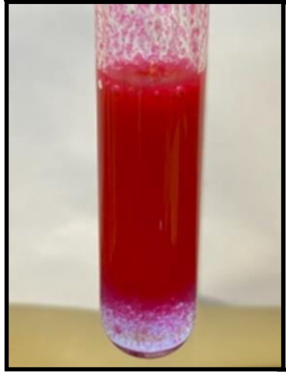
$Co^{2+} + 2\ SCN^- \rightarrow Co(SCN)_2$

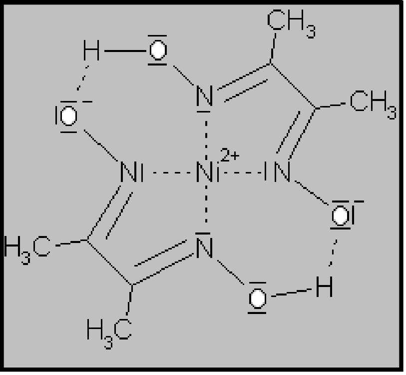
(dissolves in amyl alcohol and gives blue colour)

Detection of nickel with di-methyl glyoxime (H_2dmg)

$Ni^{2+} + 2\ H_2dmg \rightarrow [Ni^{II}(Hdmg)_2]\downarrow + 2\ H^+$

(red)

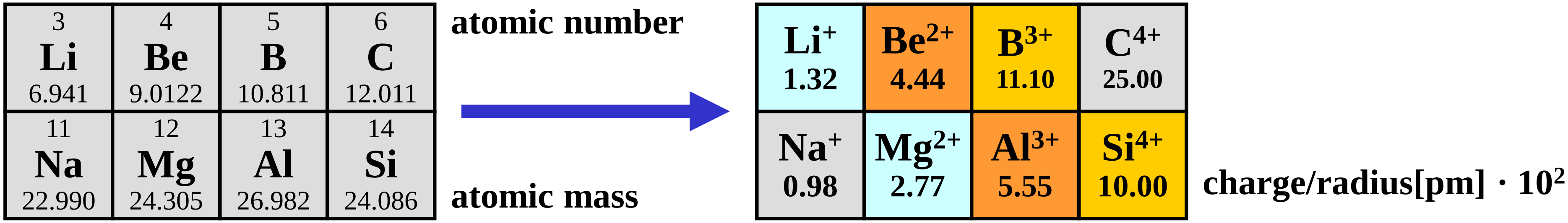




10. Separation Process for Cations

$(NH_4)_2CO_3$ Group

Cations, which form poorly soluble carbonates in ammoniacal solution belong to this group, i.e. Ba^{2+}, Sr^{2+}, and Ca^{2+}. Mg^{2+} behaves more like lithium due to the so called "Schrägbeziehung" in the periodic table.



3 **Li** 6.941	4 **Be** 9.0122	5 **B** 10.811	6 **C** 12.011
11 **Na** 22.990	12 **Mg** 24.305	13 **Al** 26.982	14 **Si** 24.086

atomic number

atomic mass

Li^+ 1.32	Be^{2+} 4.44	B^{3+} 11.10	C^{4+} 25.00
Na^+ 0.98	Mg^{2+} 2.77	Al^{3+} 5.55	Si^{4+} 10.00

charge/radius[pm] · 10^2

Filtrate/centrifugate of urotropine group: Ba^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+}, Li^+, Na^+, K^+, NH_4^+

Acidify filtrate of $(NH_4)_2S$ precipitation with 2n HCl and boil until no H_2S is released any more. Add 2n NH_4OH to the solution and heat, then add $(NH_4)_2CO_3$

$(NH_4)_2CO_3$ group

precipitate: $BaCO_3$, $SrCO_3$, $CaCO_3$

soluble group

solution: Mg^{2+}, Li^+, Na^+, K^+, NH_4^+

10. Separation Process for Cations

$(NH_4)_2CO_3$ Group

$Ba^{2+} + CO_3^{2-} \rightleftharpoons BaCO_3$ $K_L = 2.6 \cdot 10^{-9}$ mol²/l²

$Sr^{2+} + CO_3^{2-} \rightleftharpoons SrCO_3$ $K_L = 6.7 \cdot 10^{-10}$ mol²/l²

$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3$ $K_L = 1.1 \cdot 10^{-8}$ mol²/l²

Precipitate: $BaCO_3$, $SrCO_3$, $CaCO_3$

Dissolve precipitate in 2 n acetic acid

solution: Ba^{2+}, Sr^{2+}, Ca^{2+}

Add NaAc, until pH 4-5 is reached. Dropwise addition of slight excess of $K_2Cr_2O_7$

Initiate cristallisation of $BaCrO_4$ by rubbing with a glass rod

precipitate: $BaCrO_4$

solution: Sr^{2+}, Ca^{2+}

Dissolution of the carbonates

$MeCO_3 + 2\,H^+ \rightarrow Me^{2+} + H_2O + CO_2\uparrow$

Precipitation as chromate

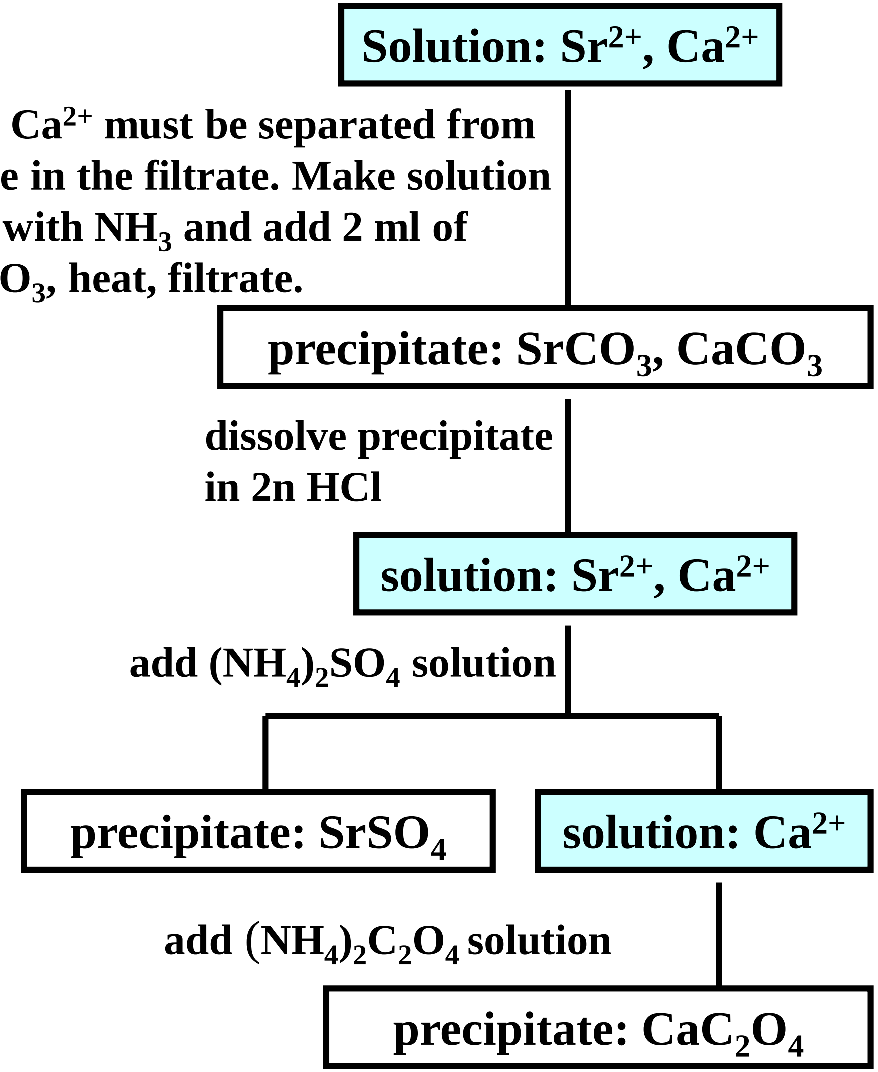
$Ba^{2+} + CrO_4^{2-} \rightleftharpoons BaCrO_4$ $K_L = 1.6 \cdot 10^{-10}$ mol²/l²

$Sr^{2+} + CrO_4^{2-} \rightleftharpoons SrCrO_4$ $K_L = 3.6 \cdot 10^{-5}$ mol²/l²

$Ca^{2+} + CrO_4^{2-} \rightleftharpoons CaCrO_4$ $K_L = 1.13$ mol²/l²

10. Separation Process for Cations

$(NH_4)_2CO_3$ Group



Solution: Sr^{2+}, Ca^{2+}

Sr^{2+} and Ca^{2+} must be separated from chromate in the filtrate. Make solution alkaline with NH_3 and add 2 ml of $(NH_4)_2CO_3$, heat, filtrate.

precipitate: $SrCO_3$, $CaCO_3$

dissolve precipitate in 2n HCl

solution: Sr^{2+}, Ca^{2+}

add $(NH_4)_2SO_4$ solution

precipitate: $SrSO_4$

solution: Ca^{2+}

add $(NH_4)_2C_2O_4$ solution

precipitate: CaC_2O_4

Dissolution of the carbonates

$SrCO_3 + 2\ H^+ \rightarrow Sr^{2+} + H_2O + CO_2\uparrow$

$CaCO_3 + 2\ H^+ \rightarrow Ca^{2+} + H_2O + CO_2\uparrow$

Precipitation as sulphates

$Sr^{2+} + SO_4^{2-} \rightarrow SrSO_4\downarrow$

Precipitation as oxalates

$Sr^{2+} + C_2O_4^{2-} \rightarrow SrC_2O_4 \quad K_L = 6.6 \cdot 10^{-8}\ mol^2/l^2$

$Ca^{2+} + C_2O_4^{2-} \rightarrow CaC_2O_4 \quad K_L = 1.78 \cdot 10^{-9}\ mol^2/l^2$

10. Separation Process for Cations

Soluble Group

The filtrate of the carbonate group still contains Mg^{2+}, Li^+, Na^+, K^+ and NH_4^+. For these ions, a separation is difficult and not necessary for their detection

NH_4^+	from primary substance → blue cross procedure: $NH_4^+ + OH^- \rightarrow NH_3\uparrow + H_2O$
Li^+	carmine red colourisation of Bunsen burner flame (670.8 nm)
Na^+	yellow colourisation of Bunsen burner flame (589.3 nm) precipitation with uranylacetate $Na^+ + Mg^{2+} + 3\ UO_2^{2+} + 9\ CH_3COO^- \rightarrow MgNa(UO_2)_3(CH_3COO)_9{\cdot}9H_2O\downarrow$
K^+	pale violet colourisation of Bunsen burner flame (Co glass needed, if Na^+ is present) forms crystals with diluted $HClO_4 \rightarrow KClO_4$ (rhombic crystals)
Mg^{2+}	addition of NH_3 and $(NH_4)_2HPO_4 \rightarrow MgNH_4PO_4{\cdot}6H_2O$ (star-shaped crystals)

11. Digestions

Transformation of poorly soluble Substances into readily soluble Compounds

Compounds, insoluble in acids

Substance	Colour
Hg_2Cl_2	white
$PbCl_2$	white
AgCl	white
AgBr	beige
AgI	yellow
$Ca/Sr/BaSO_4$	white
$PbSO_4$	white
$Cr_2(SO_4)_3$	ochre
Cr_2O_3	green
Fe_2O_3	red-brown
Al_2O_3	white
SnO_2	white
SiO_2	white
TiO_2	white

Typical digestions

Soda-potash digestion alkaline digestion	$Na_2CO_3 + K_2CO_3$ $Na_2CO_3 + NaOH$	$Ca/Sr/BaSO_4$ Al_2O_3 SiO_2 AgX
acidic digestion	$KHSO_4$	Fe_2O_3 Al_2O_3 TiO_2
oxidative digestion	$NaNO_3$ + several alkaline metal carbonates	Cr_2O_3 $Cr_2(SO_4)_3$
Freiberger digestion	$Na_2CO_3 + K_2CO_3 + S_8$	SnO_2

11. Digestions

Soda-Potash Digestion

Digestion of

Poorly soluble alkaline earth sulphates, strongly tempered oxides, silicates, silver halides

Course of action

The residue of the primary substance, that is poorly soluble in HCl, is separated, washed, dried and thoroughly ground in a crucible with a 4-6-fold excess of K_2CO_3 (pot ash) and Na_2CO_3 (soda) in a ratio of 1:1 and then molten in the flame of a Bunsen burner. The reaction has stopped after approximately 10 minutes. Thereafter, the solidified melt is ground and resorbed by water.

sulphate	$BaSO_4 + Na_2CO_3 \rightarrow BaCO_3 + Na_2SO_4$
oxide	$Al_2O_3 + Na_2CO_3 \rightarrow 2\ NaAlO_2 + CO_2\uparrow$
silver halide	$2\ AgX + Na_2CO_3 \rightarrow Ag_2CO_3 + 2\ NaX$ (X = Cl, Br, I)
	$2\ Ag_2CO_3 \rightarrow 4\ Ag + 2\ CO_2\uparrow + O_2\uparrow$

11. Digestions

Acidic Digestion

Digestion of

Alkaline oxides, e.g. Fe_2O_3 , Al_2O_3, MgO, TiO_2

Course of action

The residue of the primary substance is ground with a 6-fold excess of $KHSO_4$ and molten in a nickel or platinum crucible (no porcelain, because Al could be liberated) at as low temperatures as possible. When the reaction has stopped, the melt is heated until it is mildly glowing. If the melt is clear, one let it cool down and dissolves it in diluted H_2SO_4.

$$Fe_2O_3 + 6\ KHSO_4 \rightarrow Fe_2(SO_4)_3 + 3\ K_2SO_4 + 3\ H_2O\uparrow$$
$$Al_2O_3 + 6\ KHSO_4 \rightarrow Al_2(SO_4)_3 + 3\ K_2SO_4 + 3\ H_2O\uparrow$$

11. Digestions

Oxidative Digestion

Digestion of

Poorly soluble substances that can be oxidised, e.g. Cr_2O_3, $FeCr_2O_4$, MnO_2

Course of action

The substance is thoroughly ground and cautiously molten in a porcelain crucible (magnesia gutter) together with a 3-fold excess of a 1:1 mixture of soda (Na_2CO_3) and sodium nitrate ($NaNO_3$) (or potassium nitrate)

$$Cr_2O_3 + 3\ NaNO_3 + 2\ Na_2CO_3 \rightarrow 2\ Na_2CrO_4 + 3\ NaNO_2 + 2\ CO_2\uparrow$$

$$2\ FeCr_2O_4 + 7\ NaNO_3 + 4\ Na_2CO_3 \rightarrow Fe_2O_3 + 4\ Na_2CrO_4 + 7\ NaNO_2 + 4\ CO_2\uparrow$$

11. Digestions

Freiberger Digestion

Digestion of

Poorly soluble oxides that form water soluble thiocomplexes, e.g. SnO_2

Course of action

In a porcelain crucible, the substance is molten together with a 6-fold excess of a 1:1 mixture of sulphur and water-free Na_2CO_3

$$2\ SnO_2 + 2\ Na_2CO_3 + 9/8\ S_8 \rightarrow 2\ Na_2SnS_3 + 3\ SO_2\uparrow + 2\ CO_2\uparrow$$

The melt cake is leeched with HCl

$$Na_2SnS_3 + 2\ HCl \rightarrow SnS_2 + H_2S\uparrow + 2\ NaCl$$

The SnS_2 precipitated can subsequently be treated in the H_2S group