

Analytical Chemistry

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Literature

General Chemistry

- **E. Riedel, Allgemeine und anorganische Chemie deGruyter, 9. Auflage 2008**
- **C.E. Mortimer, U. Müller, Chemie Thieme, 8. Auflage 2003**
- **P. Paetzold, Chemie – Eine Einführung, deGruyter, 1. Auflage, 2009**

Analytical Chemistry

- **G. Jander, E. Blasius, Einführung in das anorganisch-chemische Praktikum, S. Hirzel Verlag, 16. Auflage, 2006**
- **G. Jander, K.F. Jahr, Maßanalyse, deGruyter, 17. Auflage, 2009**
- **F.J. Hahn, H. Haubold, Analytisches Praktikum: Qualitative Analyse, VCH, 2. Auflage, 1993**
- **D.C. Harris, Quantitative Chemical Analysis, W.H. Freeman and Company, 2nd Edition, 1987**
- **M. Otto, Analytische Chemie, Wiley-VCH, 3. Auflage, 2006**
- **U.R. Kunze, G. Schwedt, Grundlagen der quantitativen Analyse, Wiley-VCH, 6. Auflage, 2009**

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 $1/600000 \text{ m}^2$ 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	Pow. of ten	Prefix	Abbreviation
Force	F	kg m s ⁻²	N	10 ⁻²⁴	Yocto	y
Energy	E	N m (kg m ² s ⁻²)	J	10 ⁻²¹	Zepto	z
Power	P	J s ⁻¹ (kg m ² s ⁻³)	W	10 ⁻¹⁸	Atto	a
Pressure	p	N m ⁻²	Pa	10 ⁻¹⁵	Femto	f
Frequency	v	s ⁻¹	Hz	10 ⁻¹²	Pico	p
Electrical charge	Q	A s	C	10 ⁻⁹	Nano	n
Electrical potential	U	kg m ² A ⁻¹ s ⁻³	V	10 ⁻⁶	Micro	μ
Electrical resistance	R	kg m ² A ⁻² s ⁻³	Ω	10 ⁻³	Milli	m
Molar Mass	M	g mol ⁻¹	Da	10 ⁻²	Centi	c
Concentration	c	mol l ⁻¹	-	10 ⁻¹	Deci	d
Natural Constant	Symbol	Figure		10 ¹	Deca	da
Avogadro constant	N _A	6.022045·10 ²³ particles·mol ⁻¹		10 ²	Hecto	h
Bohr's radius	a ₀	5.2917706·10 ⁻¹¹ m		10 ³	Kilo	k
Bohr's magneton	μ _B	9.274096·10 ⁻²⁴ JT ⁻¹		10 ⁶	Mega	M
Boltzmann constant	k	1.380662·10 ⁻²³ J·K ⁻¹		10 ⁹	Giga	G
Elementary charge	e	1.6021892·10 ⁻¹⁹ C		10 ¹²	Tera	T
Standard acceleration	g	9.80665 m·s ⁻²		10 ¹⁵	Peta	P
Faraday constant	F	96485 C·mol ⁻¹		10 ¹⁸	Exa	E
Gravitational constant	G	6.6729·10 ¹¹ m ³ kg ⁻¹ s ⁻²		10 ²¹	Zetta	Z
Speed of light in vacuum	c	2.99792458·10 ⁸ m·s ⁻¹		10 ²⁴	Yotta	Y
Molar volume	V _m	22.414 l·mol ⁻¹				
Permittivity of the vacuum	ε ₀	8.854·10 ⁻¹² AsV ⁻¹ m ⁻¹				
Permeability of the vacuum	μ ₀	4π·10 ⁻⁷ VsA ⁻¹ m ⁻¹				
Planck's quantum of action	h	6.626176·10 ⁻³⁴ J·s				
Universal gas constant	R	8.31441 J·mol ⁻¹ ·K ⁻¹				

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

<p>Massenanteil w ***</p> $w = \frac{m(G)}{m(L)}$ <p style="text-align: right;">1 %</p>	<p>Massenverhältnis ζ¹⁾ ** (ζ: zeta)</p> $\zeta = \frac{m(G)}{m(LM)}$ <p>1) häufig als Gehaltsangabe für gesättigte Lösungen</p> <p style="text-align: right;">1 %</p>	<p>Massenkonzentration β ***</p> $\beta = \frac{m(G)}{V(L)}$ <p style="text-align: right;">g · l⁻¹</p>
<p>Volumenanteil φ¹⁾ ** (φ: phi)</p> $\varphi = \frac{V(G)}{V(G) + V(LM)}$ <p>1) praktisch nur für ideale Gasmischungen</p> <p style="text-align: right;">1 %</p>	<p>Volumenverhältnis ψ * (ψ: psi)</p> $\psi = \frac{V(G)}{V(LM)}$ <p style="text-align: right;">1 %</p>	<p>Volumenkonzentration σ ** (σ: sigma)</p> $\sigma = \frac{V(G)}{V(L)}$ <p style="text-align: right;">1 % „%vol“</p>
<p>Stoffmengenanteil x¹⁾ ***</p> $x = \frac{n(G)}{n(L)} = \frac{n(G)}{n(G) + n(LM)}$ <p>1) früher: Molenbruch</p> <p style="text-align: right;">1 %</p>	<p>Stoffmengenverhältnis r *</p> $r = \frac{n(G)}{n(LM)}$ <p style="text-align: right;">1 %</p>	<p>Stoffmengenkonzentration c ****</p> $c = \frac{n(G)}{V(L)}$ <p style="text-align: right;">1 mol · l⁻¹</p>
<p>Genormt sind auch Gehaltsangaben in Bezug auf Teilchenzahlen N:</p> <p>Teilchenzahlanteil X Teilchenzahlverhältnis R Teilchenzahlkonzentration C</p> <p>□ : mögliche bzw. häufigste Einheit</p>		<p>Molalität b ***</p> $b = \frac{n(G)}{m(LM)}$ <p style="text-align: right;">1 mol · kg⁻¹</p>

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 , forensic 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)**

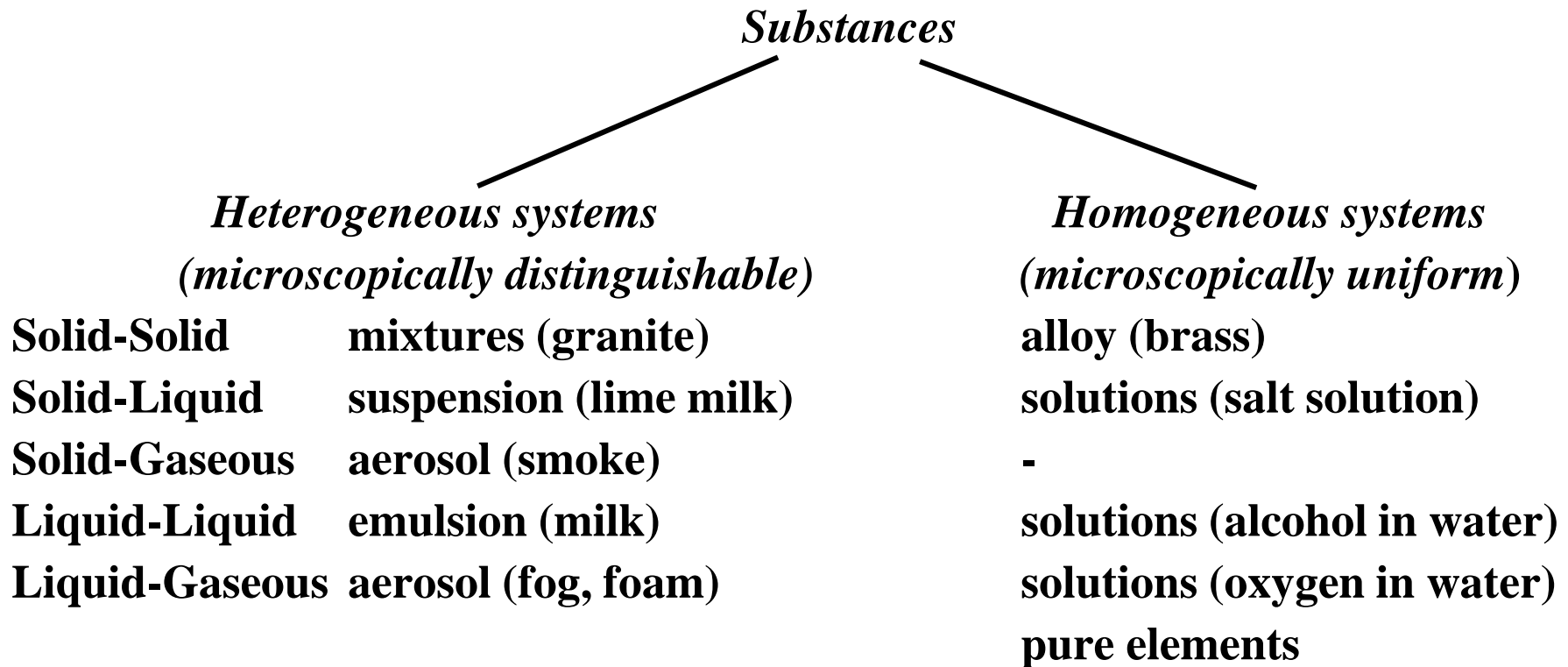
Analysis of samples

- **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, knives, quill,



3. Substances and Separation

Substances can be Classified by a Range of Physical Properties

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

3. Substances and Separation

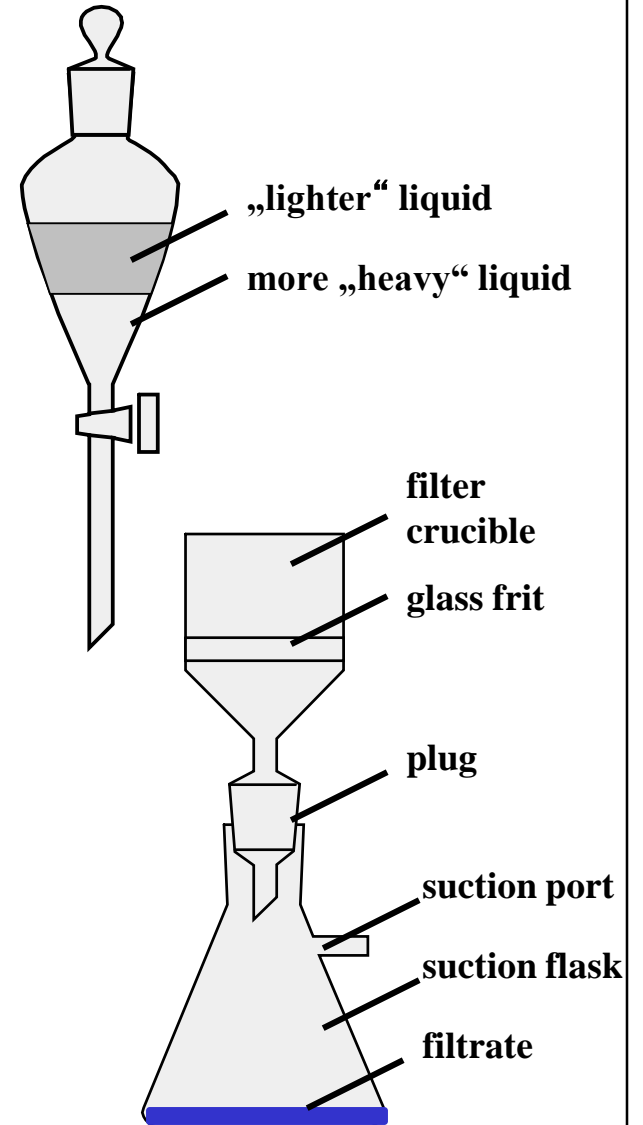
Physical Separation of Heterogeneous Systems

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. Physical methods

Vaporising and condensation:

Cooling:

Condensation and vaporising:

Adsorption and desorption

Gas chromatography

Liquid chromatography

Paper chromatography

Centrifugation (gases)

seawater → rainwater

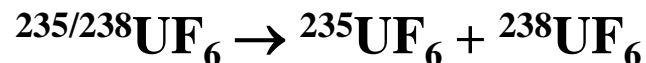
salt solutions → salt crystals

air → N₂, O₂, noble gases

dissolution of vaporisable substances

dissolution of solid substances

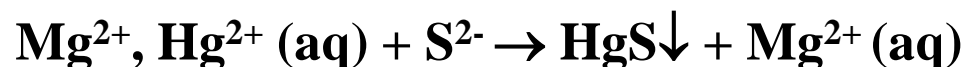
dissolution of solid substances (*β-carotene*)



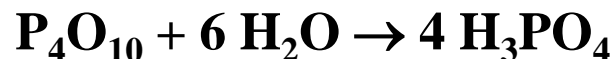
2. Chemical methods

Precipitation

Gas purification



drying of Ar via



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

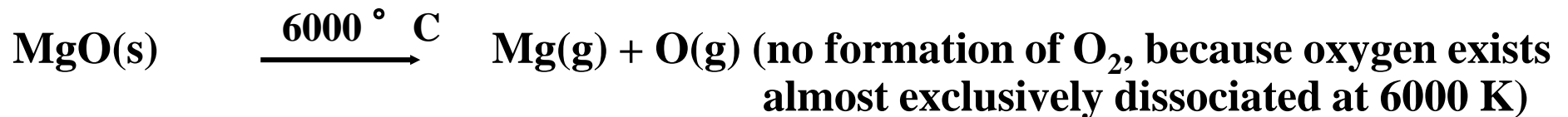
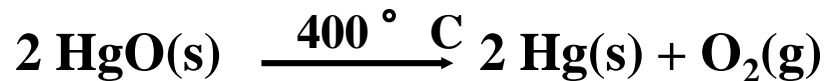
a. Compounds

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:



4. Theoretical Foundations

The Law of Mass Action \Rightarrow Quantitative Description of Reactions in Equilibrium

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

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

v = velocity

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

k = speed constant

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

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

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

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



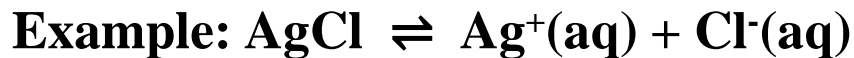
$$K = \frac{c^m(A^{n+}) \cdot c^n(B^{m-})}{c(A_m B_n)}$$

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

i.e. $K_L = K \cdot c(A_m B_n) \Rightarrow$

$$K_L = c^m(A^{n+}) \cdot c^n(B^{m-})$$

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



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

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

4. Theoretical Foundations

Solubility Products of poorly soluble Substances in H₂O 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 ₂ S	59.1	CdCO ₃	13.7
CuCl	7.4	ZnS	24.7	Ag ₂ CO 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 ₂ S ₃	71.6	PbCrO ₄	13.8
AgBr	12.3	CaSO ₄	4.6	Ag ₂ CrO ₄	11.9
AgI	16.1	SrSO ₄	6,5	Al(OH) ₃	32.3
Hg ₂ Cl ₂	17.9	BaSO ₄	10.0	Sc(OH) ₃	30.7
Hg ₂ I 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 H₂O
- Salts of heavy metals are poorly soluble (**in water**)
- Solubility of hydroxides:
NaOH > Mg(OH)₂ > Al(OH)₃ > Si(OH)₄ ⇒ 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.

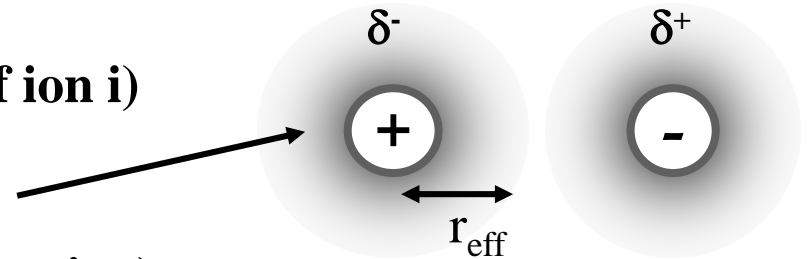
Activity: $a = \gamma \cdot c$ (effective concentration)

Magnitude of the activity coefficient γ

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

Dependence of the activity coefficient

- Ionic strength $I = 0.5 \sum c_i \cdot z_i^2$ ($z_i =$ 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 H₂O at 25 ° C

Ion	Activity coefficient for a given ionic strength I [mol/l]			
	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 ₂ PO 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 ₂ O 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

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

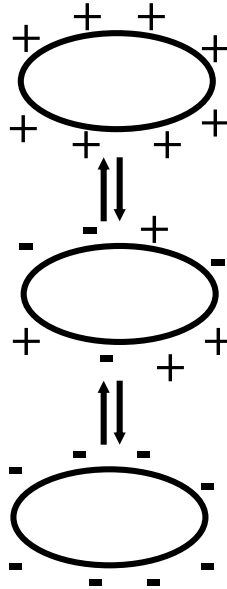
4. Theoretical Foundations

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

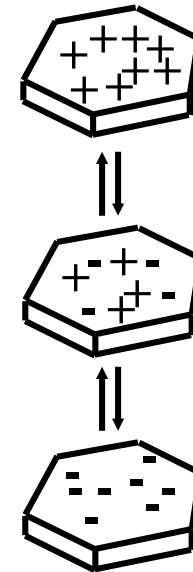
Al-salt in water



Proteins (nano particles)



Powder (micro particles)



IEP at $\text{pH} = (\text{pK}_1 + \text{pK}_2)/2$

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

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



Weight pyrite: e [g]

Weight BaSO_4 : a [g]

Stoichiometric factor: $F = A_S / M_{\text{BaSO}_4}$

Mass fraction

$$w = \frac{a \cdot F}{e} \cdot 100 \quad [\%]$$

5. Gravimetric Analysis

Course of a Gravimetric Analysis

1. **Sampling**
2. **Initial Weighing e [g]**
3. **Dissolution**
4. **Separation + Possible Masking**
5. **Precipitation \Rightarrow Precipitation Product**
6. **Filtration + Washing**
7. **Heat Treatment \Rightarrow 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



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 ($\Delta m < \pm 0.2 \text{ mg}$)

5. Gravimetric Analysis

Precipitation

Schematic course

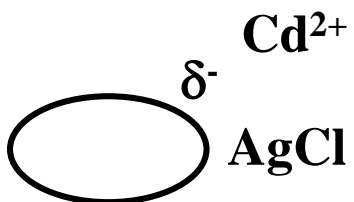
1. **Oversaturation of solution through addition of precipitation reagent**
2. **Seed formation = $f(\text{saturation concentration, impurities})$**
3. **Crystal growth = $f(T) \Rightarrow$ slow growth leads to purer precipitates, because alien substances can be excluded more easily**
4. **Crystal order = $f(T) \Rightarrow$ 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. Gravimetric Analysis

Entrainment Effects

1. Occlusion mechanical inclusion
2. Chemisorption enrichment on surface
3. Adsorption on charged colloidal particles 
4. Incorporation into lattice $\text{NH}_4\text{MgPO}_4 + \text{NH}_4\text{MgAsO}_4 \Rightarrow$ 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

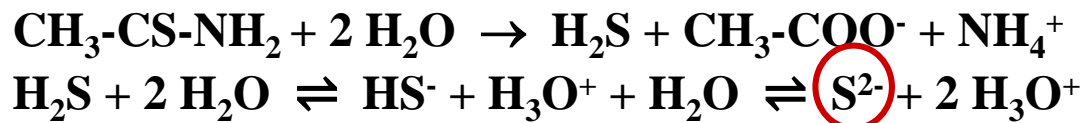
5. Gravimetric Analysis

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



Precipitation of hydroxides

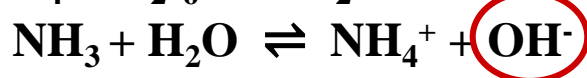
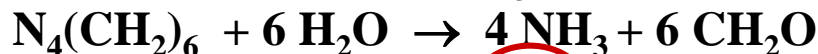
Hydrolysis of urea



Hydrolysis of potassium cyanate

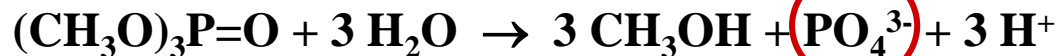


Hydrolysis of urotropine



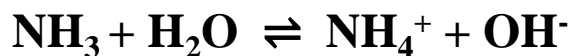
Precipitation of phosphates

Hydrolysis of tri-methylphosphate



5. Gravimetric Analysis

Precipitation of Hydroxides



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

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/mm ³]
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

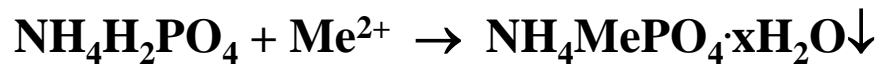


Na⁺ can not be precipitated, even in highly alkaline solutions

5. Gravimetric Analysis

Precipitation of Phosphates

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



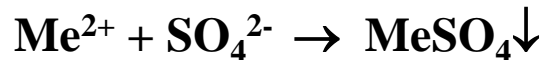
precipitation product



weighing product

Precipitation of Sulphates

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



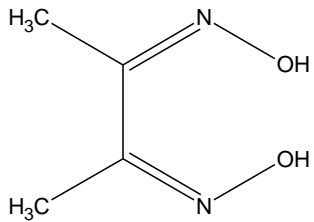
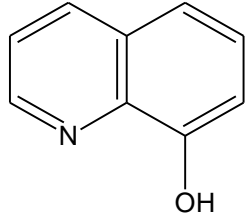
precipitation product =
weighing product

5. Gravimetric Analysis

Precipitation of Complexes with Organic Ligands

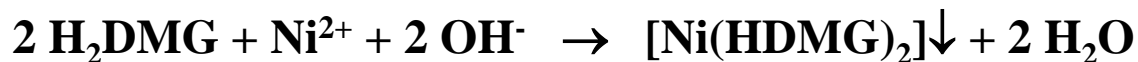
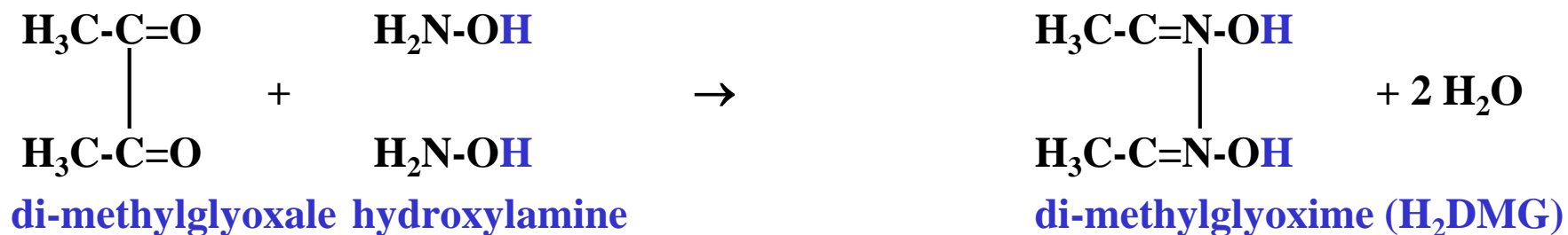
Advantages of organic reagents

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

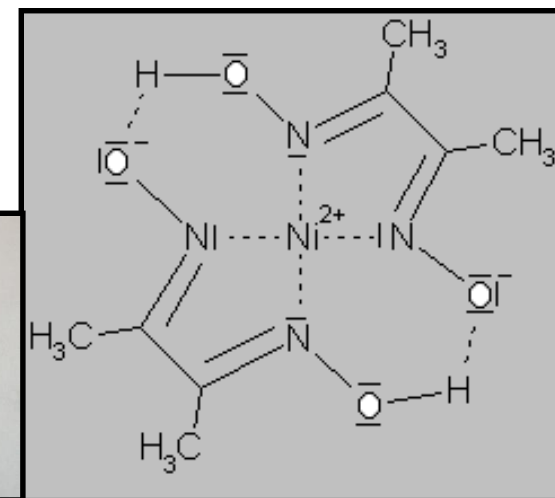
Name	Structure	Precipitation of
Di-methylglyoxime (DMG)		Ni^{2+} , Pd^{2+} , Pt^{2+}
8-hydroxyquinoline		Mg^{2+} , Zn^{2+} , Cu^{2+} , Cd^{2+} , Pb^{2+} , Al^{3+} , Fe^{3+} , Bi^{3+} , ...
Sodium tetra-phenylborate	$\text{Na}^+[\text{B}(\text{C}_6\text{H}_5)_4]^-$	K^+ , Rb^+ , Cs^+ , NH_4^+ , Ag^+

5. Gravimetric Analysis

Precipitation with Di-methylglyoxime



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

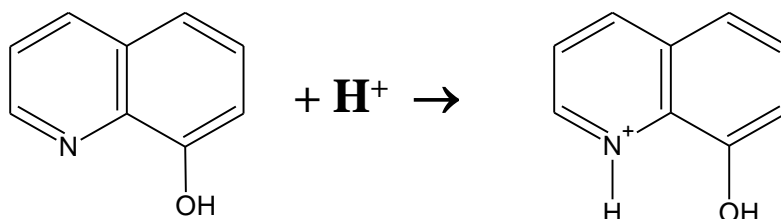


5. Gravimetric Analysis

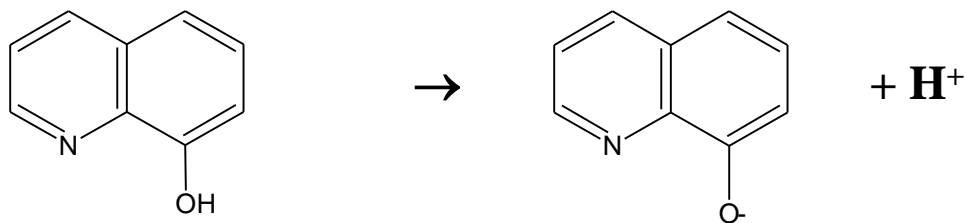
Precipitation with 8-Hydroxyquinoline (HOx) → Group Reagent

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

Reaction as base



Reaction as acid



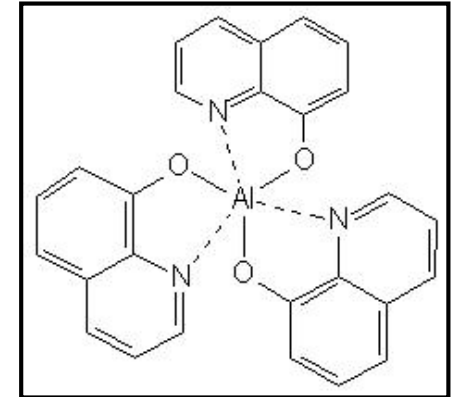
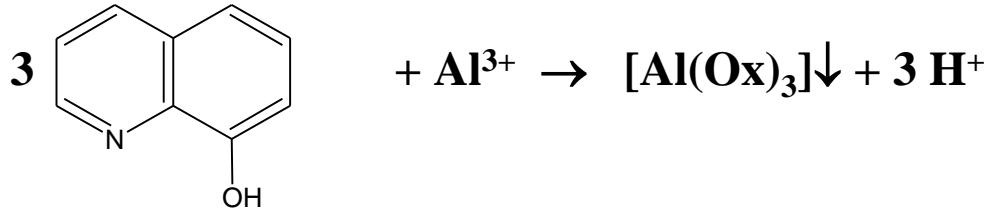
At IEP: $[\text{H}_2\text{Ox}^+] = [\text{Ox}^-]$

⇒ 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 Analysis

Precipitation with 8-Hydroxyquinoline (HOx)



⇒ Formation of highly insoluble $[\text{Al}(\text{ox})_3]$ (yellow-green and fluorescent)

„AlQ₃“

- **Beschwerungseffekt:** 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
$\text{Al}^{3+}, \text{Ga}^{3+}$	+	+	
$\text{Be}^{2+}, \text{La}^{3+}, \text{Mn}^{2+}$		+	
Mg^{2+}		+	+

6. Volumetric Analysis

Definition: The Volume of a Sample is Determined

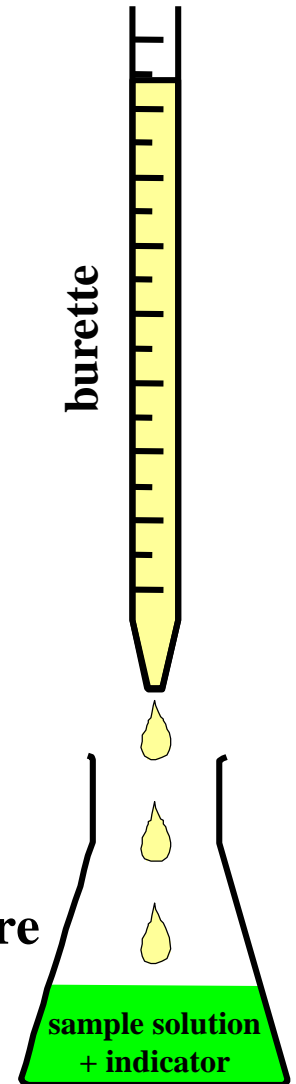
For the successful execution of a volumetric analysis, the following prerequisites must be met:

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
 $\text{nominal concentration} \times \text{titer factor (T or F)} = \text{effective concentration}$

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 weighed 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

Na_2CO_3 , NaHCO_3

NaCl

KIO_3 (potassium iodate)

Zn

$\text{C}_6\text{H}_5\text{COOH}$ (benzoic acid)

$\text{Na}_2\text{C}_2\text{O}_4$ (sodium oxalate)

standard solution to be defined

HCl , H_2SO_4 , HNO_3

AgNO_3

$\text{Na}_2\text{S}_2\text{O}_3$

EDTA (Titriplex III)

NaOH , KOH

KMnO_4

6. Volumetric Analysis

Acid-Base-Titrations

Foundation of acid-base-titrations is the neutralisation reaction



$$K = \frac{c(\text{H}^+) \cdot c(\text{OH}^-)}{c(\text{H}_2\text{O})}$$

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

$$K_{\text{W}} = c(\text{H}^+) \cdot c(\text{OH}^-)$$

$$-\log K_{\text{W}} = -\log c(\text{H}^+) - \log c(\text{OH}^-)$$

$$p = -\log_{10} c \quad (\text{p is just a mathematical operator})$$

$$pK_{\text{W}} = \text{pH} + \text{pOH}$$

6. Volumetric Analysis

Acids and Bases

1. Definition according to Arrhenius and Ostwald (1884)

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

- $\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-$
- $\text{H}_2\text{SO}_4 \rightarrow 2 \text{H}^+ + \text{SO}_4^{2-}$

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

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

Neutralisation: $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$
 $\text{HCl} + \text{NaOH} \rightarrow \text{H}_2\text{O} + \text{NaCl}$

Disadvantages of this definition

- Limited to aqueous systems
- Ammonia NH_3 is no base, although it reacts as such: $\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^-$



S. Arrhenius



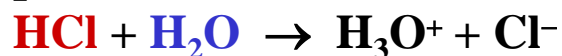
W. Ostwald

6. Volumetric Analysis

Acids and Bases

2. Definition according to Brønsted and Lowry (1923)

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

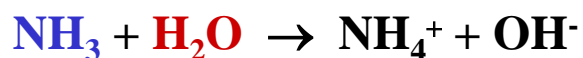


J.N. Brønstedt

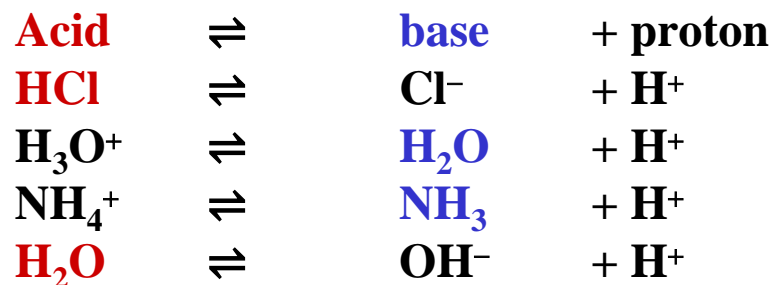


M. Lowry

Base are substances that “accept” protons from a reaction partner



Conjugated acid-base-pairs:



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

\Rightarrow 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^-

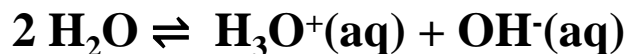
If a strong acid (completely protonated), e.g. HCl, is mixed with a strong base, e.g. NaOH, a transfer of protons from H_3O^+ -ions to OH^- -ions will occur (neutralisation)

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 ($\Delta H^0 = -57.4 \text{ kJ/mol}$)

6. Volumetric Analysis

Auto-Dissociation of Water

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



$K_{\text{W}} = c(\text{H}_3\text{O}^+) \cdot c(\text{OH}^-) = 10^{-14} \text{ mol}^2/\text{l}^2$
(ionic product of water at 22 ° C)

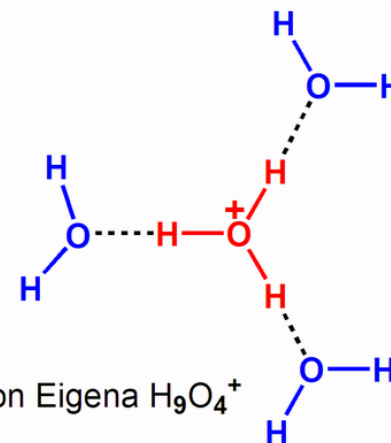
$$\Rightarrow \text{p}K_{\text{W}} = 14.00$$

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:



The total hydration enthalpy of a proton, i.e. the enthalpy of the reaction $\text{H}^+(\text{g}) + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+(\text{aq})$ is $\Delta H^0_{\text{hydr.}} = - 1091 \text{ kJ/mol}$



6. Volumetric Analysis

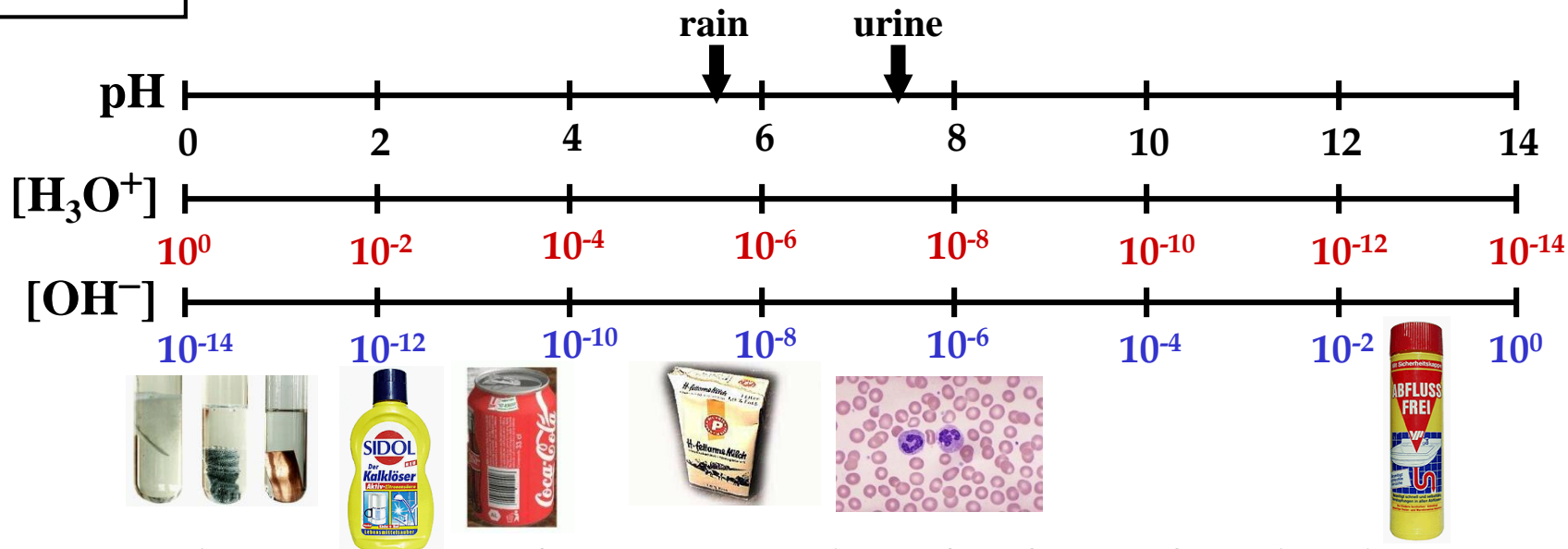
pH-Value (Latin: potentia hydrogenii)

$$\text{pH} = -\log c(\text{H}_3\text{O}^+)$$

negative decimal logarithm of hydrogen ion concentration

$$\text{pOH} = -\log c(\text{OH}^-)$$

negative decimal logarithm of hydroxide ion concentration



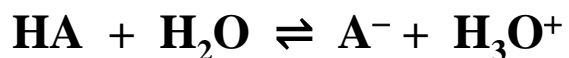
- In aqueous solution, the product of the concentrations of H₃O⁺ and OH⁻-ions is always constant: $\text{pH} + \text{pOH} = \text{p}K_{\text{W}} = 14$ at 22 ° C
- The pH-value can easily outrange the usual scale $\text{pH} = -1 \Rightarrow c(\text{H}^+) = 10 \text{ mol/l}$

6. Volumetric Analysis

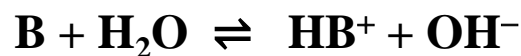
Strength of Acids and Bases

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

Strong acid (HCl)



Strong base (KOH)



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

$$K^*[\text{H}_2\text{O}] = K_s = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]}$$

$$K^*[\text{H}_2\text{O}] = K_B = \frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]}$$

$$\text{p}K_s = -\log K_s$$

$$\text{p}K_B = -\log K_B$$

K_s = acid constant

K_B = base constant

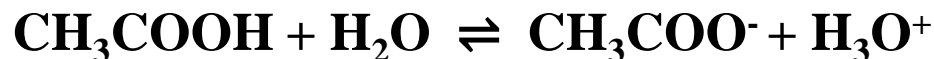
In water, the strongest acid is the H_3O^+ -ion, the strongest base is the OH^- -ion!

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



$$K_s = \frac{c(\text{H}^+) \cdot c(\text{CH}_3\text{COO}^-)}{c(\text{CH}_3\text{COOH})}$$

$$K_s = 1.8 \cdot 10^{-5}$$

$$\Rightarrow \text{p}K_s = 4.75$$

Classification according to strength in aqueous solution

Extremely strong acids	$\text{p}K_s < \text{p}K_s(\text{H}_3\text{O}^+) = -1.74$
Strong acids	$-1.74 < \text{p}K_s < 4.5$
Intermediates	$4.5 < \text{p}K_s < 9.5$
Weak acids	$9.5 < \text{p}K_s < 15.74$
Extremely weak acids	$\text{p}K_s > \text{p}K_s(\text{H}_2\text{O}) = 15.74$

6. Volumetric Analysis

Strength of Acids and Bases

pK_s	Acid	\rightleftharpoons	Base + H^+	pK_B -value	Name	
~ -10	$HClO_4$		ClO_4^-	ca. 24	perchloric acid	
~ -9	HBr		Br^-	ca. 23	hydrobromic acid	extremely strong acids
~-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	
6.92	H_2S		HS^-	7.08	hydrogen sulphide	intermediates
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)

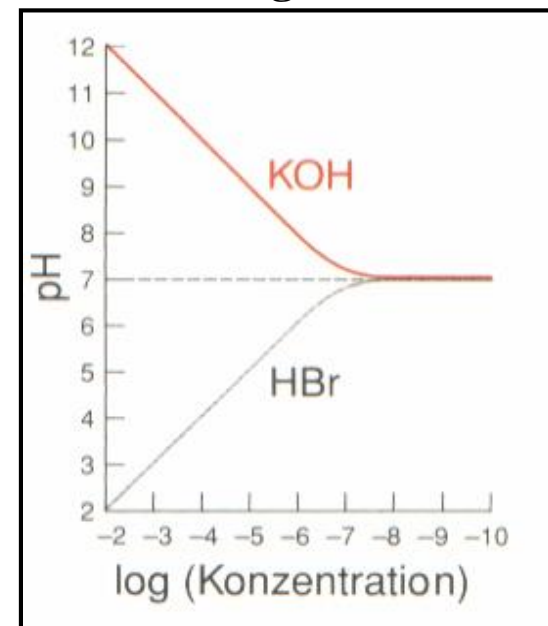
Extremely strong acids are stronger than H_3O^+ and thus completely deprotonated in aqueous solution. That implies that the H_3O^+ concentration equals the acid concentration, i.e. all extremely strong acids show the same pH-value at equal concentrations (levelling effect of water)

$c(\text{H}_3\text{O}^+) = c(\text{HA})$ is true for $c(\text{HA}) < 1 \text{ mol/l}$

pH of 0.1 M HBr: $\text{pH} = -\log(0.1) = 1$

pH of 0.001 M HBr: $\text{pH} = -\log(0.001) = 3$

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



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

$c(\text{H}_3\text{O}^+) = c(\text{HA}) + 10^{-7}$ and $\text{pH} = -\log(c(\text{HA}) + 10^{-7}) = 6.96$

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.

$$c(\text{H}_3\text{O}^+) = -\frac{K_S}{2} + \sqrt{\frac{K_S^2}{4} + K_S \cdot c_0(\text{HA})}$$

and

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

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



$$\Rightarrow K_S = \frac{c(\text{H}_3\text{O}^+) \cdot c(\text{A}^-)}{c_0(\text{HA})}$$

$$K_W = c(\text{H}_3\text{O}^+) \cdot c(\text{OH}^-)$$

Prerequisite for

electrical neutrality:

$$c(\text{H}_3\text{O}^+) = c(\text{A}^-) + c(\text{OH}^-) \Rightarrow c(\text{A}^-) = c(\text{H}_3\text{O}^+) - K_W/c(\text{H}_3\text{O}^+)$$

Substitution leads to:

$$K_S = \frac{c^2(\text{H}_3\text{O}^+) - K_W}{c_0(\text{HA})}$$

Transformation results in:

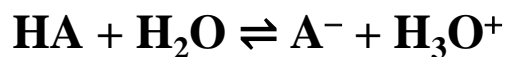
$$c(\text{H}_3\text{O}^+) = \sqrt{K_S \cdot c_0(\text{HA}) + K_W}$$

$$\Rightarrow \text{pH} = -1/2 \cdot \log(K_S c_0(\text{HA}) + K_W)$$

6. Volumetric Analysis

Intermediates

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



$$\Rightarrow \boxed{K_s = \frac{c(\text{H}_3\text{O}^+) \cdot c(\text{A}^-)}{c_0(\text{HA})}}$$

$c(\text{H}_3\text{O}^+) = c(\text{A}^-) \ll c(\text{HA})_0$ i.e. the concentration of the undissociated acid is way higher than of the deprotonated acid

$$\Rightarrow \boxed{K_s = \frac{c(\text{H}_3\text{O}^+) \cdot c(\text{A}^-)}{c_0(\text{HA})}}$$

$$\Rightarrow \boxed{c(\text{H}_3\text{O}^+) = \sqrt{K_s \cdot c_0(\text{HA})}}$$

$$\Rightarrow \text{pH} = \frac{1}{2}(\text{p}K_s - \log c_0(\text{HA}))$$

The same applies to bases

$$\Rightarrow \text{pOH} = \frac{1}{2}(\text{p}K_B - \log c_0(\text{B}))$$

6. Volumetric Analysis

Summary of pH-Values for Acids

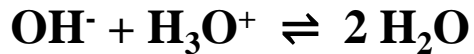
	$c(\text{H}_3\text{O}^+)$	pH-Value
Very strong $\text{pK}_s < -1.74$	$c(\text{H}_3\text{O}^+) = c_0(\text{HA}) + 10^{-7}$	$\text{pH} = -\log(c_0(\text{HA}) + 10^{-7})$
Strong $-1.74 < \text{pK}_s < 4.5$	$c(\text{H}_3\text{O}^+) = -\frac{K_s}{2} + \sqrt{\frac{K_s^2}{4} + K_s \cdot c_0(\text{HA})}$	$\text{pH} = -\log\left(-\frac{K_s}{2} + \sqrt{\frac{K_s^2}{4} + K_s \cdot c_0(\text{HA})}\right)$
Intermediate $4.5 < \text{pK}_s < 9.5$	$c(\text{H}_3\text{O}^+) = \sqrt{K_s \cdot c_0(\text{HA})}$	$\text{pH} = \frac{1}{2}(\text{pK}_s - \log(c_0(\text{HA})))$
(Very) weak $-\text{pK}_s > 9.5$	$c(\text{H}_3\text{O}^+) = \sqrt{K_s \cdot c_0(\text{HA}) + K_w}$	$\text{pH} = -\frac{1}{2} \cdot \log(K_s \cdot c_0(\text{HA}) + K_w)$

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

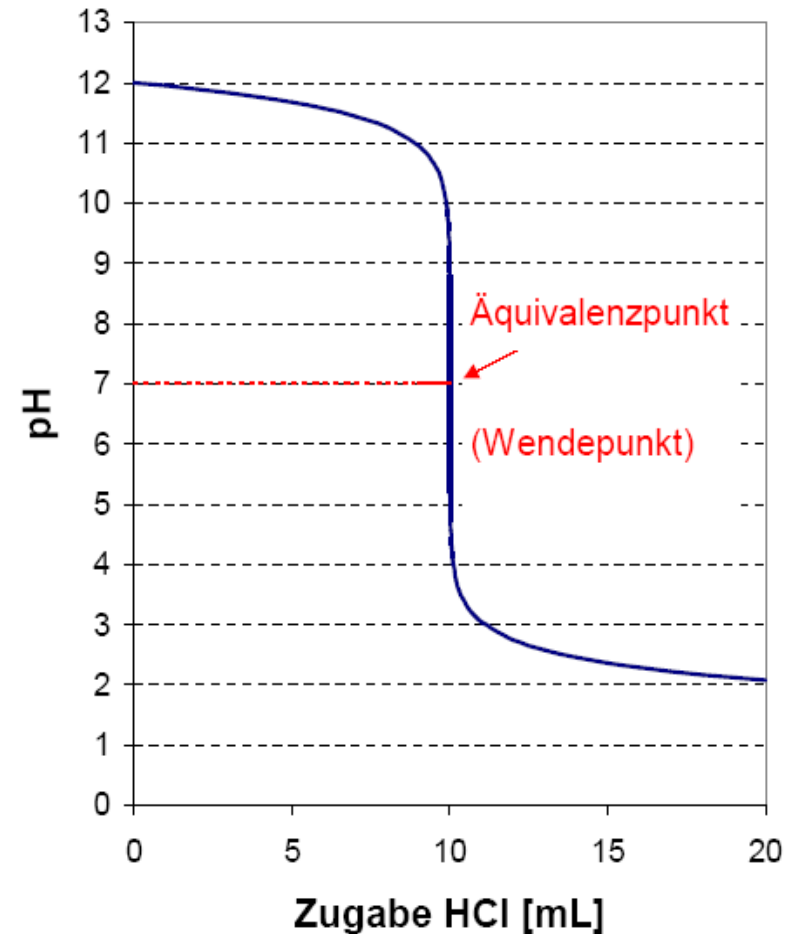
Titrant: x ml 0.1 M HCl are added



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 $T = c(\text{Acid}) \cdot V(\text{Acid}) / c(\text{Base}) \cdot V(\text{Base})$

$T = 1$ 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

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

Simplification for extremely strong acids leads to ($\text{pK}_s < -1.74$)

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

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

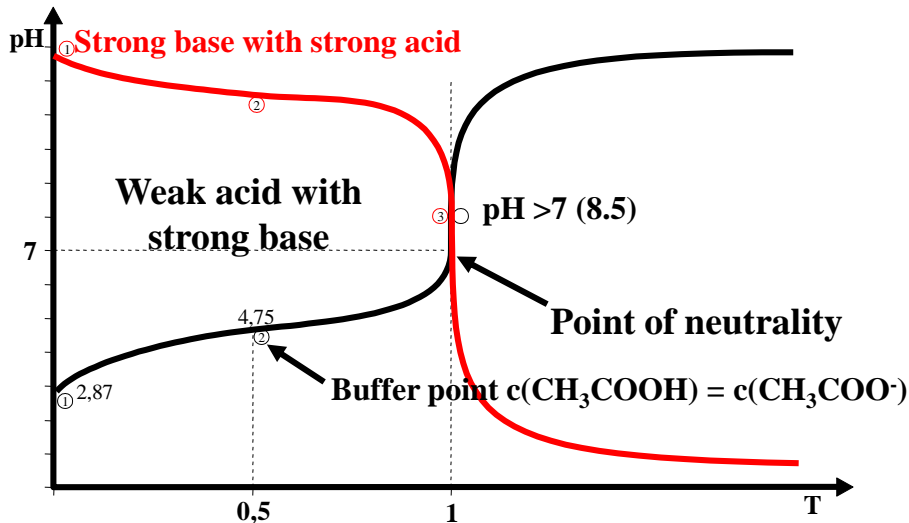
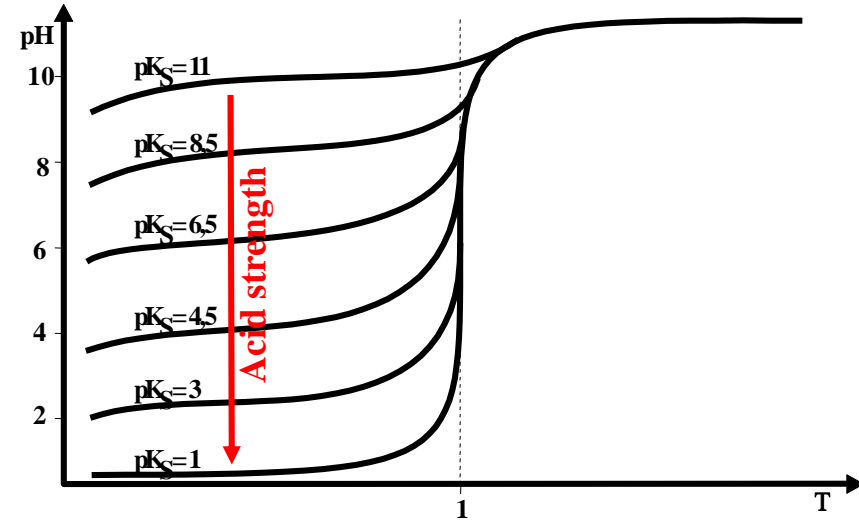
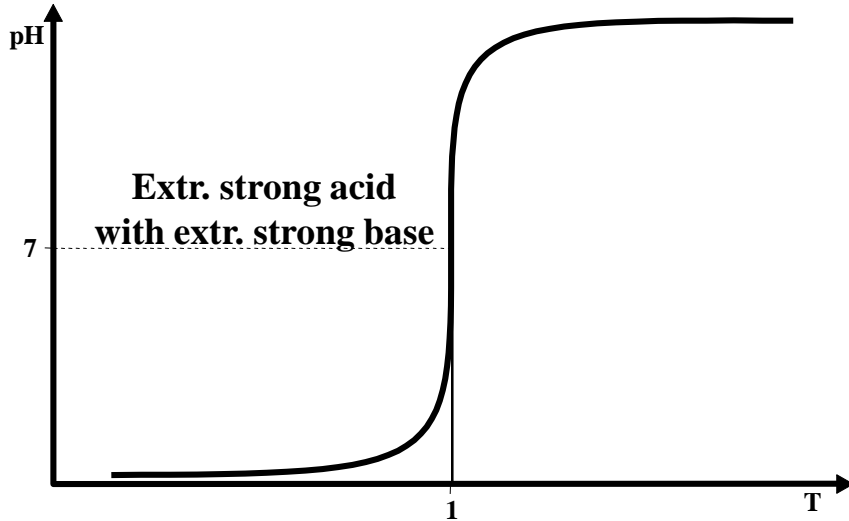
Rearrangement gives:

$$c(\text{H}_3\text{O}^+) = \frac{1-T}{2} \cdot c_0(\text{HA}) + \sqrt{\frac{(1-T)^2}{4} \cdot c_0(\text{HA}) + K_w}$$

⇒ 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
 \Rightarrow 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 $T = c(\text{acid}) \cdot V(\text{acid}) / c(\text{base}) \cdot V(\text{base})$

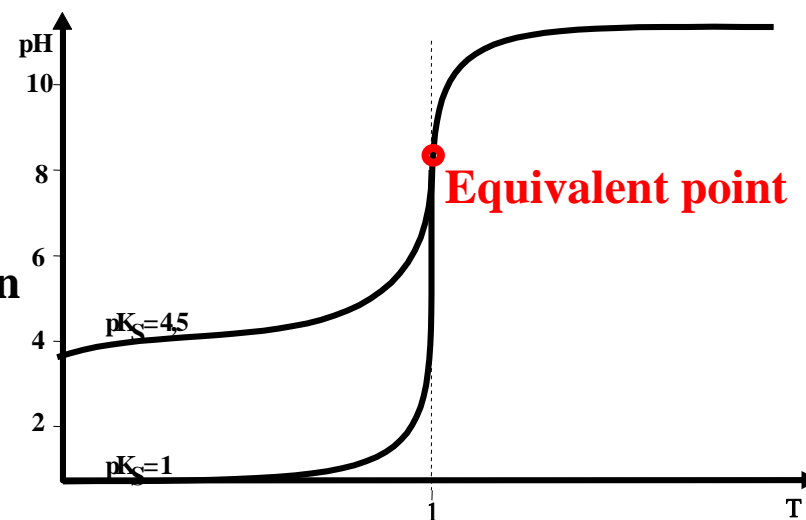
$T = 1$, meaning the neutralisation equivalent is reached after addition of only 1 ml NaOH



CH_3COO^- is a weak base ($\text{pK}_B = 9.25$)

pH-calculation analogous to 0.1 M Na-acetate solution

$$\boxed{c(\text{OH}^-) = \sqrt{K_B \cdot c_0(\text{B})}} \Rightarrow \text{pOH} = 5.1 \text{ and } \text{pH} = 8.9$$



6. Volumetric Analysis

Titration of extremely weak Acids and Bases

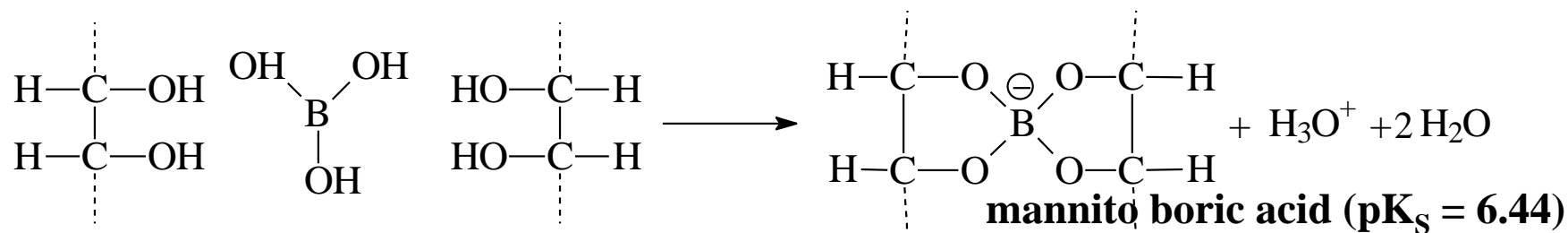
Problems

- 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 ($\text{pK}_s = 9.24$) is an extremely weak acid

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



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)

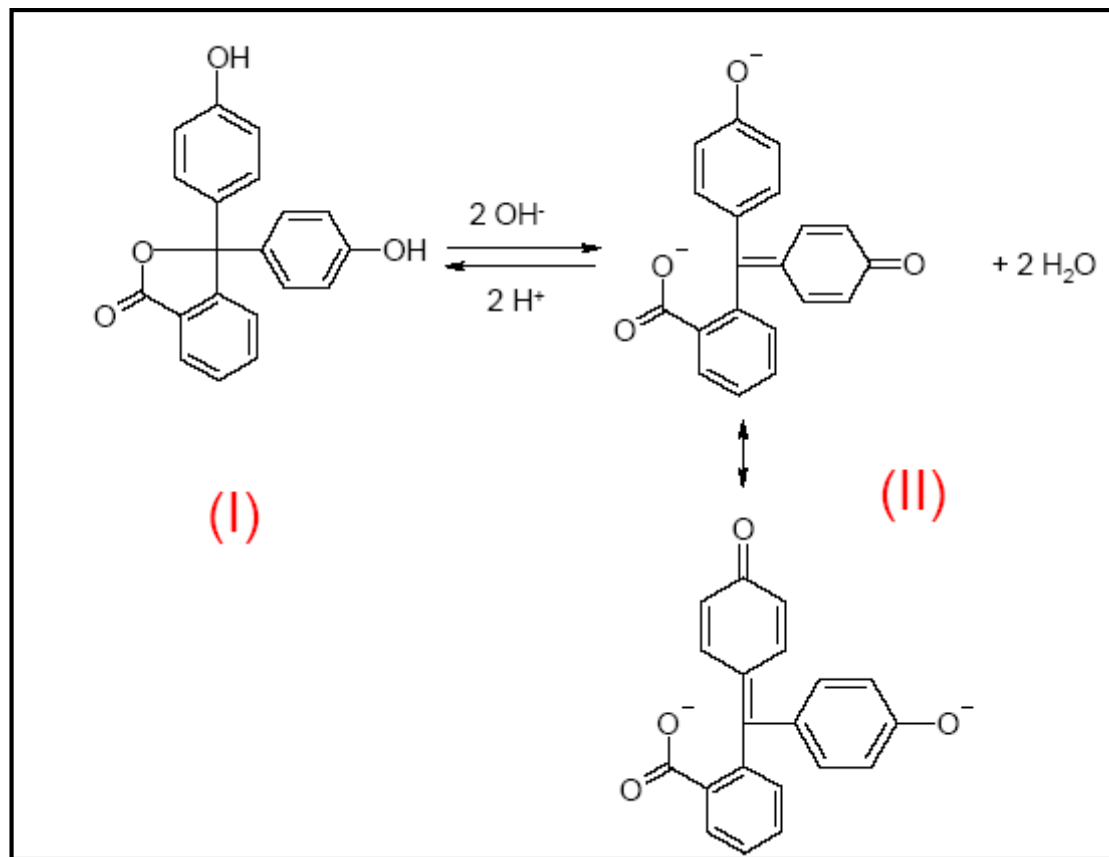
⇒ lactone ring closed

⇒ colourless

2. Alkaline solution (II)

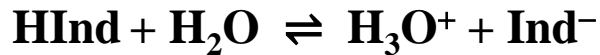
⇒ lactone ring open

⇒ red



6. Volumetric Analysis

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



⇒

$$K_{\text{Ind}} = \frac{c(\text{H}_3\text{O}^+) \cdot c(\text{Ind}^-)}{c(\text{HInd})}$$

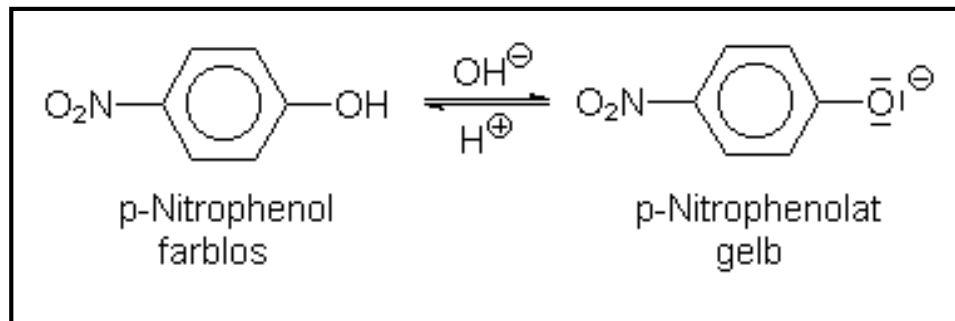
Transition range: $\text{pH} = \text{p}K_{\text{Ind}} \pm 1$

Pure colour 1: $\text{pH} = \text{p}K_{\text{Ind}} - 1$

⇒

$$\text{pH} = \text{p}K_s - \log \frac{c(\text{HInd})}{c(\text{Ind}^-)}$$

Pure colour 2: $\text{pH} = \text{p}K_{\text{Ind}} + 1$



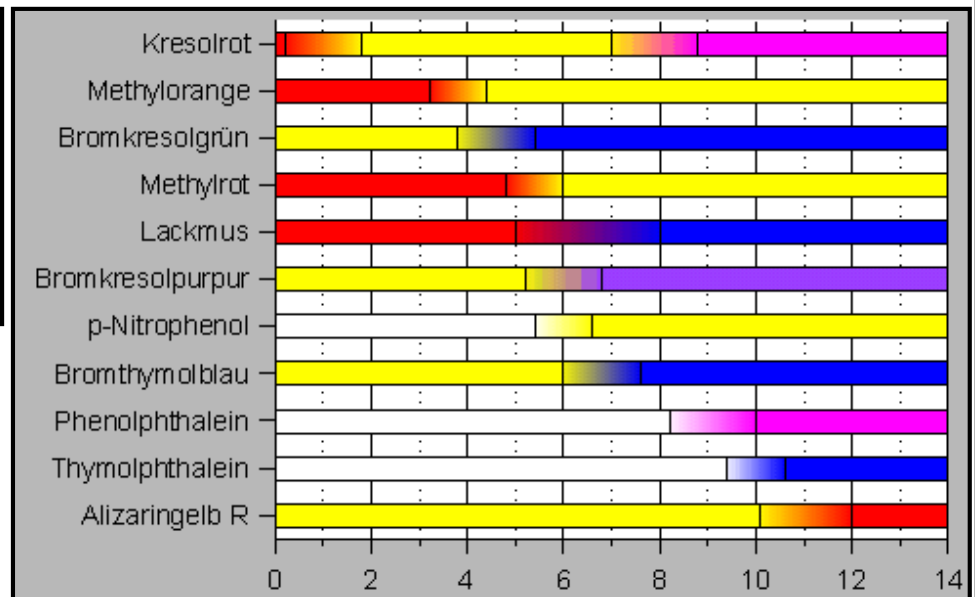
absorbs UV

absorbs blue

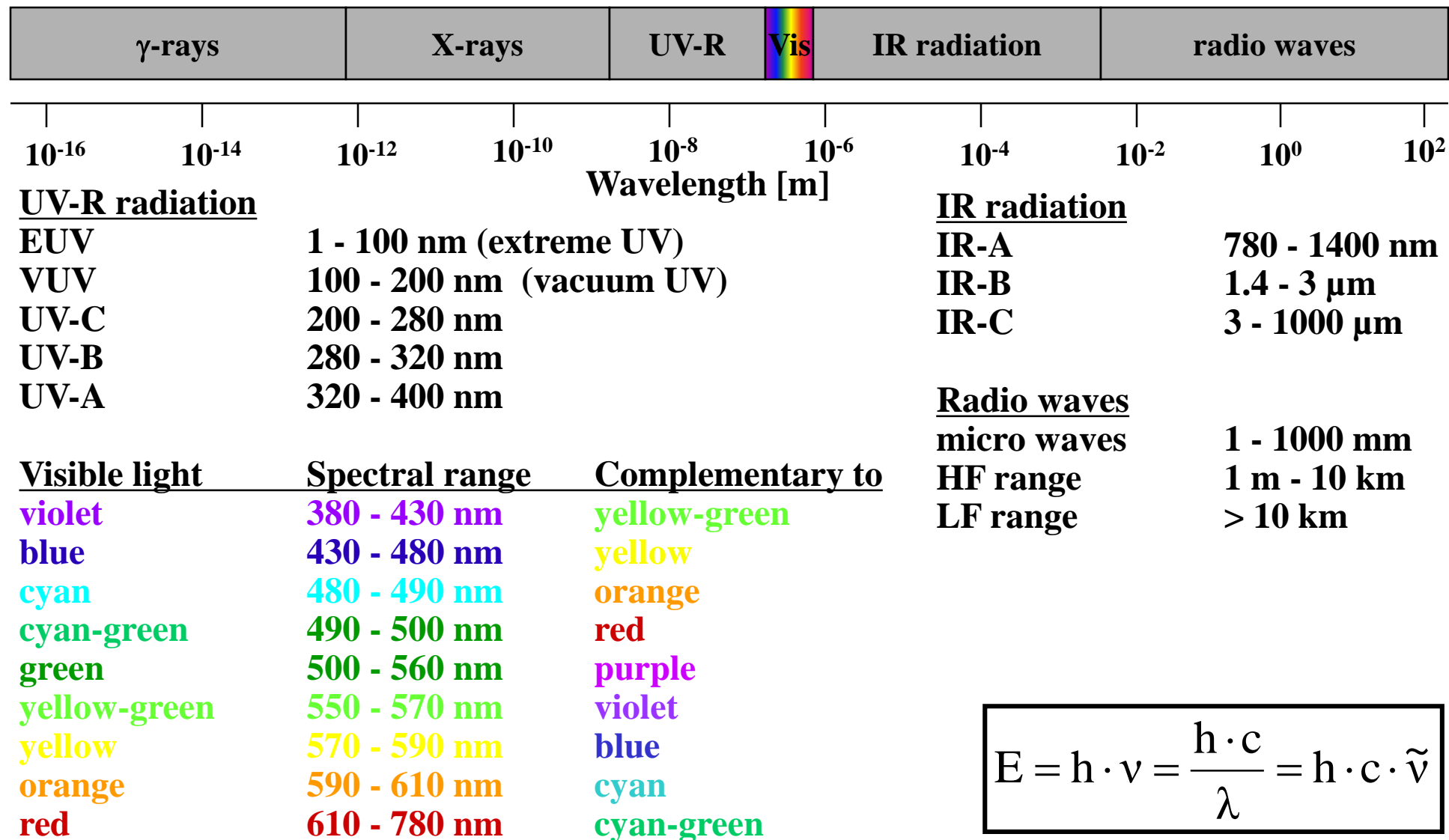
Mixed indicators

Litmus, universal indicator, red cabbage,

Tashiro (methyl red + methyl blue)



Excursion: The Electromagnetic Spectrum



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

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)

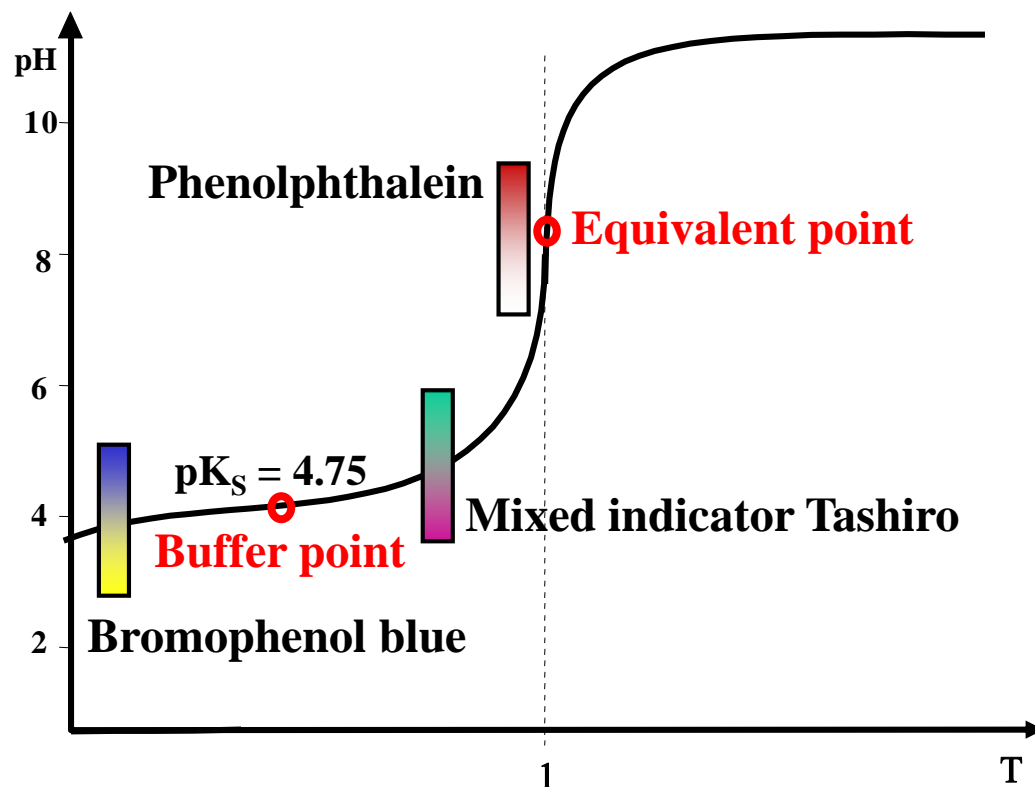
Remember: Titrations of weak bases with weak acids and the other way around lead to inconclusive results, if colorimetric means are used!

⇒ 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

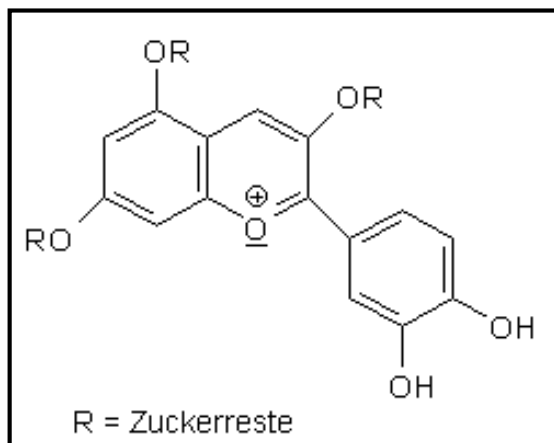


The addition of the indicator must be limited, since indicators are acids or bases themselves and thus have an impact on the protonation equilibrium

6. Volumetric Analysis

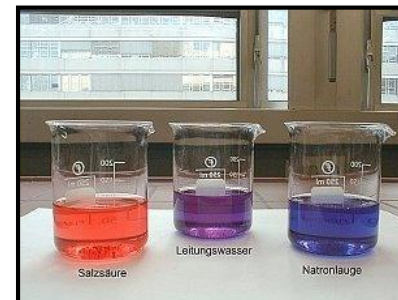
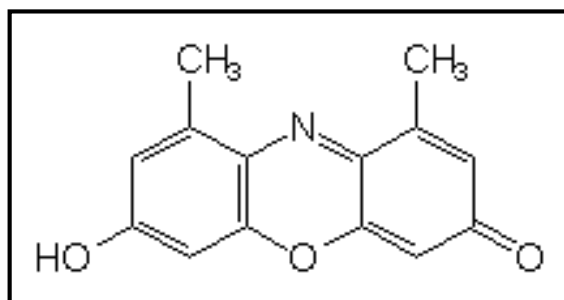
Naturally occurring Indicators

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



2. Example: Orcein from lichen (*rocella tinctoria*)

\Rightarrow 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 $\text{NO}_3^- \rightarrow \text{NH}_4^+$ Devarda alloy (50%Cu, 45%Al, 5%Zn)
amine $\text{R-NH}_2 \rightarrow \text{NH}_4^+$ catalyst: $\text{H}_2\text{SO}_4/\text{CuSO}_4$
not accessible by digestion: pyridine, R-NO_2 , R-N=N-R
- 2. Distillation**
sample: $\text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3 + \text{H}_2\text{O}$
receiver: $\text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4\text{Cl}$
- 3. Back titration** $\text{HCl (residue)} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$
- 4. Calculation**

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

6. Volumetric Analysis

Buffer Systems

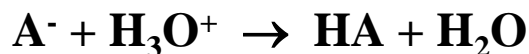
⇒ buffers are able to maintain the pH-value of a solution at a constant level, if acids or bases are added

Buffers are mixtures of

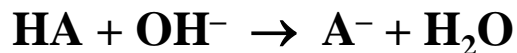
1. Weak acid HA and its anion A⁻
2. Weak base B and its cation HB⁺

On case 1)

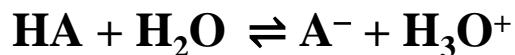
What happens upon addition of H₃O⁺?



What happens upon addition of OH⁻?



Entire equation



Henderson-Hasselbalch-Equation

$$K_s = \frac{c(\text{H}_3\text{O}^+) \cdot c(\text{A}^-)}{c(\text{HA})}$$



$$c(\text{H}_3\text{O}^+) = K_s \cdot \frac{c(\text{HA})}{c(\text{A}^-)}$$



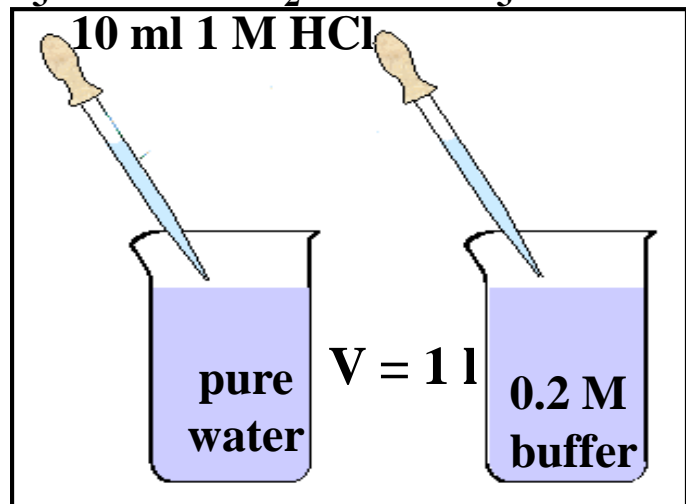
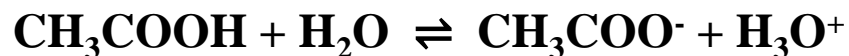
$$-\log c(\text{H}_3\text{O}^+) = -\log K_s + \log \frac{c(\text{A}^-)}{c(\text{HA})}$$



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

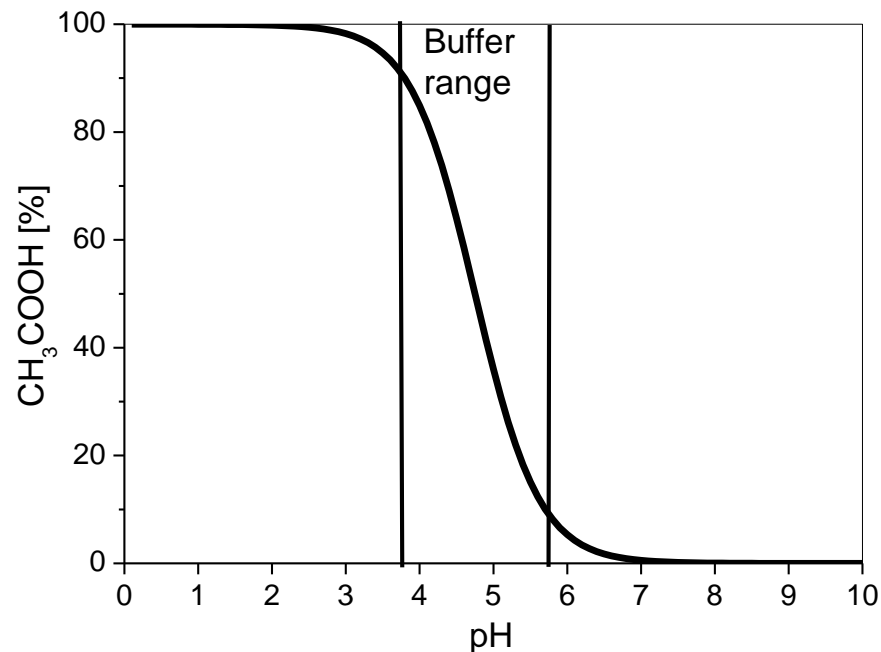
6. Volumetric Analysis

Example: Acetic Acid/Sodium Acetate Buffer



Start	pH	7.0	4.75
End	pH	2.0	4.71

Dissociation of CH_3COOH
as function of the pH-value

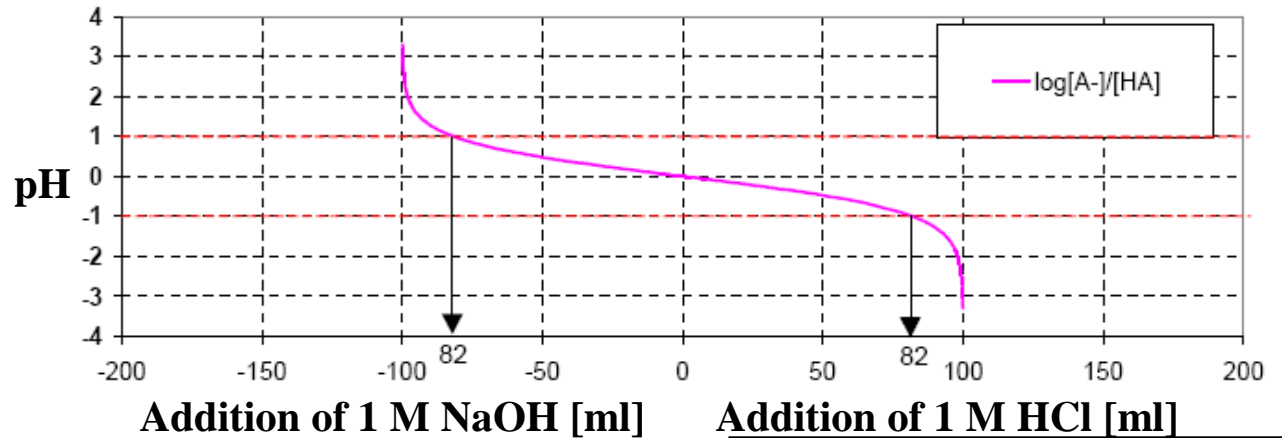


- The suitable range for a buffer is usually located at $\text{pK}_s \pm 1$
- For best results, choose the buffer system which pK_s is closest to the desired pH range!

6. Volumetric Analysis

Buffer Capacity

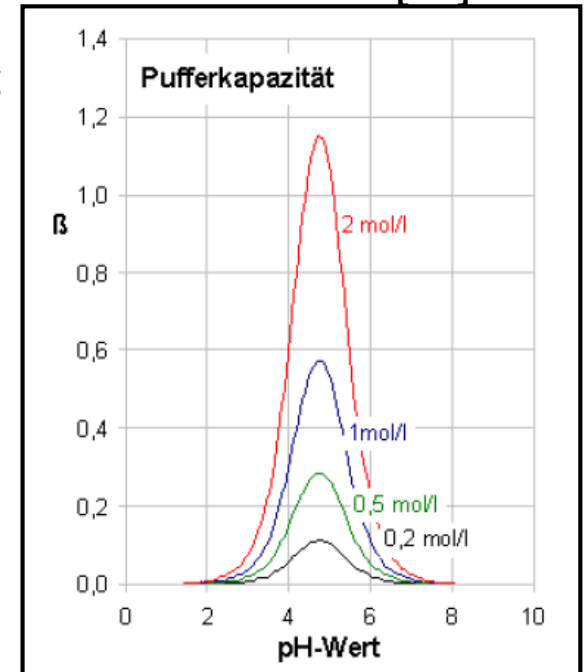
Value for the strength of the change in pH, when an acid or a base is added.



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

$C(S)$ 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

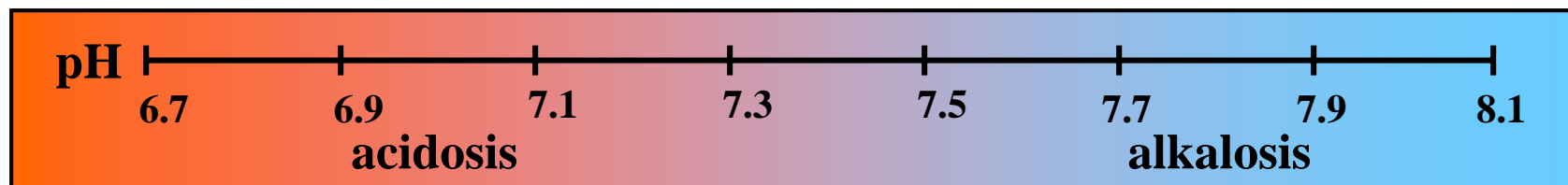


6. Volumetric Analysis

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

pH of blood plasma (human)

pH = 7.4 ± 0.03



Buffer system	pK _s	Name	Buffer capacity
$\text{H}_2\text{CO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HCO}_3^-$	6.1	carbonate	75%
$\text{HbH}^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Hb}$	8.25	haemoglobin	24%
$\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HPO}_4^{2-}$	6.8	phosphate	1%

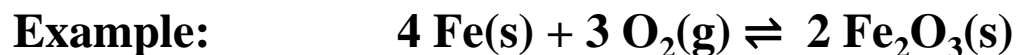
6. Volumetric Analysis

Redox Titration – Theoretical Foundations

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



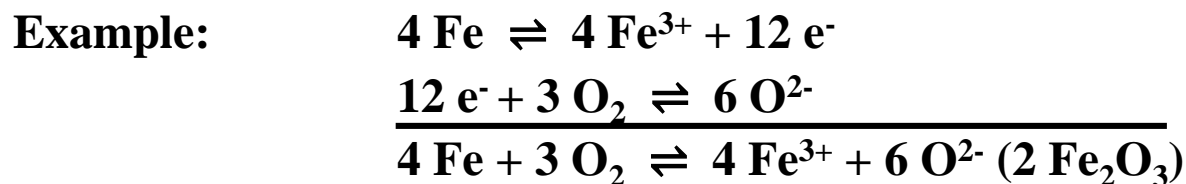
A. Lavoisier



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



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

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

<i>Formula</i>	<i>Name</i>	<i>Oxidation state</i>
H_2SO_2	sulphinic acid	+II
H_2SO_3	sulphurous acid	+IV
H_2SO_4	sulphuric acid	+VI
$\text{H}_2\text{S}_2\text{O}_3$	thiosulphuric acid	+II
$\text{H}_2\text{S}_2\text{O}_4$	di-thionous acid	+III
$\text{H}_2\text{S}_2\text{O}_6$	di-thionite acid	+V
$\text{H}_2\text{S}_2\text{O}_7$	di-sulphuric acid	+VI

6. Volumetric Analysis

Redox Reactions: Participation of two Redox Systems \Rightarrow Separate Description of both Redox Systems

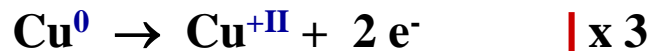
General approach to establish a valid redox reaction

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:



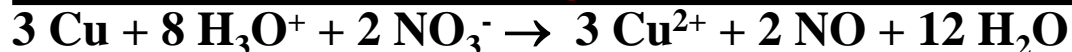
Redox system 1:



Redox system 2:



Redox equation:

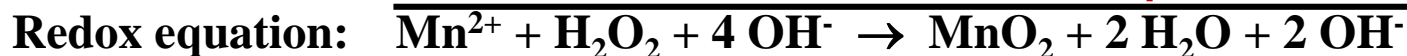
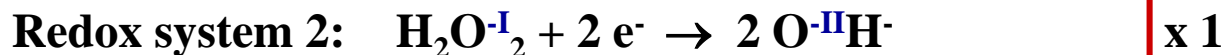


6. Volumetric Analysis

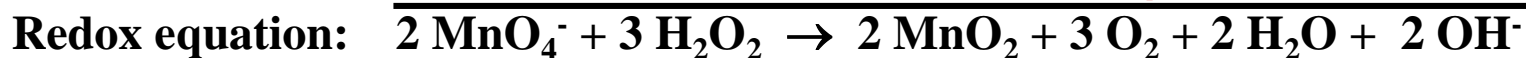
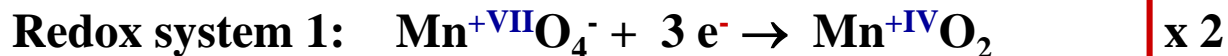
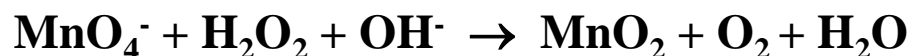
Redox Reactions

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

1. Example: Reaction of hydrogen peroxide with Mn²⁺



2. Example: Reaction of hydrogen peroxide with MnO₄⁻

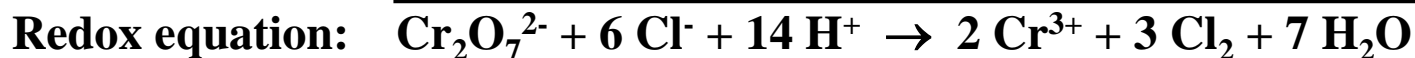
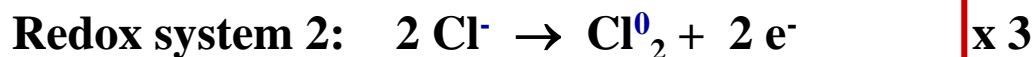
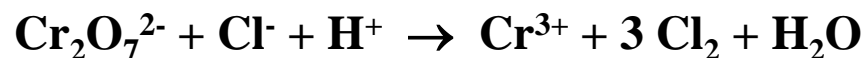


6. Volumetric Analysis

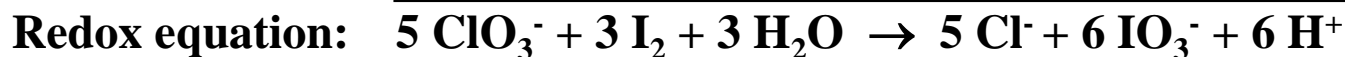
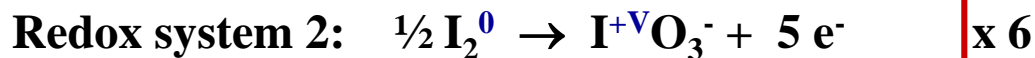
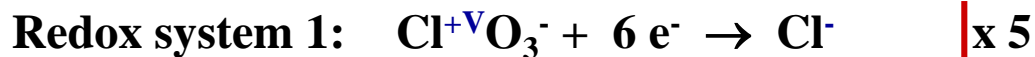
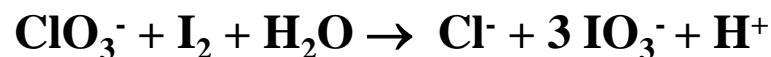
Redox Reactions

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

1. Example: Reaction of dichromate with chloride



2. Example: Reaction of chlorate with iodine



6. Volumetric Analysis

Redox Titrations: Manganometry



⇒ 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 $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$
- 2) Determination of oxalate through titration ⇒ direct titration $\text{C}_2\text{O}_4^{2-} \rightarrow 2 \text{CO}_2 + 2 \text{e}^-$

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):

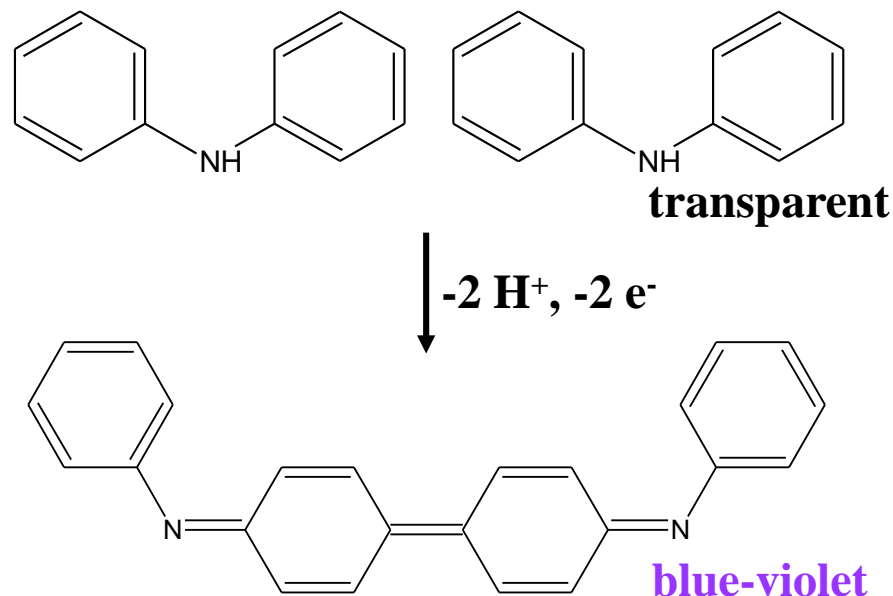


Advantages over manganometry

- 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-ylidene)-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):



Advantage compared to manganometry

- Cerium(IV)-sulphate solutions are stable

Disadvantages compared to manganometry

- Ce^{4+} is yellow and Ce^{3+} is colourless

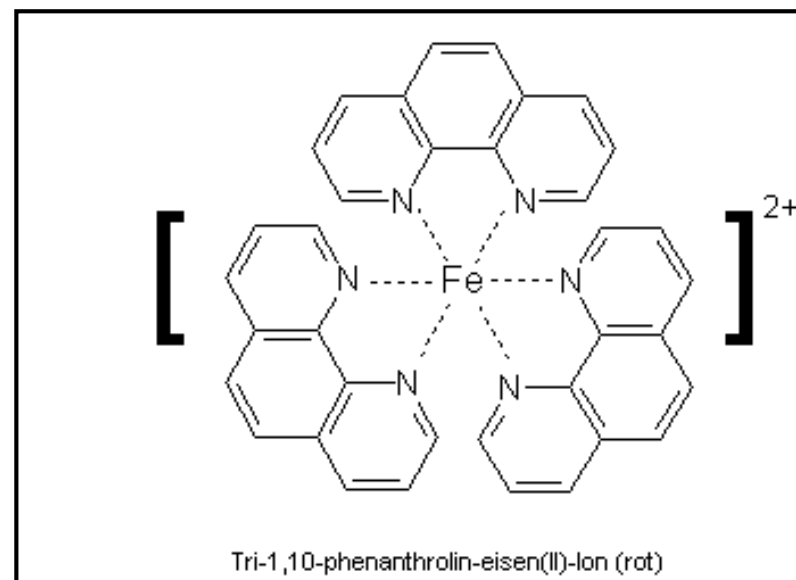
⇒ use of redox indicator

⇒ Ferroine



(red)

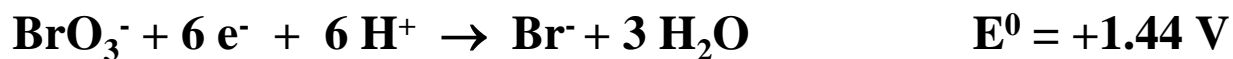
(light blue)



6. Volumetric Analysis

Redox Titrations: Oxidation with Potassium Bromate KBrO_3 (Bromatometry)

Possible applications are again similar to manganometry:



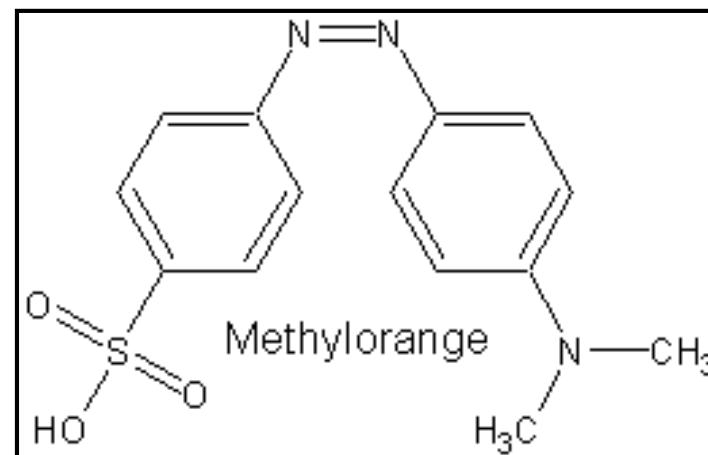
At the end point, residual bromate reacts as following:



Redox indicator is needed, too:

Methyl orange + $\text{Br}_2 \rightarrow$ transparent compound

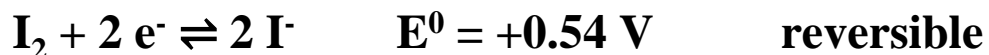
This reaction is irreversible!



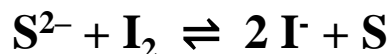
6. Volumetric Analysis

Redox Titrations: Iodometry

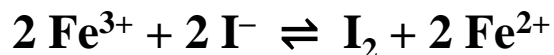
Versatile redox titration method, because iodine itself exhibits oxidising properties, whilst iodide solution shows reductive behaviour:



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



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



The resulting iodine is subsequently titrated with a standard solution of a suitable reduction agent, e.g. sodium thiosulphate $\text{Na}_2\text{S}_2\text{O}_3$:



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

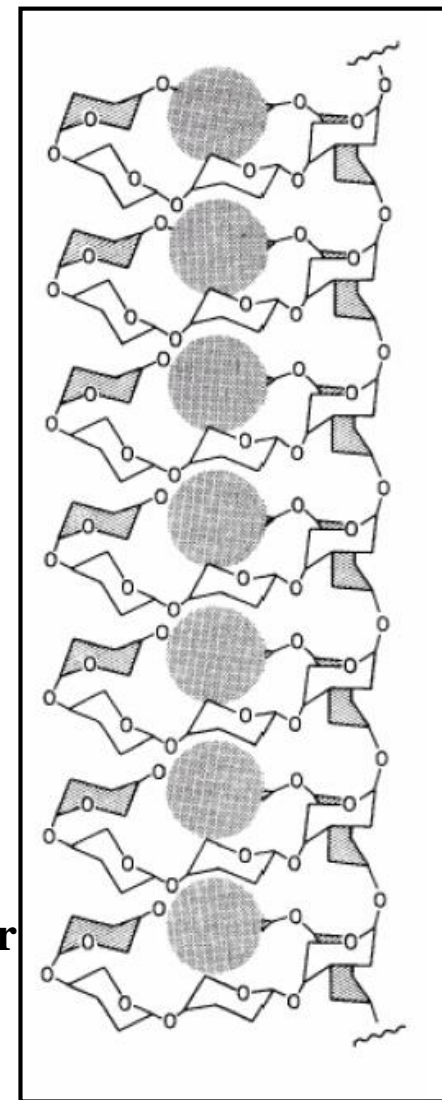
The iodine solutions used in iodometry always comprise potassium iodide apart from iodine, and thus the dark brown tri-iodide anion I_3^-

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: $\text{Me}^+ + \text{X}^- \rightleftharpoons \text{MeX} \downarrow$

$$K_L(\text{MeX}) < 10^{-9} \text{ mol}^2/\text{l}^2$$

No determination of:

sulphides, hydroxides, phosphates \Rightarrow delayed precipitation

Determination of X^-

Cl^- , Br^- , I^- , OCN^- , SCN^- , $\text{CN}^- \Rightarrow$ halides and pseudo-halides with Ag^+

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

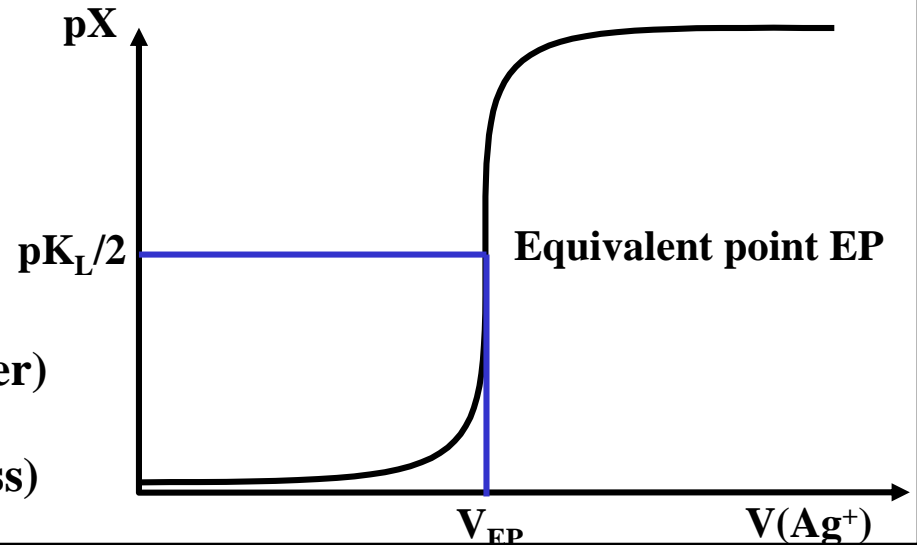
$$K_L(\text{AgX}) = c(\text{Ag}^+) \cdot c(\text{X}^-) = c^2(\text{X}^-)$$

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

$$\Rightarrow \text{pX} = \text{p}K_L/2$$

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

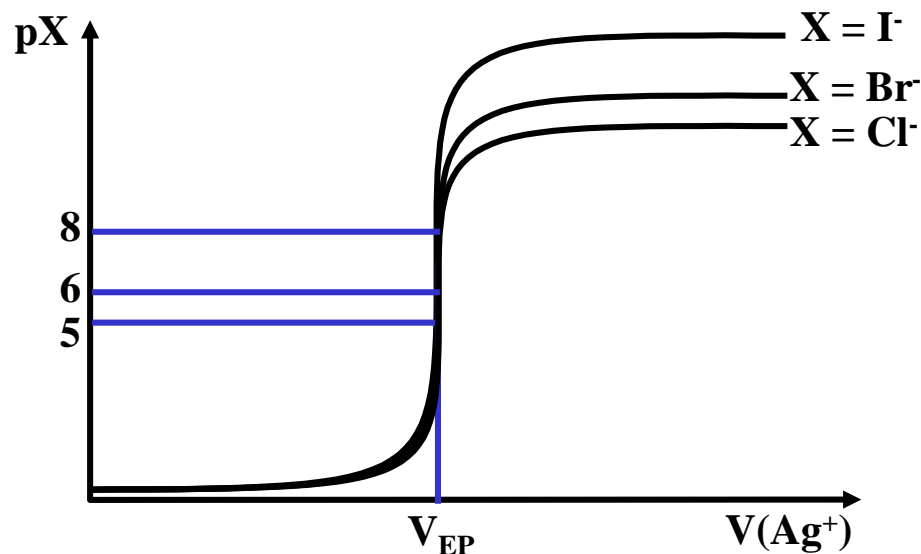
Posterior to EP: $\text{Ag}^+ + \text{X}^- \rightleftharpoons \overset{+}{\text{Ag}}\overset{+}{\text{X}} + \text{Ag}^+$ (excess)



6. Volumetric Analysis

Precipitation Titration

MeX	$K_L(\text{MeX})$
AgCl	$\sim 10^{-10} \text{ mol}^2/\text{l}^2$
AgBr	$\sim 10^{-12} \text{ mol}^2/\text{l}^2$
AgI	$\sim 10^{-16} \text{ mol}^2/\text{l}^2$



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

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

Prior to EP $\text{Ag}^+ + \text{X}^- \rightleftharpoons \text{AgX} \downarrow + \text{X}^- (\text{receiver}) \rightarrow \text{charged particles (colloids)}$

At EP $\text{Ag}^+ + \text{X}^- \rightleftharpoons \text{AgX} \downarrow \rightarrow \text{no charged particles} \Rightarrow \text{unobscured point}$

Posterior to EP: $\text{Ag}^+ + \text{X}^- \rightleftharpoons \text{AgX} + \text{Ag}^+ (\text{excess}) \rightarrow \text{charged particles (colloids)}$

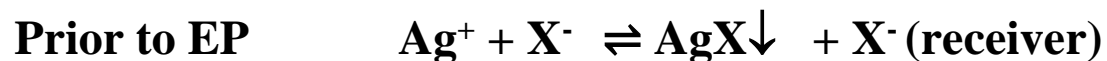
6. Volumetric Analysis

Precipitation Titration

2. Approach: titration according to Mohr (1856)



Ag₂CrO₄ is soluble more readily than AgX, i.e. precipitates posterior to the EP of the silver halides and pseudo-halides



Caution! Error of titration

When Ag₂CrO₄ precipitates, there is already a small excess of Ag⁺ present in the solution

6. Volumetric Analysis

Precipitation Titration

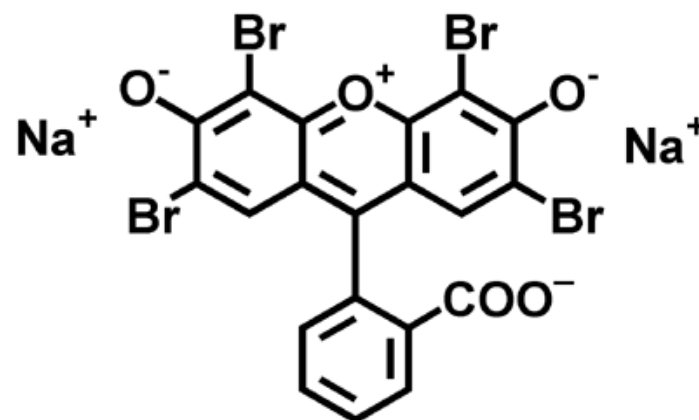
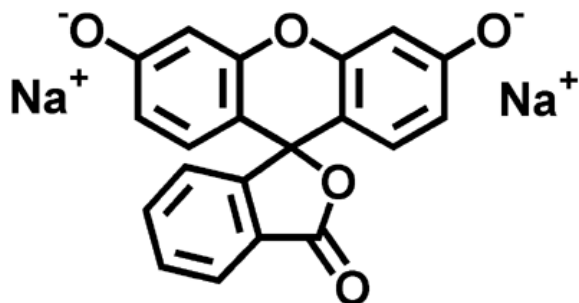
3. Approach: titration according to Fajans (1923)

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



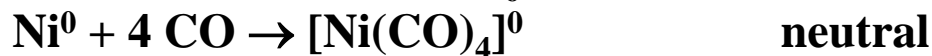
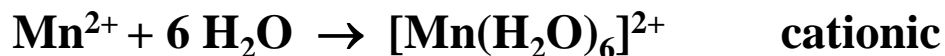
6. Volumetric Analysis

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 $\Rightarrow ZL_n$

Examples



\Rightarrow result of Lewis acid-base-reaction $Z + |L \rightarrow Z-L$

Ligands

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

Neutral molecules: NH₃ (ammine-), H₂O (aqua-)

6. Volumetric Analysis

Complexometry

Coordination number

Geometry

2

linear

3

trigonal planar

4

tetrahedral, square planar

5

trigonal bi-pyramidal, square pyramidal

6

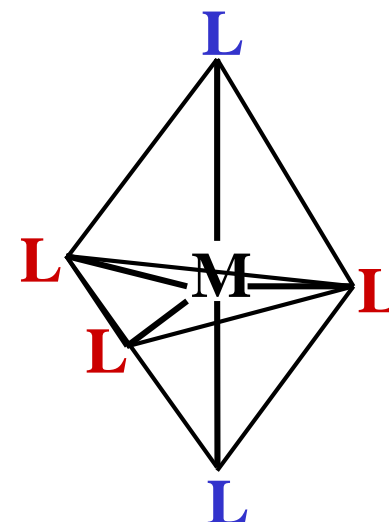
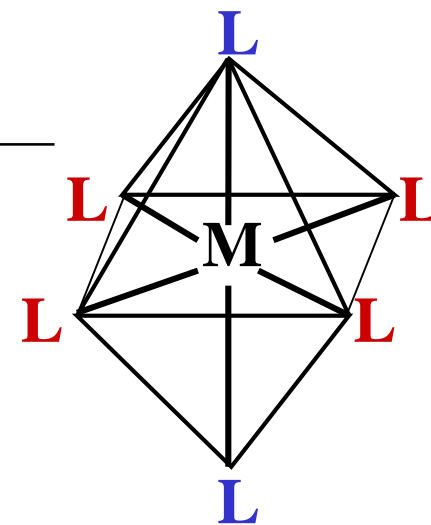
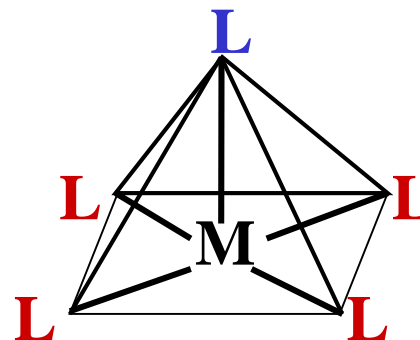
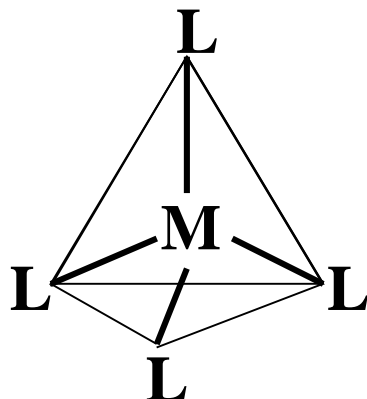
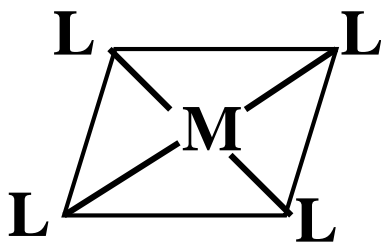
octahedral

7

pentagonal bi-pyramidal

8

cubic, dodecahedral



6. Volumetric Analysis

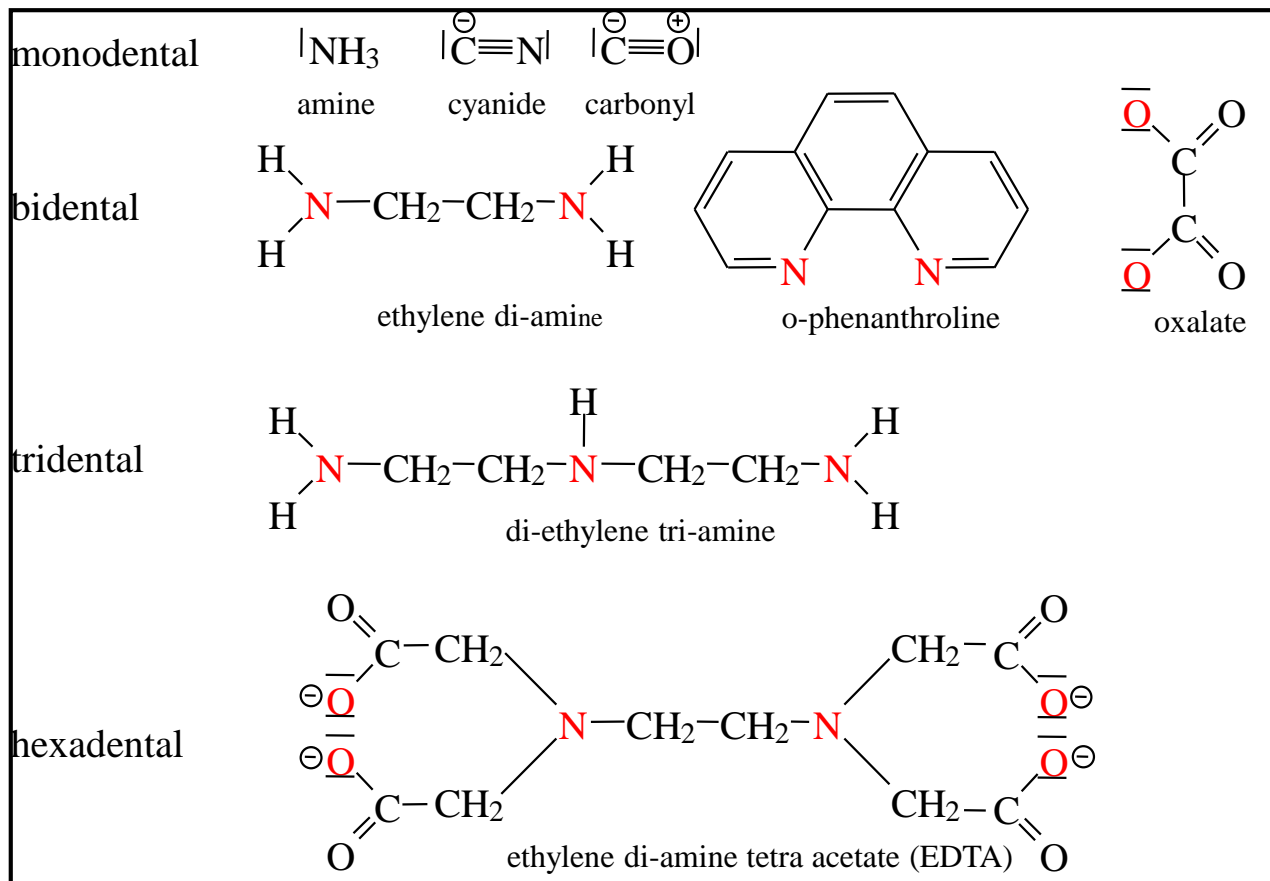
Complexometry

Denticity

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

Multidental ligands are also called chelating ligands

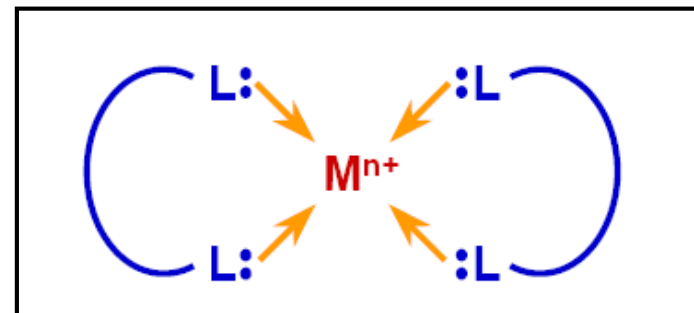
Chelating complexes are more stable than complexes with monodental ligands



6. Volumetric Analysis

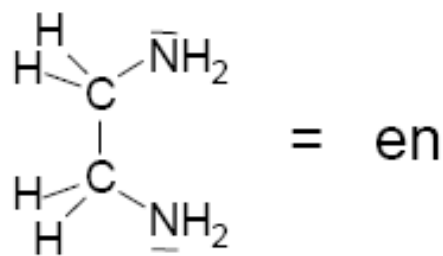
Complexometry

Composition of chelating ligands and complexes

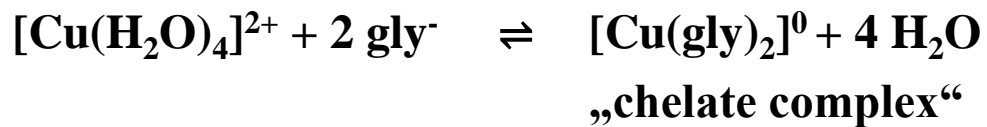
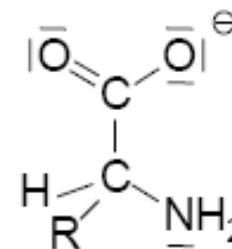


Examples

ethylene diamine (en)



amino acids $\text{NH}_2\text{-CHR-COO}^-$



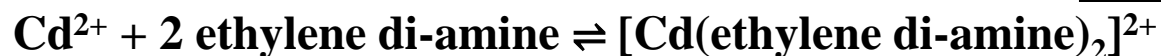
6. Volumetric Analysis

Complexometry

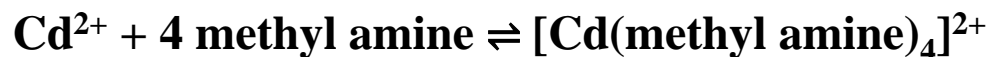
Chelating effect

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

Example



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



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

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

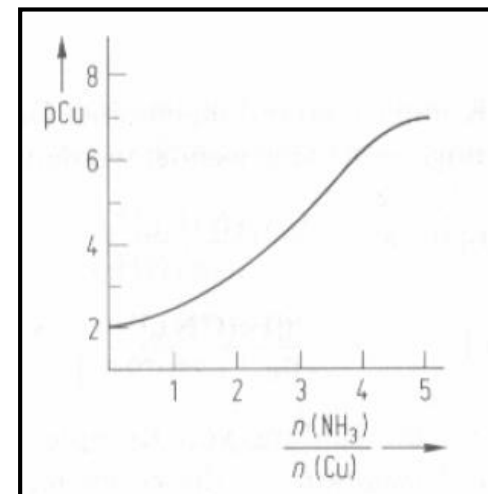
Central atom:	analyte
Ligand:	titration agent, e.g. multidental ligands of the like of EDTA
Complex formation:	central atom Z + n ligand \rightarrow complex ZL_n

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!



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

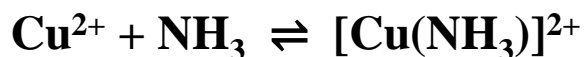
Reason: stepwise course of the complex formation reaction



6. Volumetric Analysis

Complexometry

Stepwise complex formation reactions



$$K_1 = 1.35 \cdot 10^4$$



$$K_2 = 3.02 \cdot 10^3$$



$$K_3 = 7.41 \cdot 10^2$$



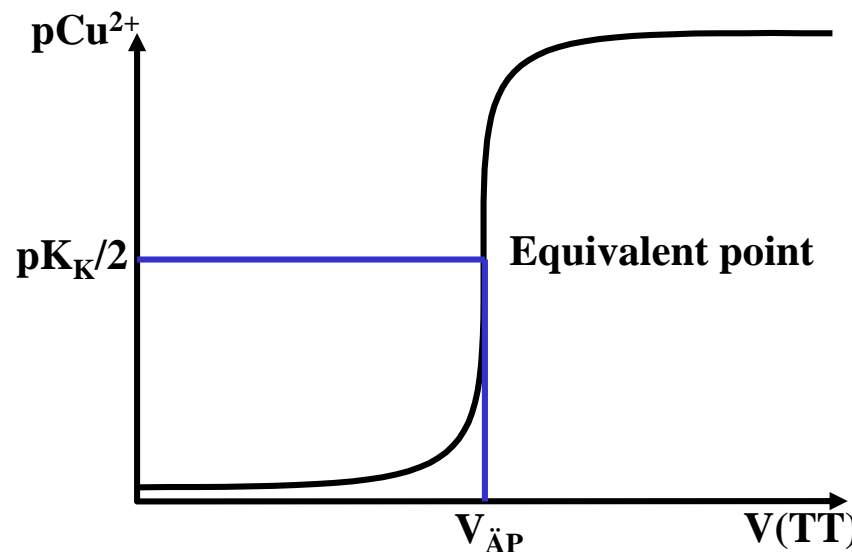
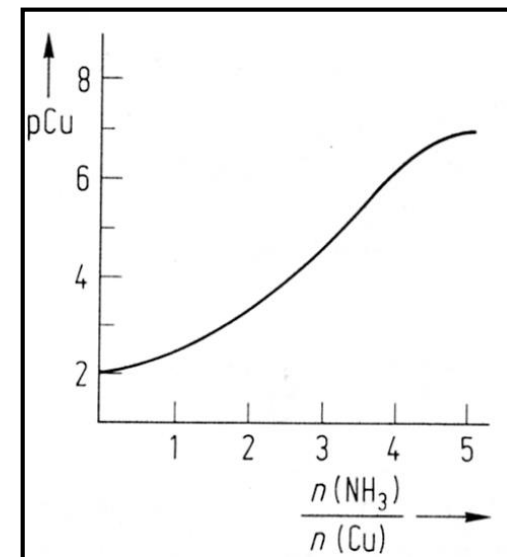
$$K_4 = 1.29 \cdot 10^2$$

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

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)

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

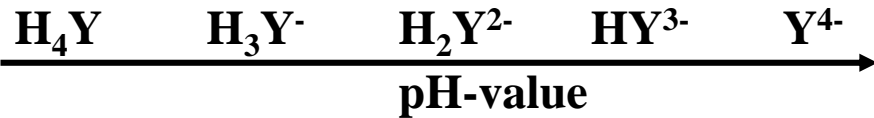


6. Volumetric Analysis

Complexometry

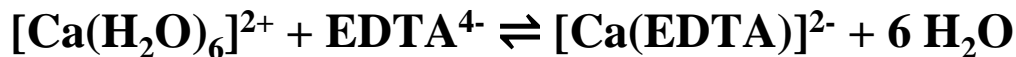
Ethylene diamine tetra acetic acid (EDTA, H_4Y)

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

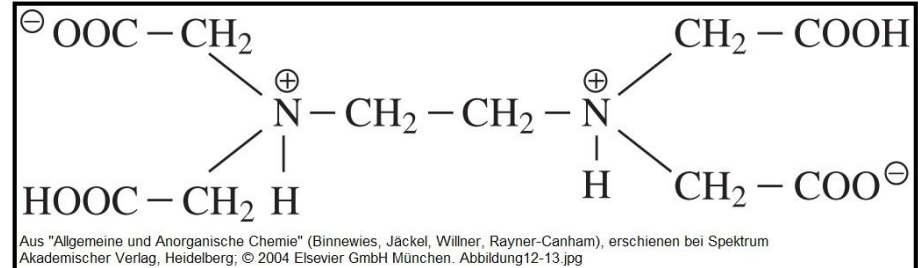


In highly alkaline environments only $[Y]^{4-}$ is present, which is the actual ligand

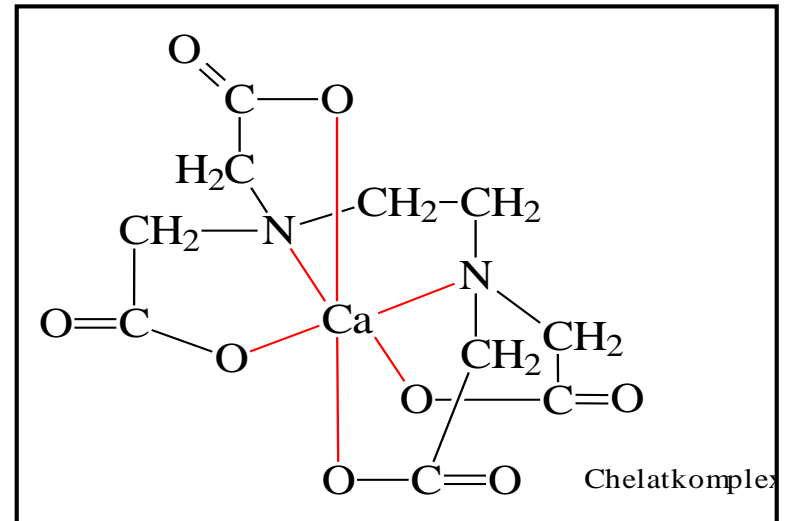
Example for a complex formation with EDTA



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



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



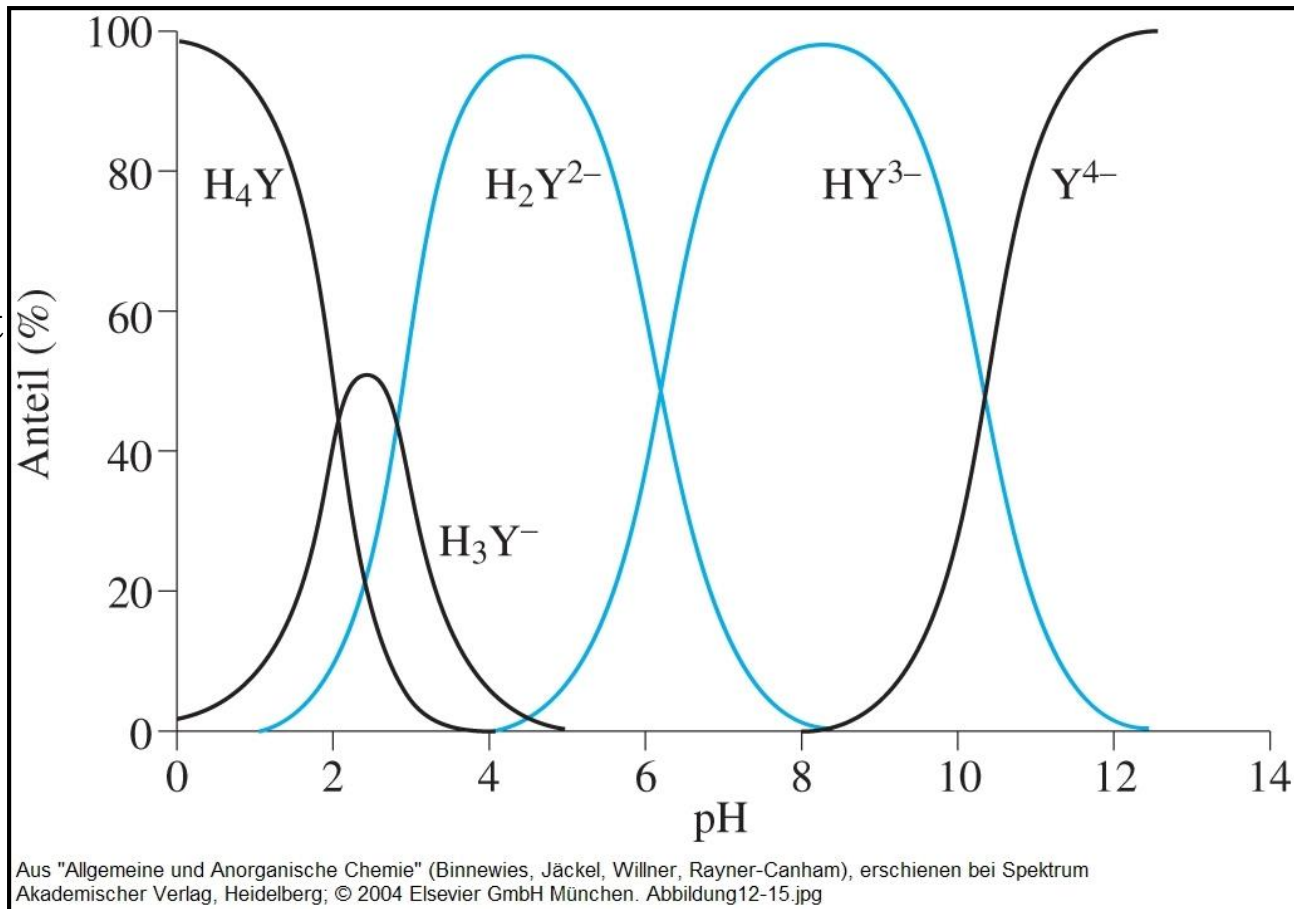
6. Volumetric Analysis

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+}



6. Volumetric Analysis

Complexometry

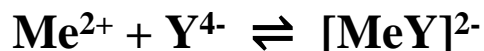
pH dependence of the reaction with EDTA

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)

$$c(Y^{4-})_H = \alpha_Y^{4-} \cdot c_0(\text{EDTA}) \quad \text{with } c_0(\text{EDTA}) = c(\text{H}_4\text{Y}) + c(\text{H}_3\text{Y}^-) + c(\text{H}_2\text{Y}^{2-}) + c(\text{HY}^{3-}) + c(\text{Y}^{4-})$$

α_Y^{4-} describes the pH-dependant concentration (activity) of Y^{4-}



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

$$\Rightarrow K_{\text{eff}} = K_K \cdot \alpha_Y^{4-}$$

(effective stability constant)

6. Volumetric Analysis

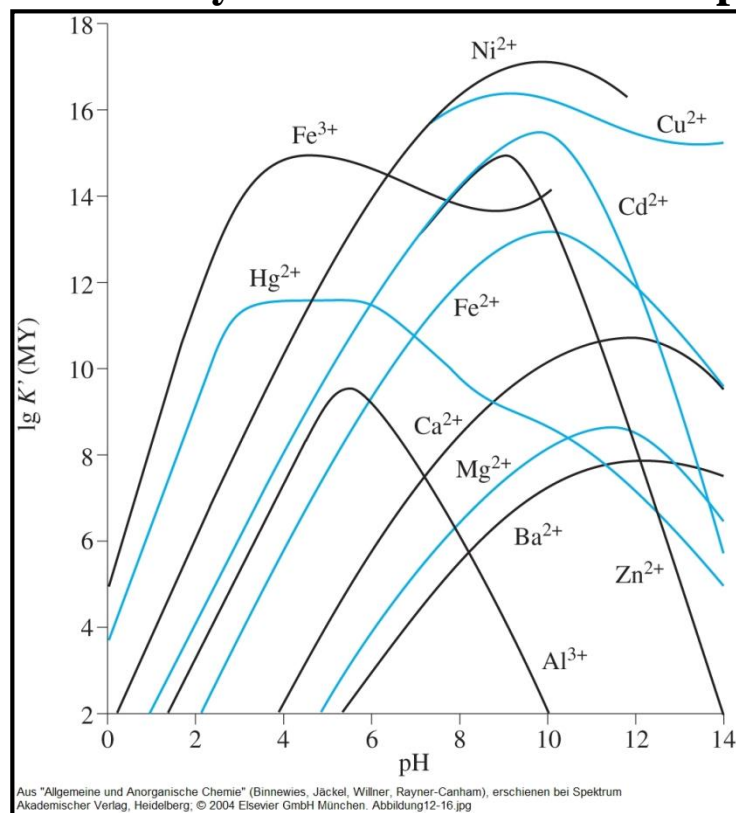
Complexometry

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

Effective stability constant of EDTA complexes



Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung12-16.jpg

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
 - Freiburger 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 **CoCl₂, Cu(II) salts**

Brown **CoSO₄, Ag₂O, CdO, PbO₂, Ag₃AsO₄, SnS, Fe(OH)₃, MnO₂, Bi₂S₃, V₂S₅, Mo(OH)₃, PbCr₂O₇, Ag₂CrO₄**

Crème **V₂O₅**

Yellow **As₂S₃, Bi₂O₃, FeSO₄, K₂CrO₄, NiCl₂, NiSO₄, PbO, WO₃, CdS, PbI₂, AgI, PbCrO₄, BaCrO₄, HgO, Ag₂HPO₄, CdO**

Green **Cr₂O₃, FeSO₄, Ni(NO₃)₂, NiCO₃, NiCl₂, NiSO₄, Cr(OH)₃**

Orange **Sb₂S₃, HgO, HgI₂, Hg₂CrO₄**

Pink **MnCl₂, MnCO₃, MnSO₄, CoCl₂**

Red **Fe₂O₃, HgI₂, HgS, Cu₂O, MnS, Co(OH)₂, Fe-thiocyanates, K₂Cr₂O₇**

Black **Co₂O₃, CuO, HgS, Sb₂S₃, PbS, CuS, NiS, CoS, FeS, FeI₂, Co(OH)₃, Cu(SCN)₂, Ag₂S₃, Mn(OH)₃, MnO(OH)₂**

Violet **CoCO₃, KCr(SO₄)₂, KMnO₄**

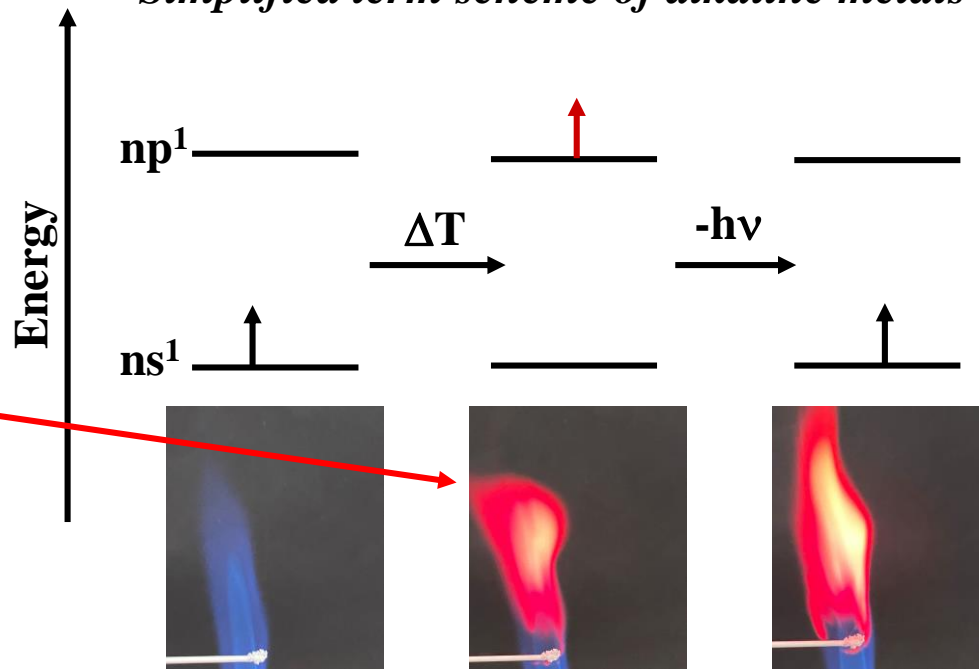
⇒ **If there are several distinguishable agglomerates present, it is recommended to separate them and to investigate them individually**

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

Simplified term scheme of alkaline metals

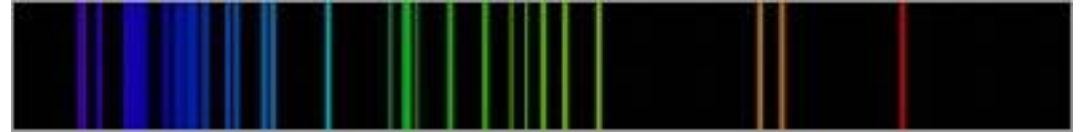


In the case of the alkaline metals, it is always the electron farthest from the core (ns^1) that is thermally excited. On relaxation, a photon with a distinct energy, which corresponds to the energy difference $\Delta E = h\nu$ between the first excited and the ground state, is emitted.

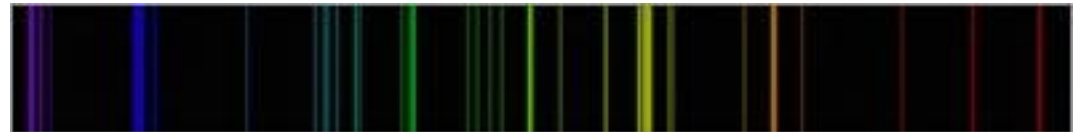
8. Preliminary Tests

The Flame Colourisation is like a Fingerprint for each Element

Emission spectrum of arsenic



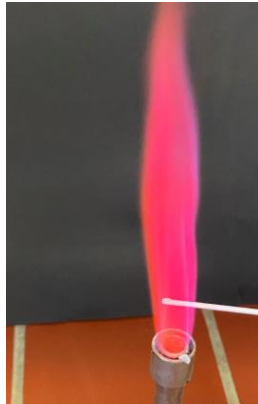
Emission spectrum of lead



Emission spectrum of mercury



Flame colored by lithium



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

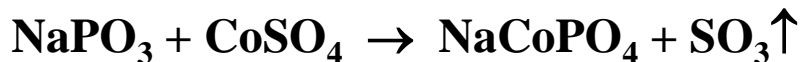
If one melts borax ($\text{Na}_2\text{B}_4\text{O}_7$) or a phosphor salt (e.g. $\text{NaNH}_4\text{HPO}_4$) and adds a heavy metal salt, characteristic colourisations can occur (depends if the melting takes place in an oxidative or a reductive flame) through the formation of heavy metal borates or phosphates

Phosphor salt pearl ($\text{NaNH}_4\text{HPO}_4$)

Upon heating, $\text{NaNH}_4\text{HPO}_4$ transforms into meta- or polyphosphate (NaPO_3)_x (x = 3 - 12)



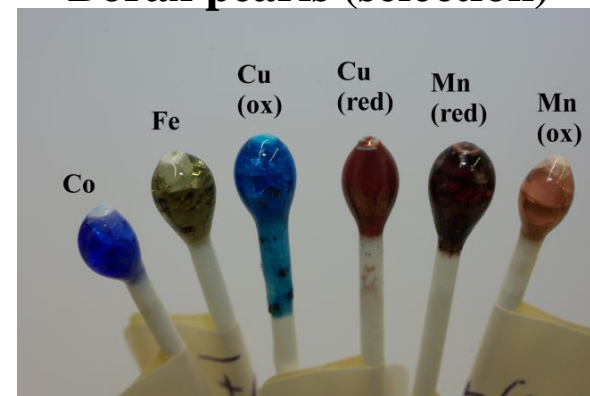
In the heat, meta phosphate is able to dissolve oxides and to drive out volatile acids from their respective salts



Borax pearl ($\text{Na}_2\text{B}_4\text{O}_7$)



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)

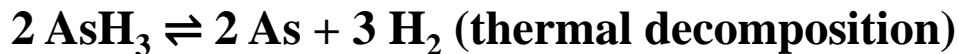
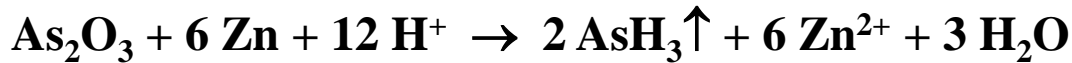
<u>Cation</u>	<u>Oxidative flame</u>	<u>Reductive flame</u>
Fe	yellow	light green
Mn	violet	colourless
Co	blue	blue
Ni	yellow-red	brown
Cr	emerald green	emerald green

Caution: this test is only valid for **Co²⁺ (blue)** and **Cr³⁺ (green)**

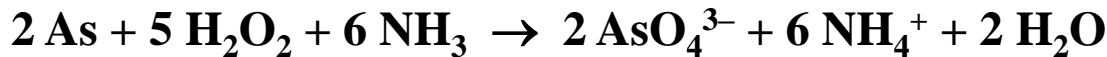
8. Preliminary Tests

Specialised Preliminary Tests

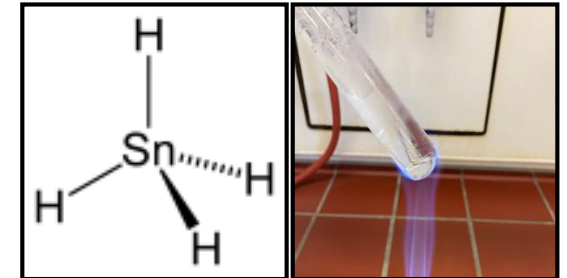
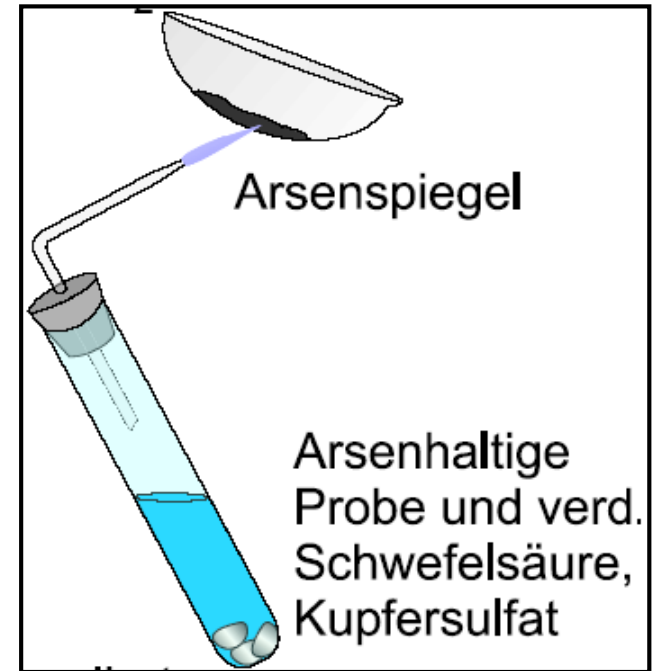
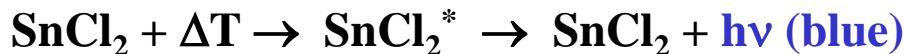
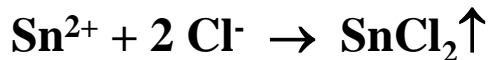
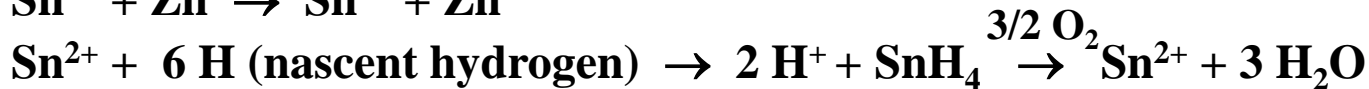
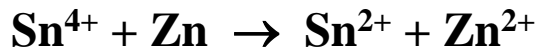
Marsh's test (detection of As and Sb)



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



Glow test (detection of Sn through luminescence)

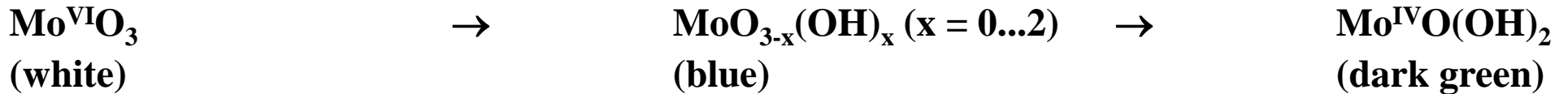


8. Preliminary Tests

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



Interferences

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

Sequence

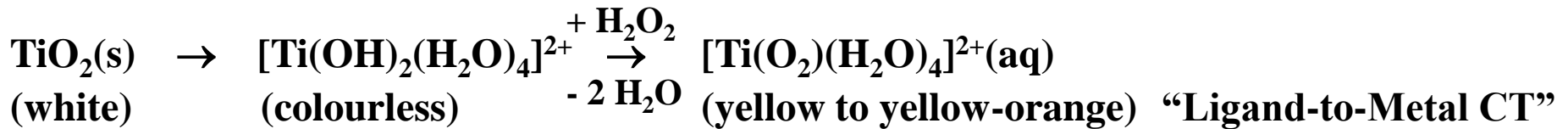
- Primary substance + some SnCl_2 + 20 ml conc. H_2SO_4 in an open pod, heated upon dryness, let it cool down \Rightarrow blue colour

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



Disturbances

- Titanium forms colourless $[\text{TiF}_6]^{2-}$ 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 \Rightarrow 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. $\text{H}_2\text{O} \Rightarrow$ measure pH value
2. HCl (diluted)
3. HCl (conc.)
4. HNO_3 (diluted)
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 \Rightarrow separation \Rightarrow washing \Rightarrow 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: $\text{S}_2\text{O}_3^{2-}$, 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 $\text{MA}_2 + \text{Na}_2\text{CO}_3(\text{soda}) \rightarrow \text{MCO}_3\downarrow + 2 \text{Na}^+ + 2 \text{A}^-$ (M = metal cation)

Example $\text{BaCl}_2(\text{aq}) + \text{Na}_2\text{CO}_3(\text{aq}) \rightarrow \text{BaCO}_3(\text{s})\downarrow + 2 \text{Na}^+(\text{aq}) + 2 \text{Cl}^-(\text{aq})$

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** $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$
- **green** $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$

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

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

9. Detection of Anions

Soda Extraction

Treatment with AgNO₃

- Acidify filtrate of soda extraction with HNO₃ until pH \cong 0
- Dropwise addition of AgNO₃ solution

Colour of precipitate

white

light yellow

yellow

orange to red

black

caused by

Cl⁻, ClO₃⁻, BrO₃⁻, IO₃⁻, CN⁻, SCN⁻, SO₃²⁻

Br⁻

I⁻

CrO₄²⁻

S²⁻

Salt	K_L [mol ² /l ²]
AgCl	1·10 ⁻¹⁰
AgCN	4·10 ⁻¹²
AgSCN	1·10 ⁻¹²
AgBr	4·10 ⁻¹³
AgI	1·10 ⁻¹⁶

AgX	Colour	Absorption of	Photo sensitivity of silver halides
AgCl	white	UV	⇒ photographic pigments ⇒ sluggish decomposition ⇒ formation of Ag ⁰
AgBr	light yellow	violet	
AgI	yellow	blue	



9. Detection of Anions

Soda Extraction

Addition of AgNO₃

- The obtained precipitate must be filtered off and washed
- Subsequently treat with NH₃



⇒ in solution: AgCl, AgBr, AgBrO₃, AgIO₃ and Ag₂SO₃

⇒ in residue: AgI, Ag₂S

- Treatment with cyanide



⇒ even AgI is dissolved

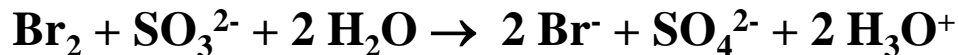
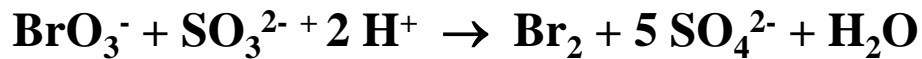
Principle: the amount of free Ag⁺ is decreased by complexation, which allows the more readily soluble precipitates to dissolve

9. Detection of Anions

Soda Extraction

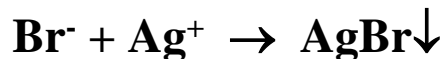
Addition of AgNO₃

- Acidify filtrate of soda extraction with HNO₃ until pH \cong 0
- Dropwise addition of Na₂SO₃ solution



⇒ reduction of Br^{+V}O₃⁻ (bromate) to Br⁻ (bromide)

- Dropwise addition of AgNO₃



⇒ light yellow precipitate

9. Detection of Anions

Soda Extraction

Treatment with CaCl₂

- Acidify filtrate of soda extraction with acetic acid until $\text{pH} \cong 5$
 - Dropwise addition of CaCl₂ solution
- ⇒ observation of white precipitate

Precipitate consists of

MoO₄²⁻ (molybdate), WO₄²⁻ (tungstate), PO₄³⁻ (phosphate), P₂O₇⁴⁻ (di-phosphate), VO₄³⁻ (vanadate), F⁻ (fluoride), C₂O₄²⁻ (oxalate), C₄H₄O₆²⁻ (tartrate)

- In high concentrations: SO₄²⁻
- At elevated temperatures: SO₃²⁻

Note: do not use too much acetic acid, otherwise the dilution will be too 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 $\text{pH} \cong 0$
- 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), $\text{S}_2\text{O}_3^{2-}$ (thiosulphate), $\text{C}_2\text{O}_4^{2-}$ (oxalate), NO_2^- (nitrite), AsO_3^{3-} (arsenide)

At elevated temperatures

$\text{S}_2\text{O}_8^{2-}$ (peroxo di-sulphate), $\text{C}_4\text{H}_4\text{O}_6^{2-}$ (tartrate)

Note: no precipitation but redox reactions!

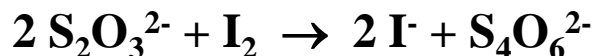
9. Detection of Anions

Soda Extraction

Treatment with I₂/starch (test on reducing substances)

- Acidify filtrate of soda extraction with HCl until pH \cong 0
- Dropwise addition of I₂/starch solution (blue)

⇒ If the I₂/starch solution decolours, there are reducing anions present in the soda extraction



Reduction of: I⁰ to I⁻

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

Note: Cl₂ and Br₂ will be reduced by S₂O₃²⁻, too
thereby S₂O₃²⁻ is oxidised to SO₄²⁻

9. Detection of Anions

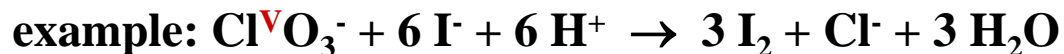
Soda Extraction

Treatment with KI/starch (test on oxidising substances)

- Acidify filtrate of soda extraction with HCl until $\text{pH} \cong 0$
- Dropwise addition of KI/starch solution

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

I⁻ is oxidised to I₂, which forms a blue inclusion compound with starch (amylose)



Oxidation of iodide to iodine through:

- ClO⁻ (hypochlorite), CrO₄²⁻, NO₂⁻, S₂O₈²⁻, ClO₃⁻, BrO₃⁻, IO₃⁻, MnO₄⁻, NO₃⁻, Cu²⁺, Fe³⁺
- Weak reaction for: AsO₄³⁻ (arsenate)

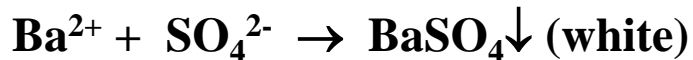
Note: no precipitation but redox reaction!

9. Detection of Anions

Detection of individual Anions (from Soda Extraction)

Sulphate SO_4^{2-}

- Acidify soda extraction with diluted HCl until $\text{pH} \cong 0$
- Dropwise addition of BaCl_2 solution (10%)



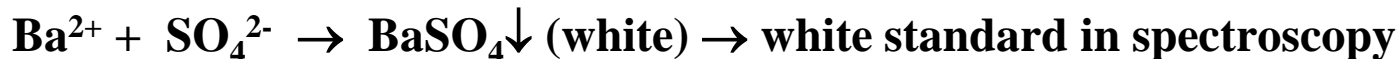
Barium sulphate is poorly soluble in diluted mineral acids and concentrated HCl, but it readily dissolves in hot concentrated H_2SO_4 under formation of a complex

Peroxo di-sulphate $\text{S}_2\text{O}_8^{2-}$

- Acidify soda extraction and reflux



- Dropwise addition of BaCl_2 solution (10%)



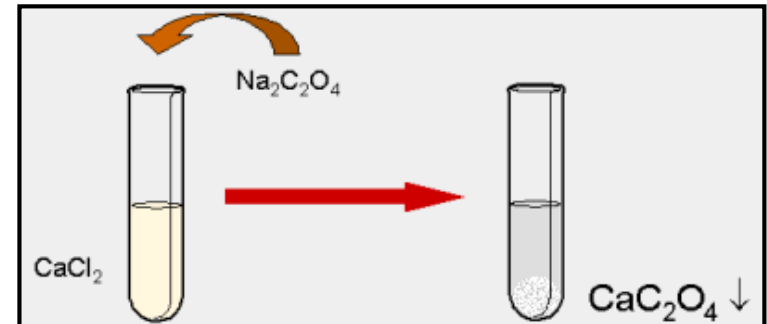
9. Detection of Anions

Detection of individual Anions (from Soda Extraction)

Oxalate $C_2O_4^{2-}$

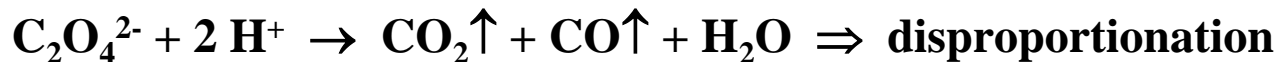
- Acidify filtrate of soda extraction with acetic acid until $pH \cong 5$
- Dropwise addition of $CaCl_2$ solution

$Ca^{2+} + C_2O_4^{2-} \rightarrow CaC_2O_4 \downarrow$ (white)
(forms kidney stone in kidney or bladder)

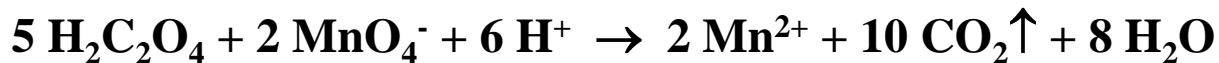


Additional probing for oxalate

1. With concentrated H_2SO_4



2. With $KMnO_4$



9. Detection of Anions

Detection of individual Anions (from Soda Extraction)

Thiocyanate SCN⁻

- Acidify filtrate of soda extraction with diluted HNO₃ until pH ≈ 0
- Dropwise addition of FeCl₃ solution (freshly made!)

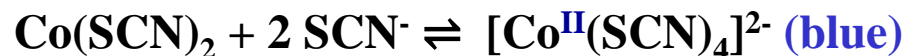
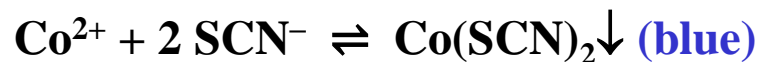


Additional tests for thiocyanate

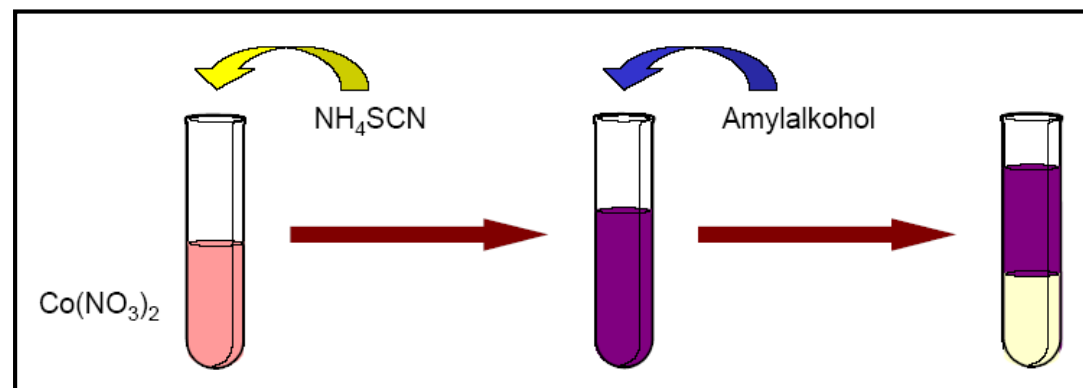
1. With CuSO₄



2. With Co(NO₃)₂



Co(SCN)₂ is neutral and soluble in amyl alcohol (amyl alcohol = 1-pentanol C₅H₁₁OH)



9. Detection of Anions

Detection of individual Anions (from Soda Extraction)

Nitrite NO_2^- and nitrate NO_3^-

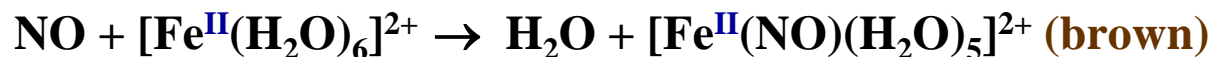
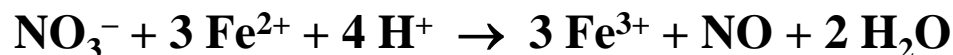
Since nitrite disturbs the detection of nitrate (ring test or Lunge's reagent), it must be removed prior to detection:

- $\text{HNO}_2 + \text{NH}_3 \rightarrow \text{N}_2 + 2 \text{H}_2\text{O}$
- $\text{HNO}_2 + \text{HN}_3 \rightarrow \text{N}_2 + \text{N}_2\text{O} + \text{H}_2\text{O}$
- $2 \text{HNO}_2 + (\text{NH}_2)_2\text{CO} \rightarrow \text{N}_2 + \text{CO}_2 + 3 \text{H}_2\text{O}$

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



9. Detection of Anions

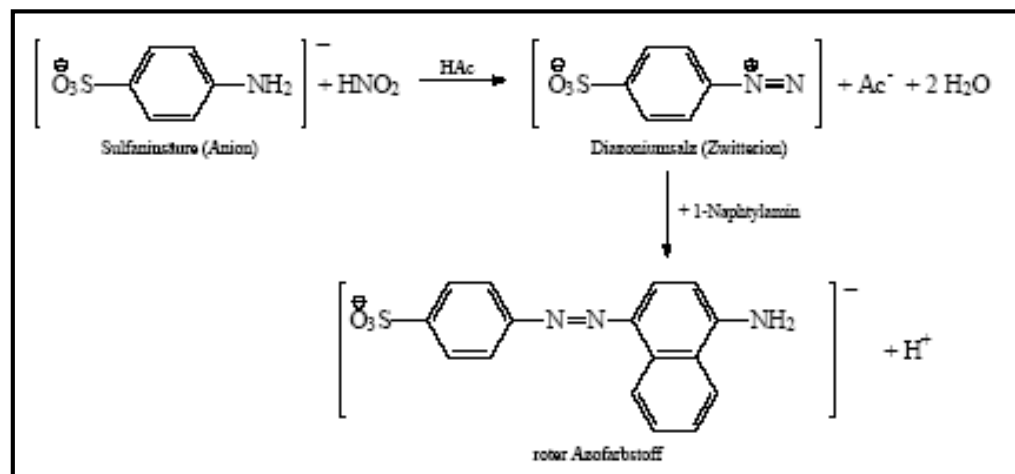
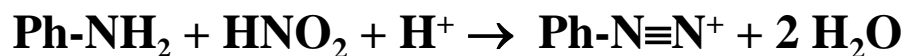
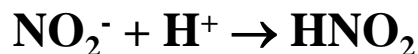
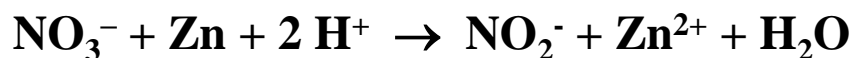
Detection of individual Anions (from Soda Extraction)

Nitrite NO_2^- and nitrate NO_3^-

2. Lunge's reagent

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

⇒ formation of red colour upon presence of $\text{NO}_2^-/\text{NO}_3^-$



9. Detection of Anions

Detection of individual Anions (from Soda Extraction)

Chloride Cl⁻

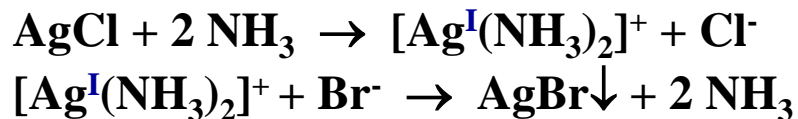
- Acidify filtrate of soda extraction with diluted nitric acid
- Dropwise addition of AgNO₃ solution

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

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

- Wash with (NH₄)₂CO₃ solution
- Addition of NaBr or KBr solution

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



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 CCl₄ (carbon tetrachloride) or CHCl₃ (chloroform) underneath solution
- Slow dropwise addition of Cl₂ water

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



- Further addition of Cl₂ water ⇒ decolouring



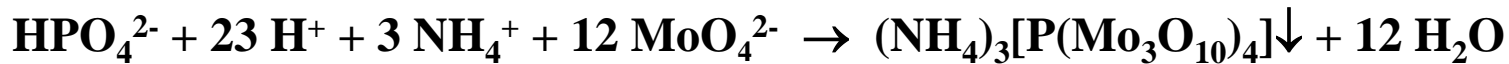
9. Detection of Anions

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



$[\text{P}(\text{Mo}_3\text{O}_{10})_4]^{3-}$ 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 CH₃COO⁻

- 0.1 - 0.2 g of primary substance are ground together with KHSO₄

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



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



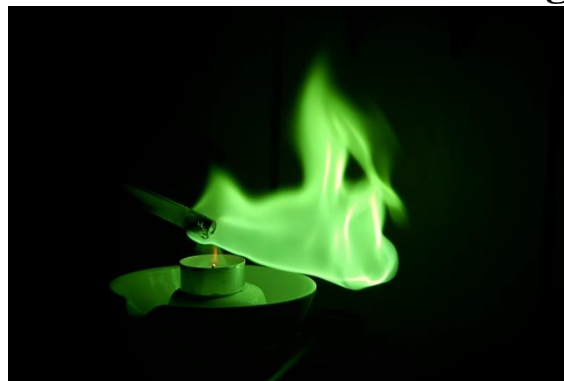
9. Detection of Anions

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



⇒ 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)

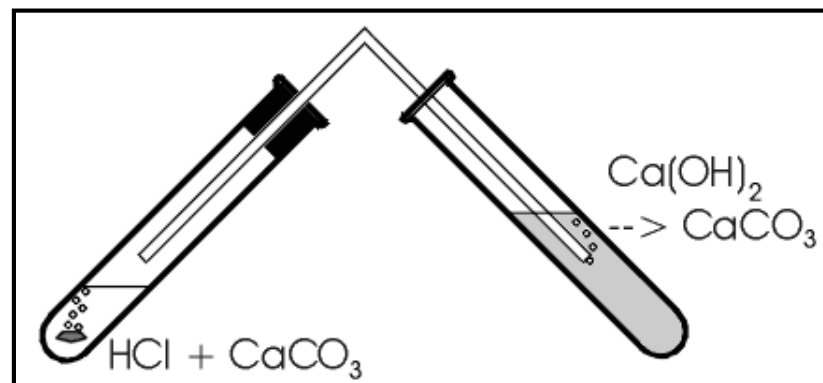
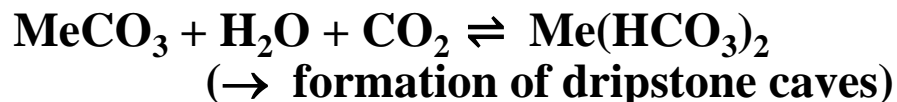
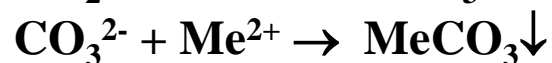
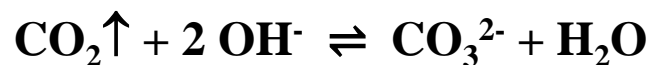
Carbonate CO_3^{2-}

- 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. $\text{Ba}(\text{OH})_2$ or $\text{Ca}(\text{OH})_2$ 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



Reactions in fermentation tube:



upon CO_2 excess, carbonates dissolve as hydrogen carbonates

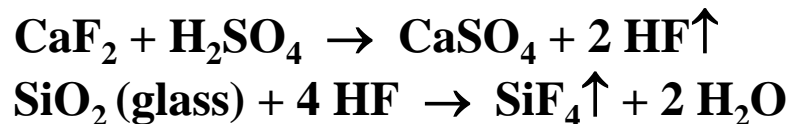
9. Detection of Anions

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)



Creep test

- Some mg of primary substance are heated in a dried test tube together with a small amount of concentrated H₂SO₄
 - Originating HF etches the inner wall of the test tube, so that H₂SO₄ can not wet the glass wall any more
- ⇒ if the test tube is then turned upside down, the H₂SO₄ drips off the test tube wall

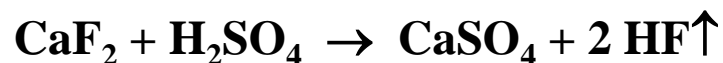
9. Detection of Anions

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



SiF_4 is hydrolysed on moist filter paper:

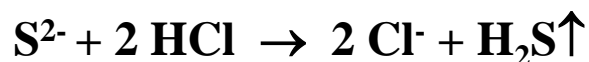


9. Detection of Anions

Detection of individual Anions (from Primary Substance)

Sulphide S²⁻

- 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



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



Complementary tests

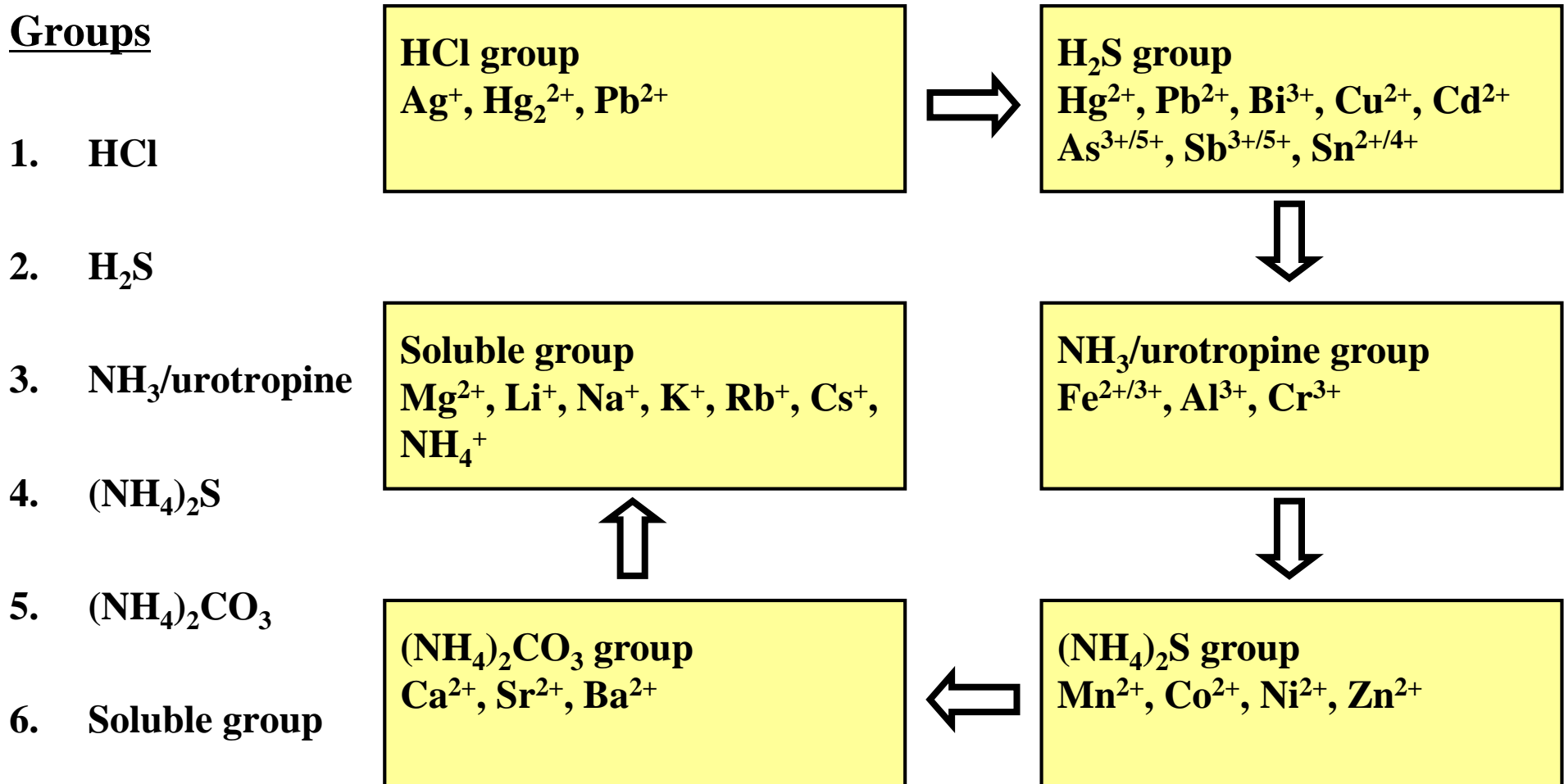
- Addition of Cd(CH₃COO)₂ solution to soda extraction



10. Separation Process for Cations

Overview of the Separation Process for Cations

Groups



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+} , $\text{Hg}_2^{2+} \Rightarrow$ precipitation as chlorides

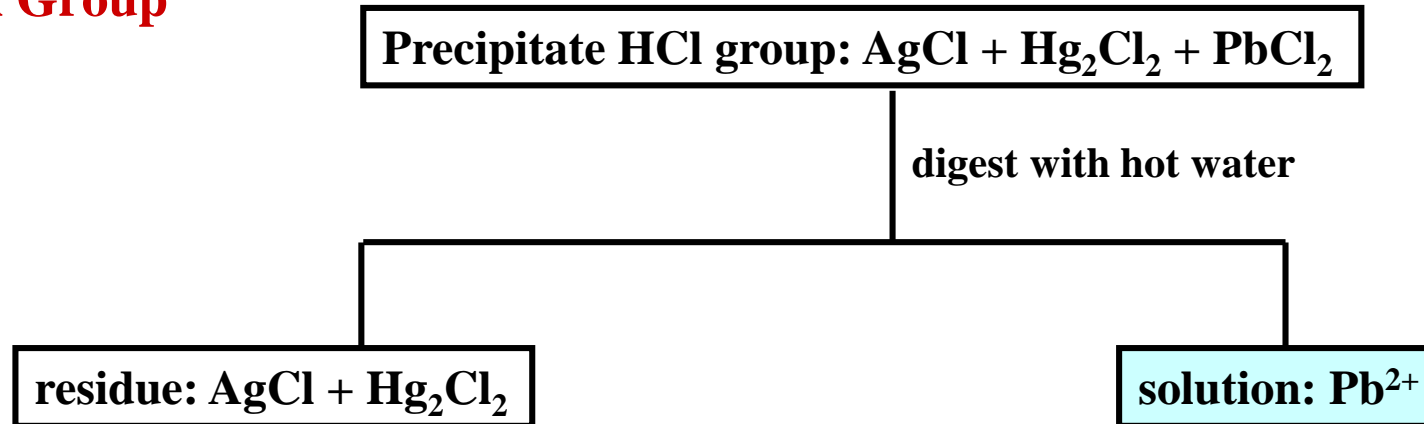
<u>Reaction</u>	<u>pK_L</u>	
$\text{Hg}_2^{2+} + 2 \text{Cl}^- \rightarrow \text{Hg}_2\text{Cl}_2 \downarrow$	17.9	
$\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl} \downarrow$	9.7	
$\text{Pb}^{2+} + 2 \text{Cl}^- \rightarrow \text{PbCl}_2 \downarrow$	4.8	incomplete precipitation!

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



Solubility increases with increasing temperature

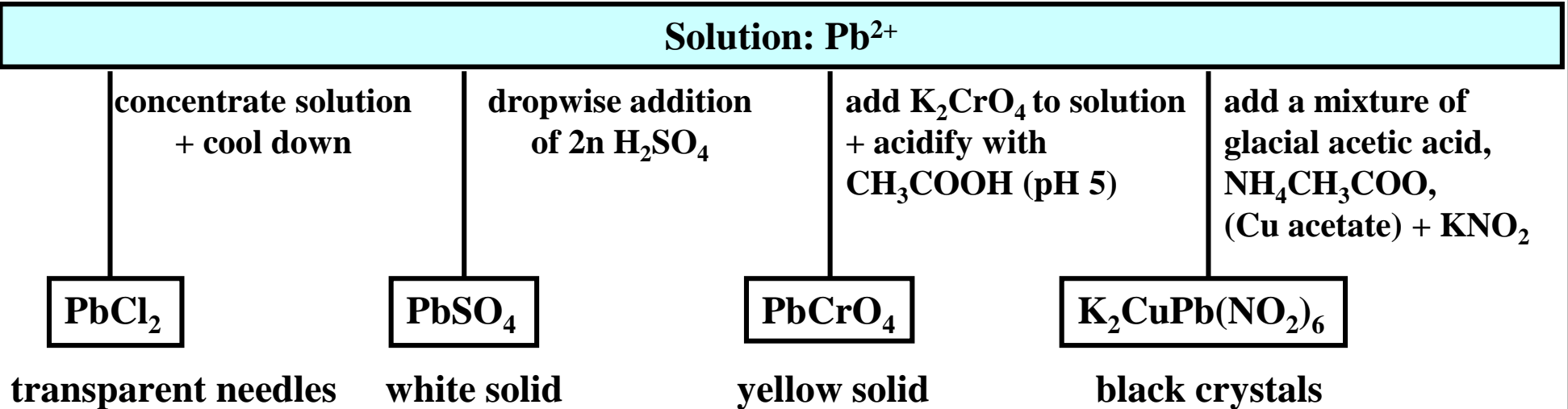


Problems

- 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

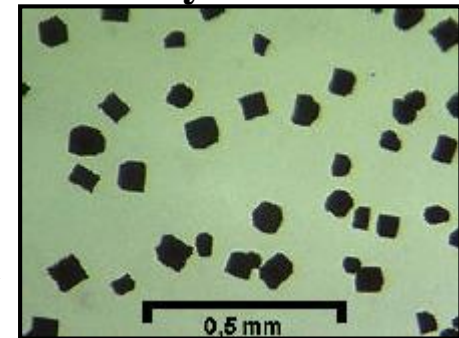


Problems

- PbSO₄ dissolves in concentrated H₂SO₄ and forms the complex acid H₂[Pb(SO₄)₂]
- Lead chromate is poorly soluble, but lead di-chromate is not

$$\text{Pb}^{2+} + \text{CrO}_4^{2-} \rightarrow \text{PbCrO}_4 \quad K_L = 3.2 \cdot 10^{-11}$$
 poorly soluble in CH₃COOH, NH₃
 soluble in NaOH, HNO₃

$$2 \text{CrO}_4^{2-} + 2 \text{H}_3\text{O}^+ \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + 3 \text{H}_2\text{O} \quad K = 3.5 \cdot 10^{14}$$



10. Separation Process for Cations

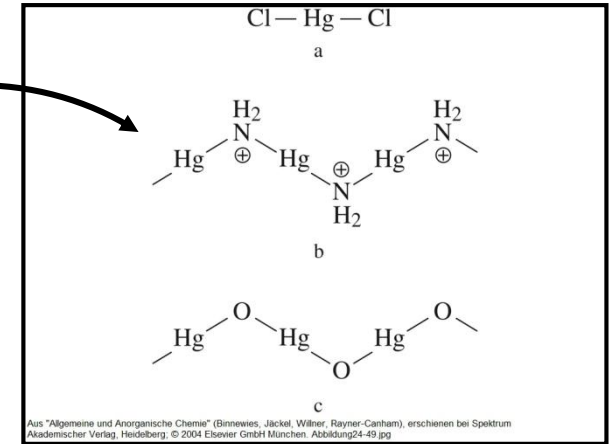
HCl Group

Residue: $\text{AgCl} + \text{Hg}_2\text{Cl}_2$

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

solution: $[\text{Ag}(\text{NH}_3)_2]^+$

$\text{Hg} + [\text{Hg}(\text{NH}_2)]\text{Cl}$

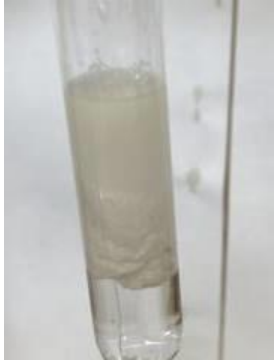


1. Formation of poorly soluble silver di-amine complex $[\text{Ag}(\text{NH}_3)_2]^+$
 $\text{AgCl} + 2 \text{NH}_3 \rightarrow [\text{Ag}^{\text{I}}(\text{NH}_3)_2]^+ + \text{Cl}^-$
2. Blackening of white residue due to formation of metallic Hg^0
 $\text{Hg}_2^{2+} + 2\text{Cl}^- + 2 \text{NH}_3 \rightarrow [\text{Hg}^{\text{II}}(\text{NH}_3)_2]\text{Cl}_2 + \text{Hg}^0$
 $[\text{Hg}^{\text{II}}(\text{NH}_3)_2]\text{Cl}_2 \rightarrow [\text{Hg}^{\text{II}}(\text{NH}_2)]\text{Cl} + \text{NH}_4^+ + \text{Cl}^-$
 Combination of black metallic mercury and white mercury(II)-amide chloride = calomel („pleasant black“)

10. Separation Process for Cations

HCl Group

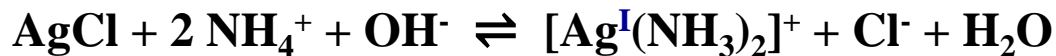
Solution: $[\text{Ag}(\text{NH}_3)_2]^+$



acidify with 2n HCl

AgCl

decomposition of $[\text{Ag}(\text{NH}_3)_2]^+$ leads to precipitation of white AgCl

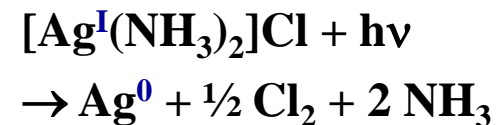


acidification decreases concentration of OH^-
 \Rightarrow shifting the equilibrium to the left side

heat upon dryness

$[\text{Ag}(\text{NH}_3)_2]\text{Cl}$

octahedral, transparent to black crystals



10. Separation Process for Cations

H₂S Group

Filtrate/centrifugate of HCl group: Hg²⁺, Pb²⁺, Bi³⁺, Cu²⁺, Cd²⁺, As^{3+/5+}, Sb^{3+/5+}, Sn^{2+/4+}

pass H₂S through the hydrochloric solution
(pH 0-2)

add thio-acetic amide CH₃CSNH₂ + hydrolyse:
CH₃CSNH₂ + 2 H₂O → CH₃COO⁻ + NH₄⁺ + H₂S

precipitate: HgS, PbS, Bi₂S₃, CuS, CdS, As₂S₃, As₂S₅, Sb₂S₃, Sb₂S₅, SnS, SnS₂

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:



otherwise sulphides will be oxidised to sulphur (this also happens, if H₂O₂ is present)

- Solution can be yellow (CrO₄²⁻) or violet (MnO₄⁻). 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

H₂S Group

Precipitate: HgS, PbS, Bi₂S₃, CuS, CdS, As₂S₃, As₂S₅, Sb₂S₃, Sb₂S₅, SnS, SnS₂

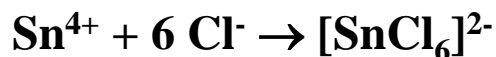
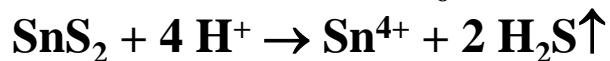
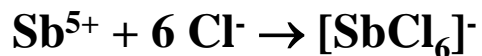
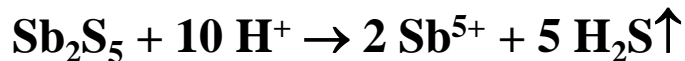
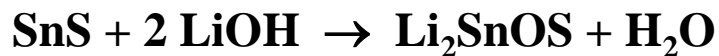
1. reflux with ca. 10 ml LiOH/KNO₃ solution
2. filtrate

copper group

arsenic group

precipitate: HgS, PbS, Bi₂S₃, CuS, CdS

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



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

precipitate: As₂S₅, Sb₂S₅, SnS₂

**digest with hot
conc. HCl**

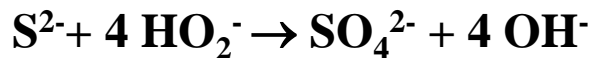
solution: [SbCl₆]⁻ + [SnCl₆]²⁻

precipitate: As₂S₅

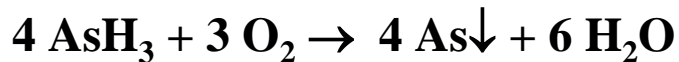
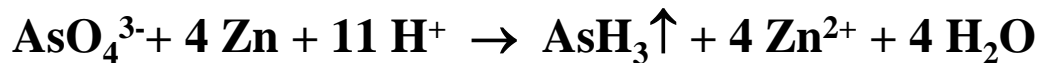
10. Separation Process for Cations

H₂S Group

Oxidation of sulphides



Marsh's test

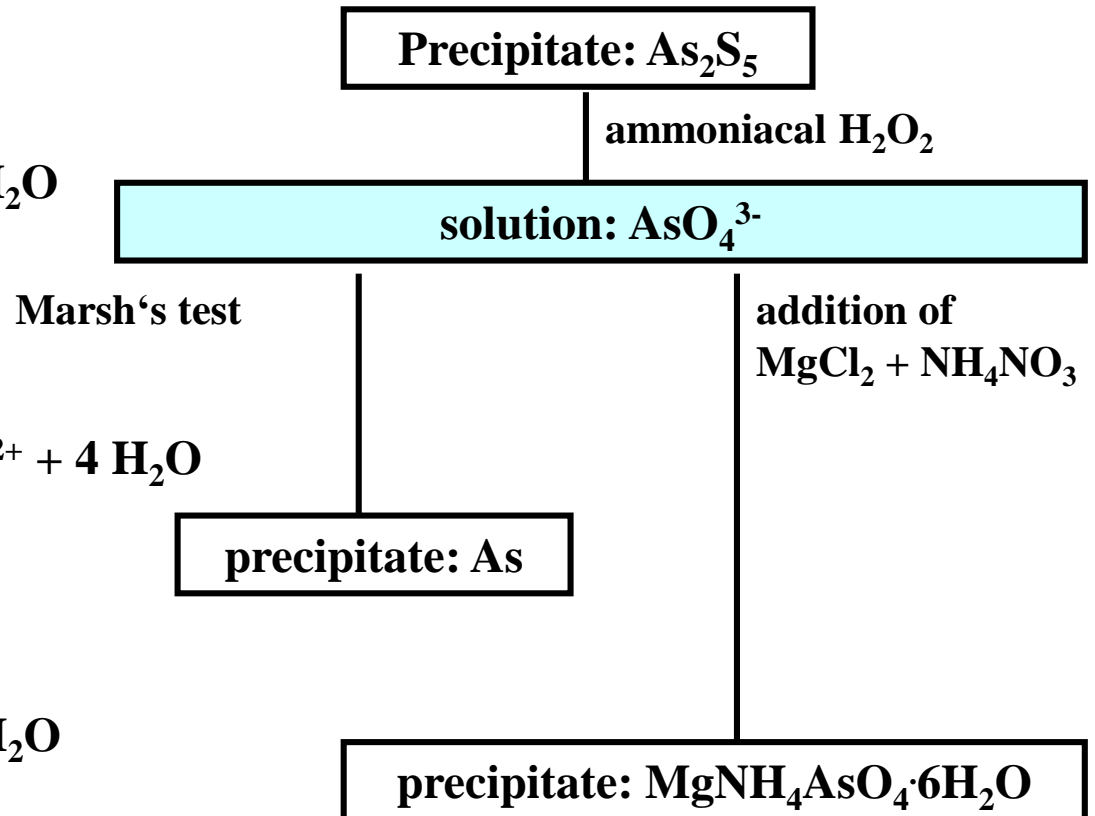


As-mirror, soluble in ammoniacal H₂O₂

solution:



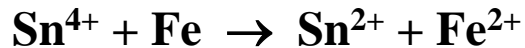
Precipitation as magnesium ammonium arsenate



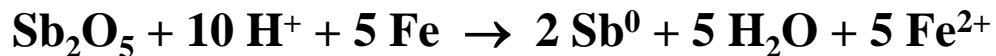
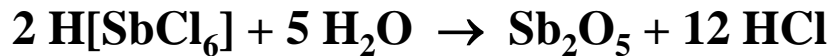
10. Separation Process for Cations

H₂S Group

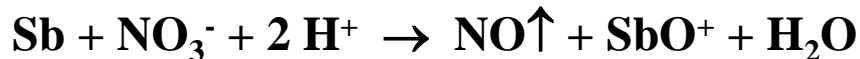
Reduction of Sn⁴⁺



Reduction of Sb⁵⁺



Oxidation of Sb

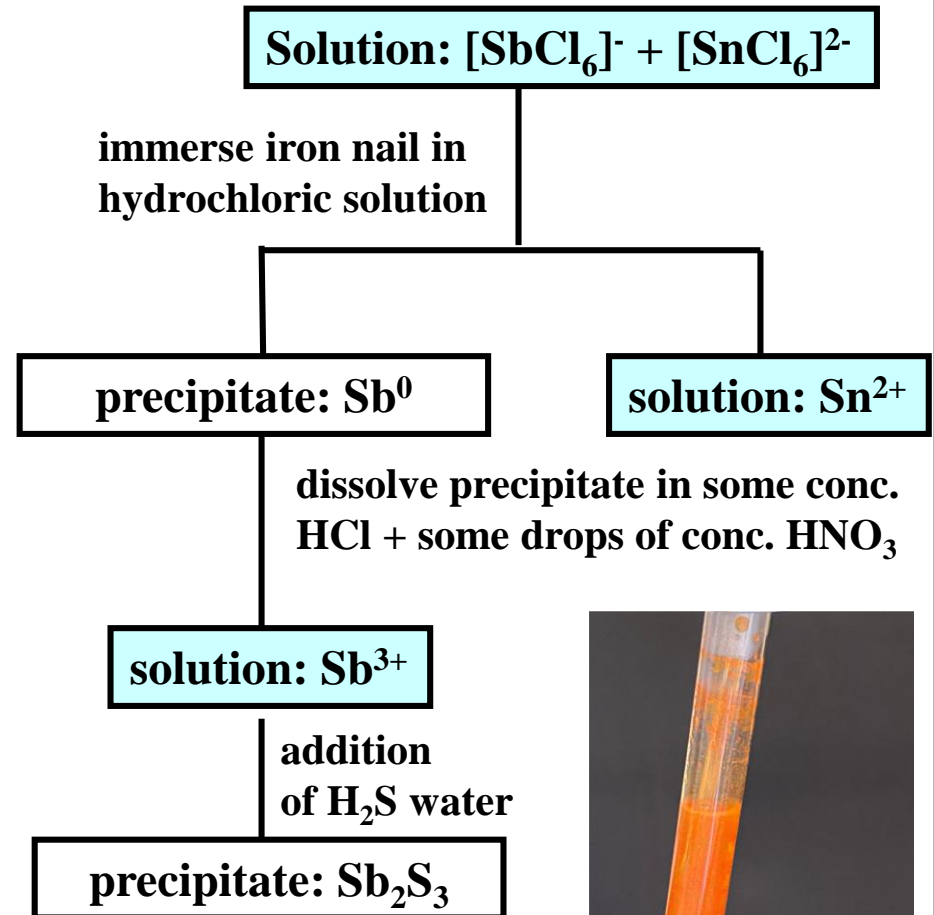
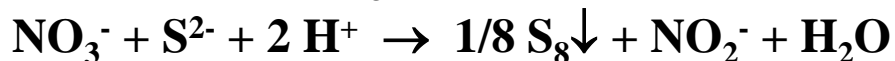


Precipitation of Sb³⁺ as sulphide



Problem

If too much HNO₃ was used:



10. Separation Process for Cations

H₂S Group

Solution: Sn²⁺

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



gas phase: SnCl₂↑

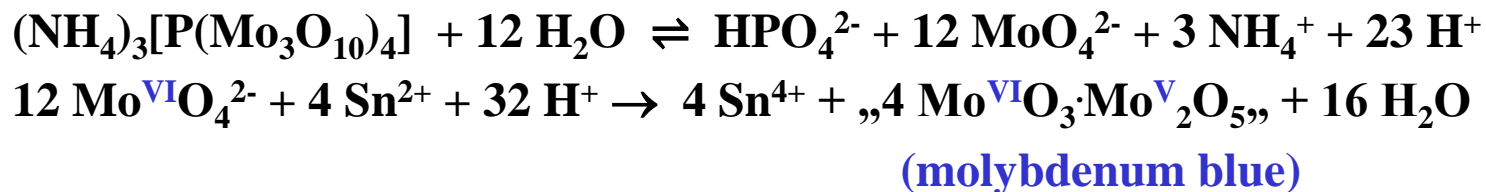
add ammonium molybdate and di-sodium hydrogenphosphate to the solution

solution: Sn⁴⁺ + „Mo^{VI}O₃·Mo^V₂O₅“

Glow tests



Detection through formation of molybdenum blue



10. Separation Process for Cations

H₂S Group

Precipitate: HgS, PbS, Bi₂S₃, CuS, CdS

residue of polysulphide treatment is heated cautiously with conc. HNO₃:H₂O (1:2) in a porcelain pod

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

- $\text{Hg}^{2+} + \text{S}^{2-} \rightleftharpoons \text{HgS} \quad K_L = 1.3 \cdot 10^{-44} \text{ mol}^2/\text{l}^2$
- $\text{Pb}^{2+} + \text{S}^{2-} \rightleftharpoons \text{PbS} \quad K_L = 1.9 \cdot 10^{-24} \text{ mol}^2/\text{l}^2$
- $\text{Cu}^{2+} + \text{S}^{2-} \rightleftharpoons \text{CuS} \quad K_L = 2.9 \cdot 10^{-31} \text{ mol}^2/\text{l}^2$
- $\text{Cd}^{2+} + \text{S}^{2-} \rightleftharpoons \text{CdS} \quad K_L = 2.6 \cdot 10^{-24} \text{ mol}^2/\text{l}^2$
- $2 \text{Bi}^{3+} + 3 \text{S}^{2-} \rightleftharpoons \text{Bi}_2\text{S}_3 \quad K_L = 2.3 \cdot 10^{-72} \text{ mol}^5/\text{l}^5$

(all values for T = 90 ° C)

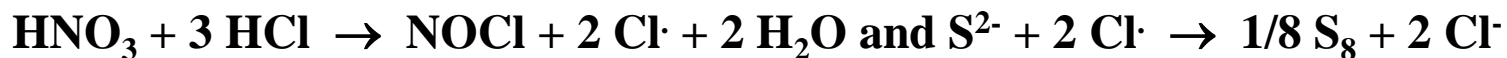
residue: HgS

solution:
Pb²⁺, Bi³⁺, Cu²⁺, Cd²⁺

residue is dissolved in some aqua regia at elevated temperatures, subsequently heated upon near dryness and collected with H₂O

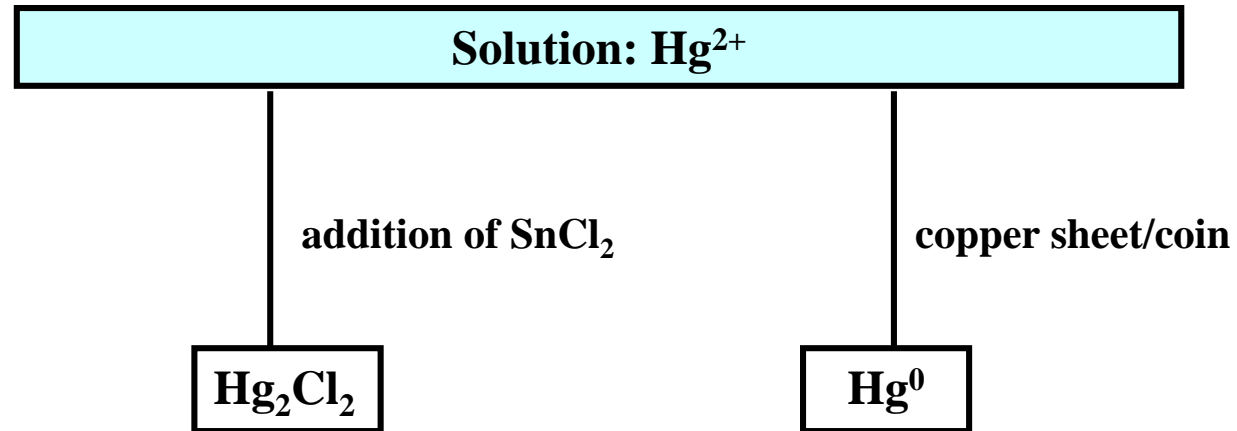
solution: Hg²⁺

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

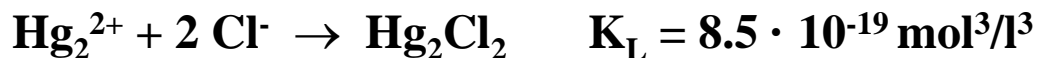
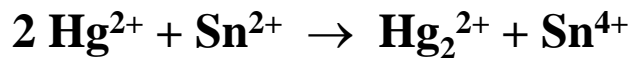


10. Separation Process for Cations

H₂S Group

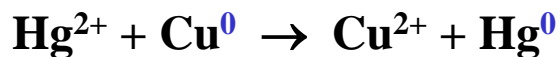


Reduction and subsequent precipitation as chloride



Reduction to elemental Hg

Hg is more noble than Cu

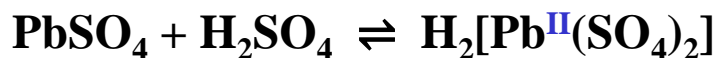


The segregated metallic Hg forms a shiny silver alloy together with Cu (amalgam)

10. Separation Process for Cations

H₂S Group

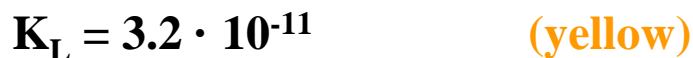
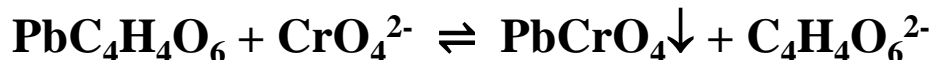
Precipitation of PbSO₄



Dissolution with ammonium tartrate



Precipitation with potassium chromate



Solution: Pb²⁺, Bi³⁺, Cu²⁺, Cd²⁺

addition of H₂SO₄

precipitate: PbSO₄

solution: Bi³⁺, Cu²⁺, Cd²⁺

pour ammoniacal ammonium tartrate solution over the precipitate

solution: [PbC₄H₄O₆]⁰

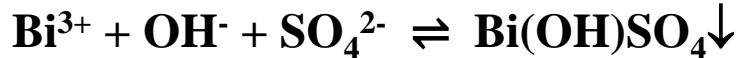
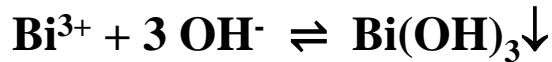
add K₂CrO₄ solution and acidify with acetic acid (pH = 5)

precipitate: PbCrO₄

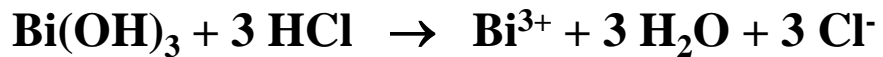
10. Separation Process for Cations

H₂S Group

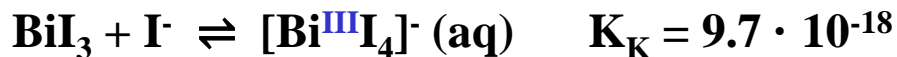
Precipitation of bismuth hydroxide/hydroxy sulphate



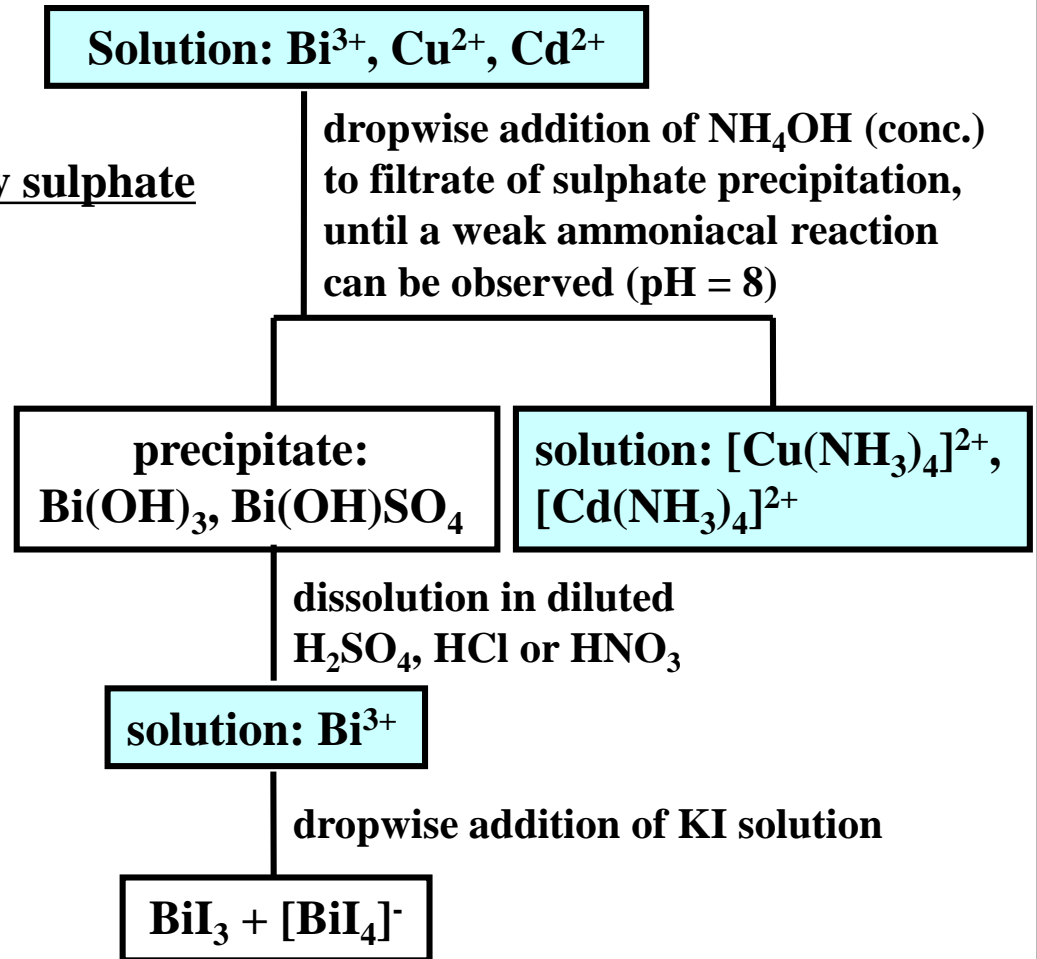
Dissolution in HCl



Reaction with iodide



(yellow-orange solution)

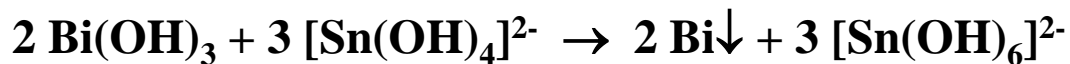


10. Separation Process for Cations

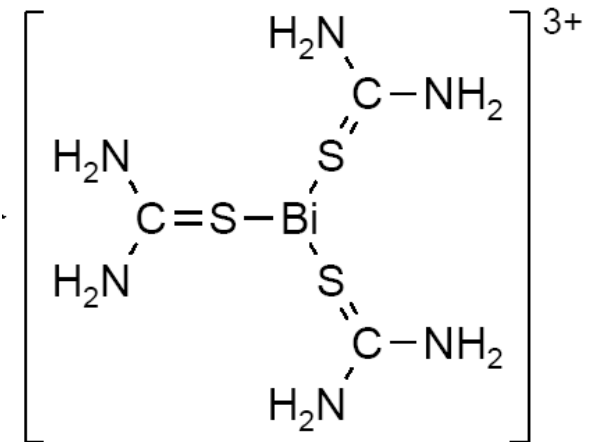
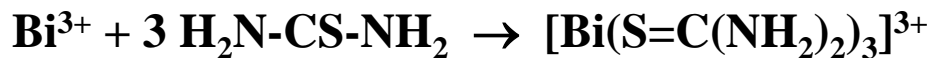
H₂S Group

Complementary tests for Bi³⁺

1. Through reduction to the metal

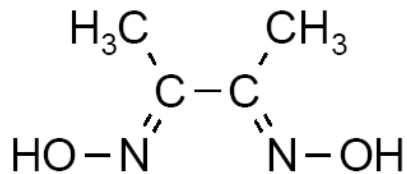
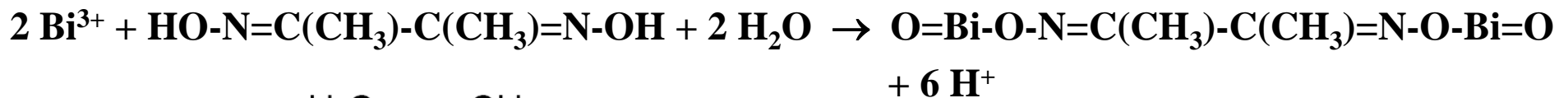


2. Via reaction with thio-urea H₂N-CS-NH₂



gelb

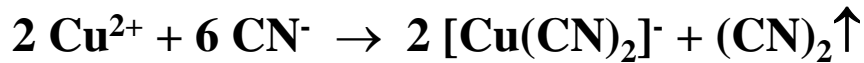
3. Through reaction with di-methyl glyoxime



10. Separation Process for Cations

H₂S Group

Masking of copper



The copper cyanide complex is more stable than the corresponding cadmium complex. Upon introduction of H₂S, the solubility product of copper sulphide is not reached, in contrast to that of CdS

⇒ yellow cadmium sulphide precipitates:



Solution: [Cu(NH₃)₄]²⁺, [Cd(NH₃)₄]²⁺

if the solution is coloured deep blue by [Cu(NH₃)₄]²⁺, some small amount of KCN should be added to decolourise the solution (masking of Cu²⁺)

solution: [Cu(CN)₄]³⁻, [Cd(CN)₄]²⁻

H₂S water is added dropwise to the transparent solution

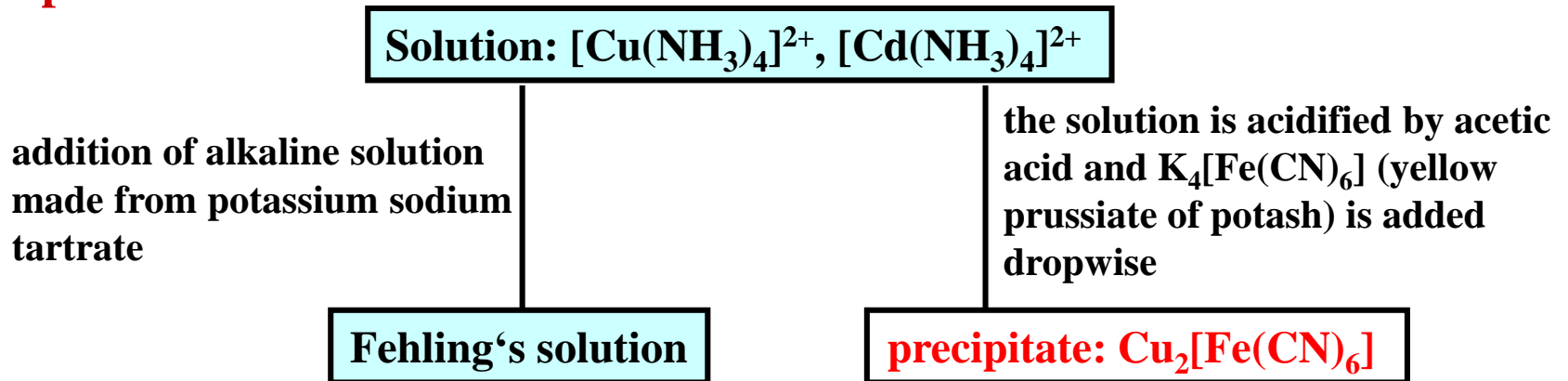
precipitate: CdS

solution: [Cu(CN)₄]³⁻

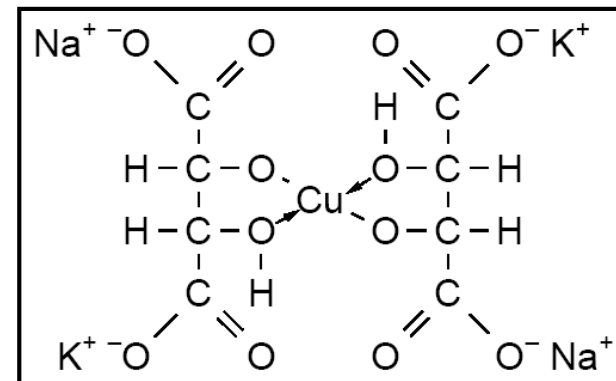
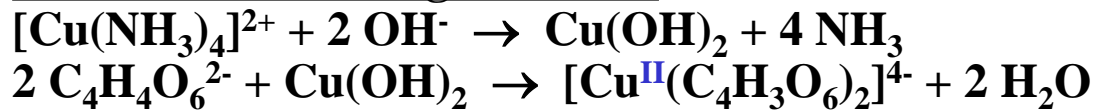


10. Separation Process for Cations

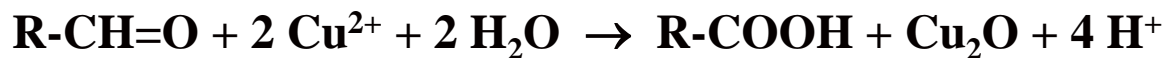
H₂S Group



Formation of Fehling's solution



Fehling's solution is reduced by sugar/aldehyde \Rightarrow formation of yellow-red Cu₂O



(sugar)

10. Separation Process for Cations

Urotropine and $(\text{NH}_4)_2\text{S}$ 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: $\text{Fe}^{2+/3+}$, 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
 $\Rightarrow \text{pH} > 7$

urotropine group

$(\text{NH}_4)_2\text{S}$ group

precipitate: $\text{Fe}(\text{OH})_3$, $\text{Cr}(\text{OH})_3$, $\text{Al}(\text{OH})_3$

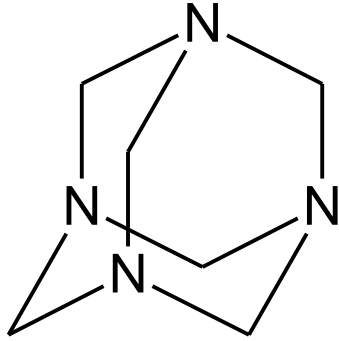
solution: Mn^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+}

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

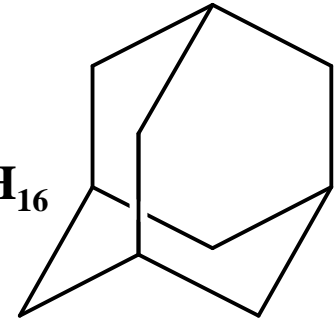


10. Separation Process for Cations

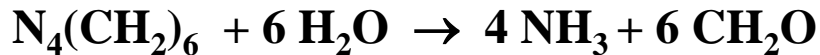
Urotropine (hexamethylenetetramine)



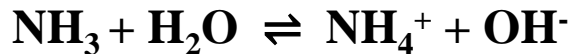
adamantane structure → adamantane $C_{10}H_{16}$



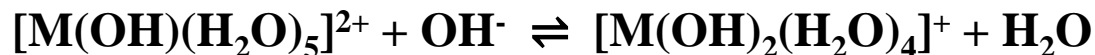
Hydrolysis of urotropine



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

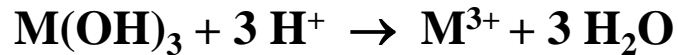


Hydrolysis of acidic aqua complexes

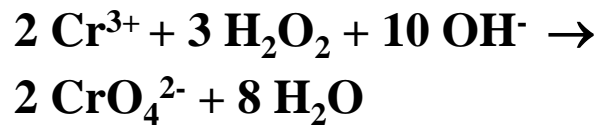
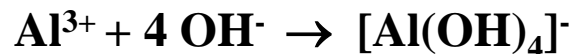
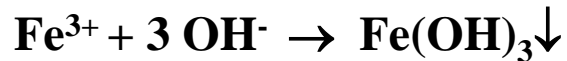


10. Separation Process for Cations

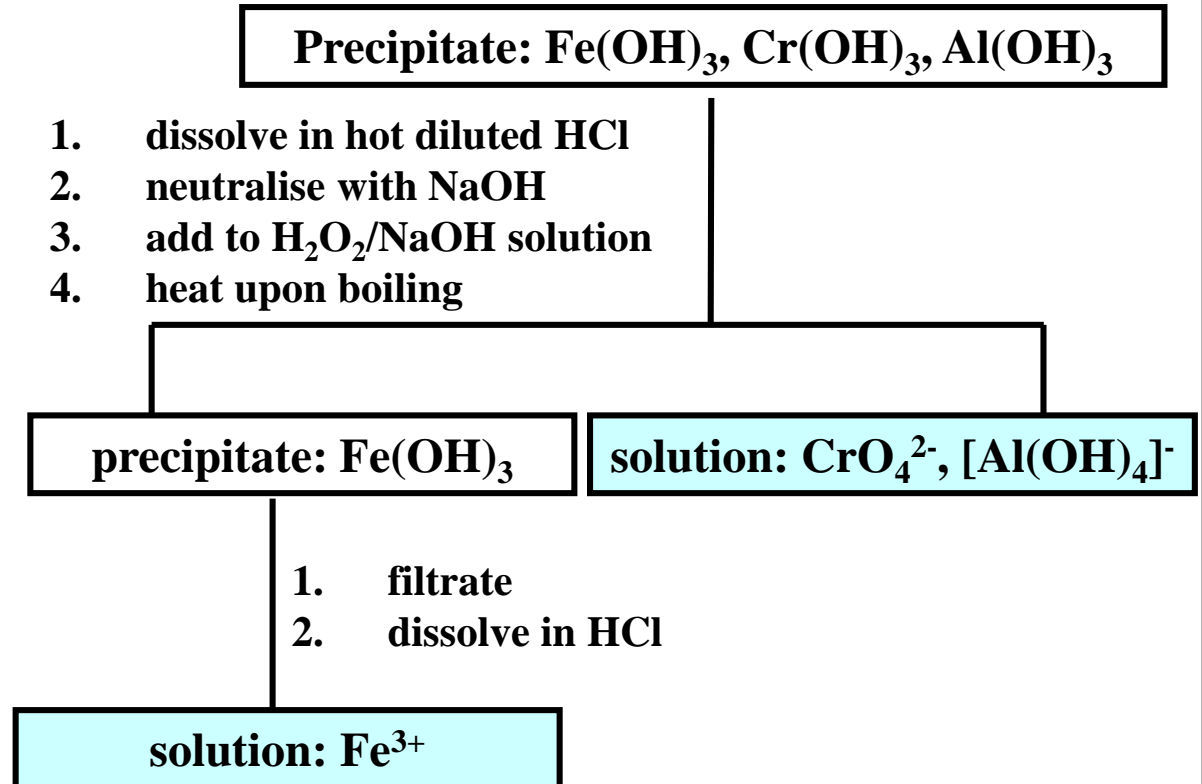
Urotropine Group



Alkaline precipitation



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



10. Separation Process for Cations

Urotropine Group

Solution: Fe³⁺

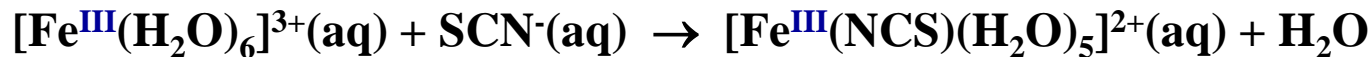
dilute solution with H₂O
and add KSCN



dilute with H₂O and add
K₄[Fe(CN)₆]
(yellow prussiate of potash)



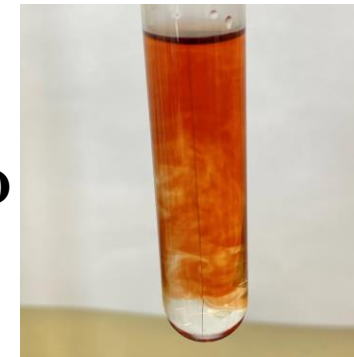
Verification as penta aqua thiocyanato(III)-ions



Detection as Prussian blue

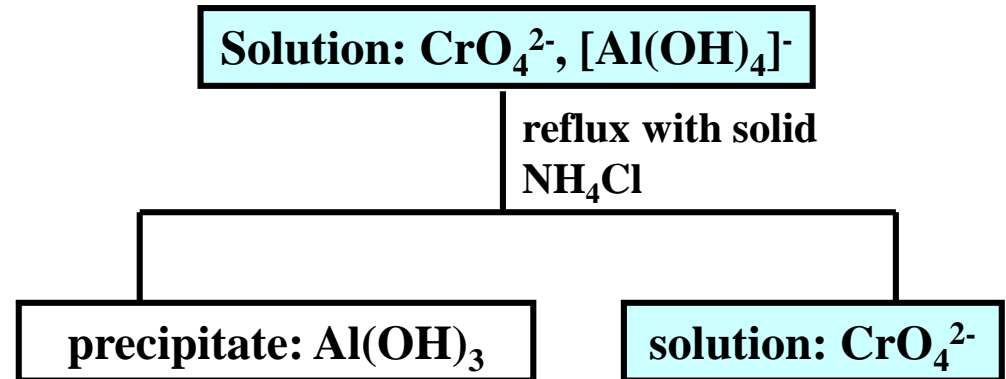
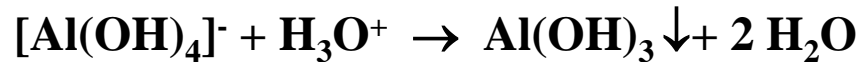
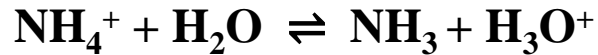


⇒ charge-transfer absorption in the yellow range of the spectrum

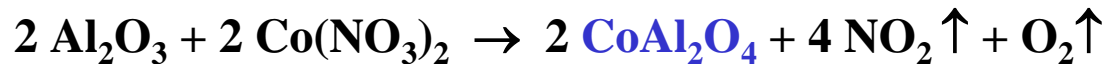


10. Separation Process for Cations

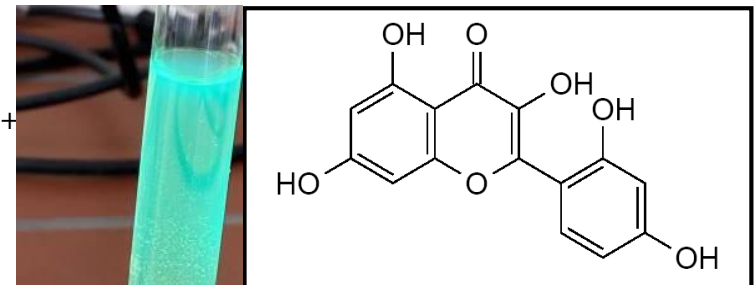
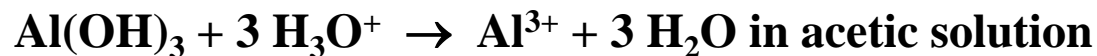
Urotropine Group



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



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



10. Separation Process for Cations

Urotropine Group

Solution: CrO_4^{2-}

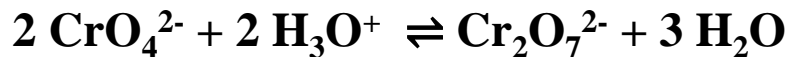
1. acidify with H_2SO_4
2. add 3 drops of H_2O_2
3. add amyl alcohol (1-pentanol) and shake

blue solution: CrO_5

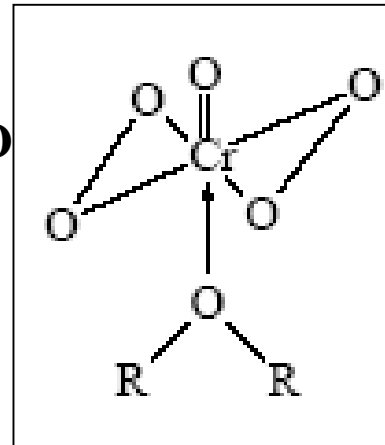
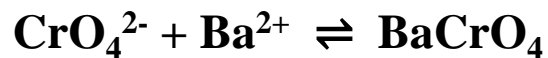
1. acidify with CH_3COOH
2. add BaCl_2

precipitate: BaCrO_4

Detection as CrO_5



Detection as barium chromate



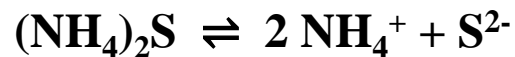
10. Separation Process for Cations

$(\text{NH}_4)_2\text{S}$ 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

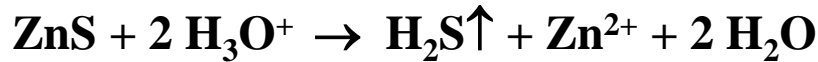


Precipitation of sulphides

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

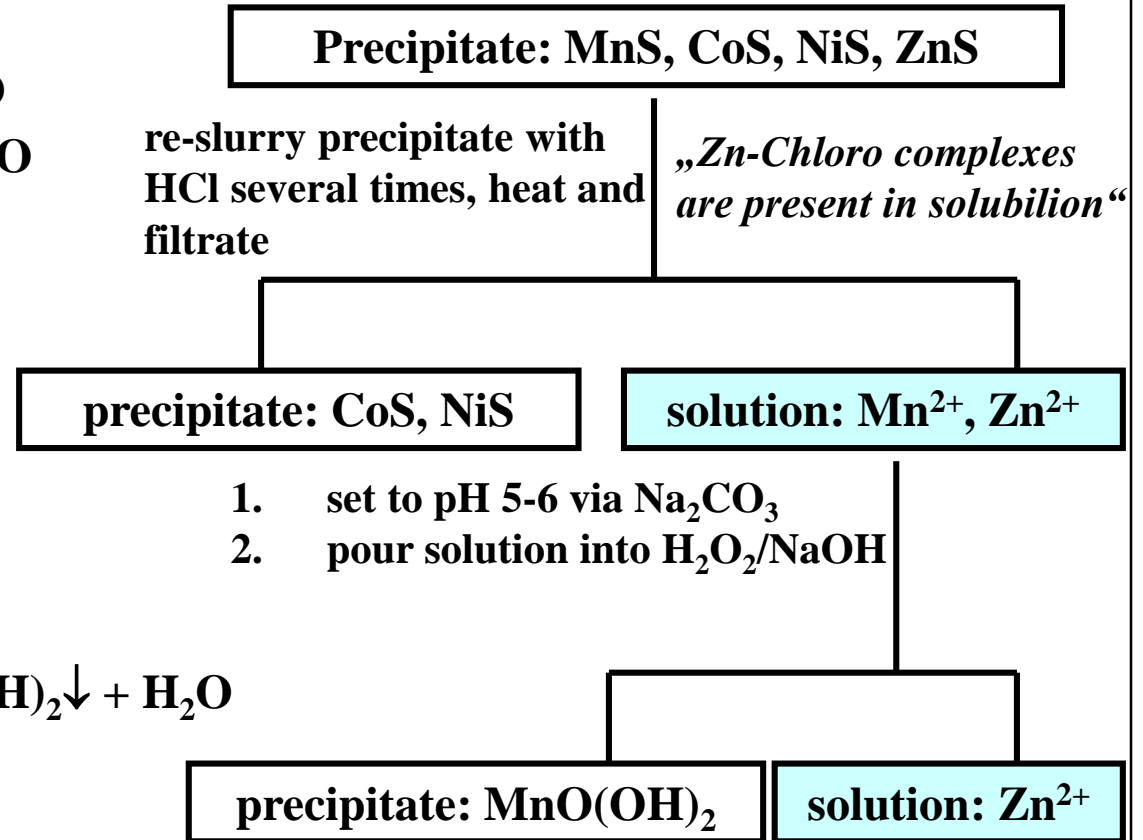
10. Separation Process for Cations

$(\text{NH}_4)_2\text{S}$ Group



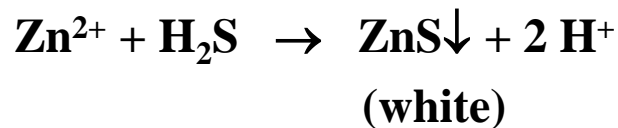
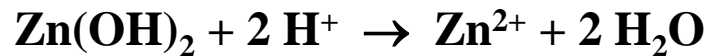
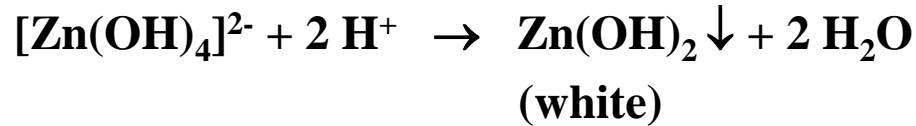
Separation of zinc and manganese

- $\text{Mn}^{2+} + \text{H}_2\text{O}_2 + 2 \text{OH}^- \rightarrow \text{MnO}(\text{OH})_2\downarrow + \text{H}_2\text{O}$
- $\text{Zn}^{2+} + 2 \text{OH}^- \rightarrow \text{Zn}(\text{OH})_2\downarrow$
- $\text{Zn}(\text{OH})_2 + 2 \text{OH}^- \rightarrow [\text{Zn}(\text{OH})_4]^{2-}$
(tetra hydroxozincate)

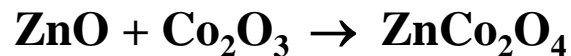


10. Separation Process for Cations

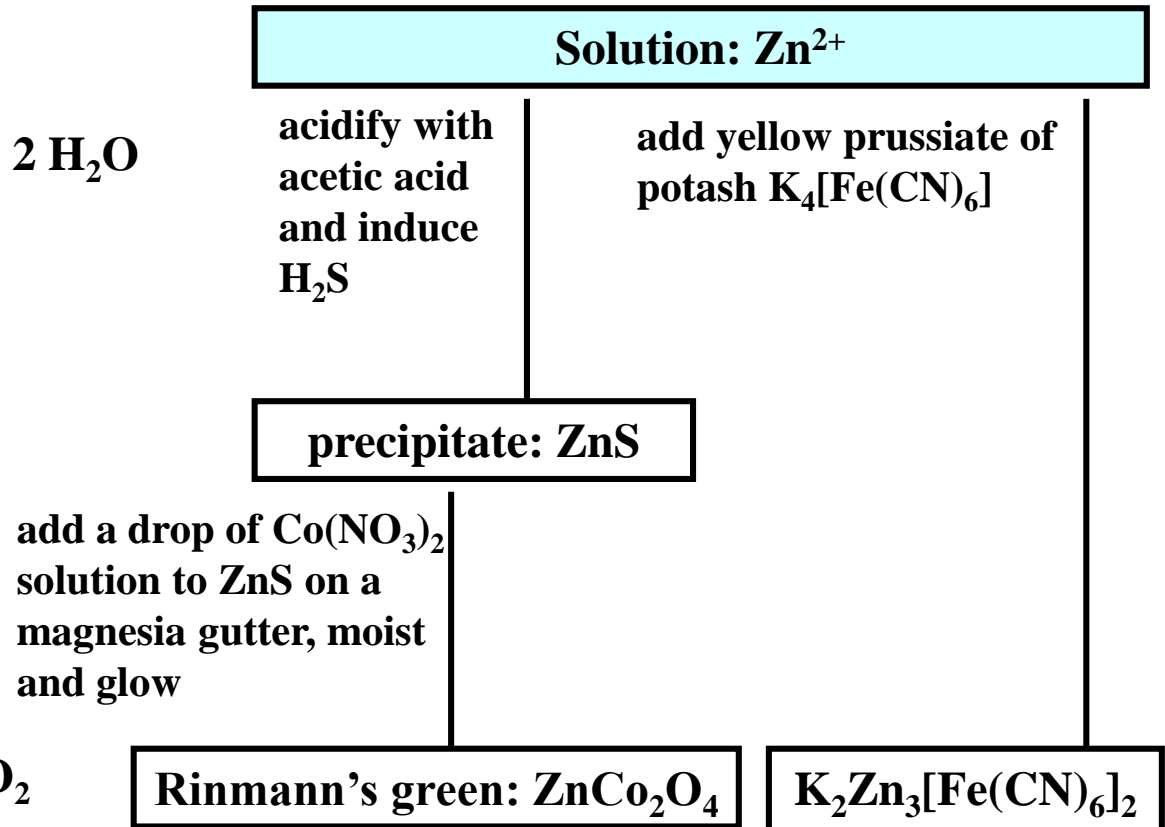
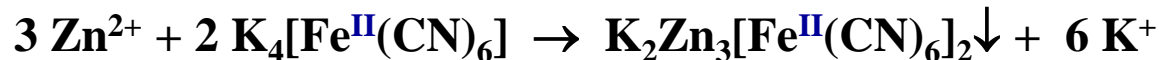
(NH₄)₂S Group



Detection of Rinmann's green



Detection as stained-white potassium zinc hexacyanoferrate



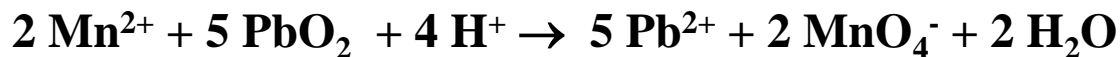
10. Separation Process for Cations

(NH₄)₂S Group



Detection as permanganate

1. Oxidation with lead oxide



2. Oxidation with ammonium peroxy-di-sulphate



Precipitate: MnO(OH)₂

wash precipitate
with some
conc. HCl

solution: Mn²⁺

acidify with conc.
HNO₃, add PbO₂
and reflux

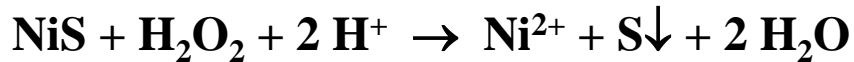
acidify with conc.
H₂SO₄, add (NH₄)₂S₂O₈
and reflux

solution: MnO₄⁻



10. Separation Process for Cations

$(\text{NH}_4)_2\text{S}$ Group



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: $\text{Co}(\text{SCN})_2$

make solution alkaline and add di-methyl glyoxime

Detection of cobalt with thiocyanate



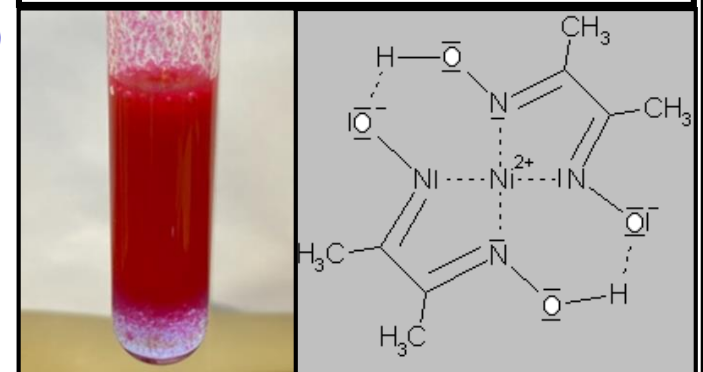
(dissolves in amyl alcohol and gives blue colour)

Detection of nickel with di-methyl glyoxime (H_2dmg)



(red)

precipitate: $[\text{Ni}(\text{Hdmg})_2]$



10. Separation Process for Cations

$(\text{NH}_4)_2\text{CO}_3$ 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	atomic number	Li⁺ 1.32	Be²⁺ 4.44	B³⁺ 11.10	C⁴⁺ 25.00	charge/radius[pm] · 10 ²
11 Na 22.990	12 Mg 24.305	13 Al 26.982	14 Si 24.086		atomic mass	Na⁺ 0.98	Mg²⁺ 2.77	Al³⁺ 5.55	

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

Acidify filtrate of $(\text{NH}_4)_2\text{S}$ 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 $(\text{NH}_4)_2\text{CO}_3$

$(\text{NH}_4)_2\text{CO}_3$ group

soluble group

precipitate: BaCO_3 , SrCO_3 , CaCO_3

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

10. Separation Process for Cations

$(\text{NH}_4)_2\text{CO}_3$ Group



Precipitate: BaCO_3 , SrCO_3 , CaCO_3

Dissolve precipitate
in 2 n acetic acid

Dissolution of the carbonates



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

Add NaAc, until pH 4-5
is reached. Dropwise
addition of slight excess
of $\text{K}_2\text{Cr}_2\text{O}_7$

Precipitation as chromate



Initiate cristallisation of
 BaCrO_4 by rubbing with
a glass rod



precipitate: BaCrO_4

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

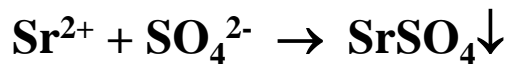
10. Separation Process for Cations

$(\text{NH}_4)_2\text{CO}_3$ Group

Dissolution of the carbonates



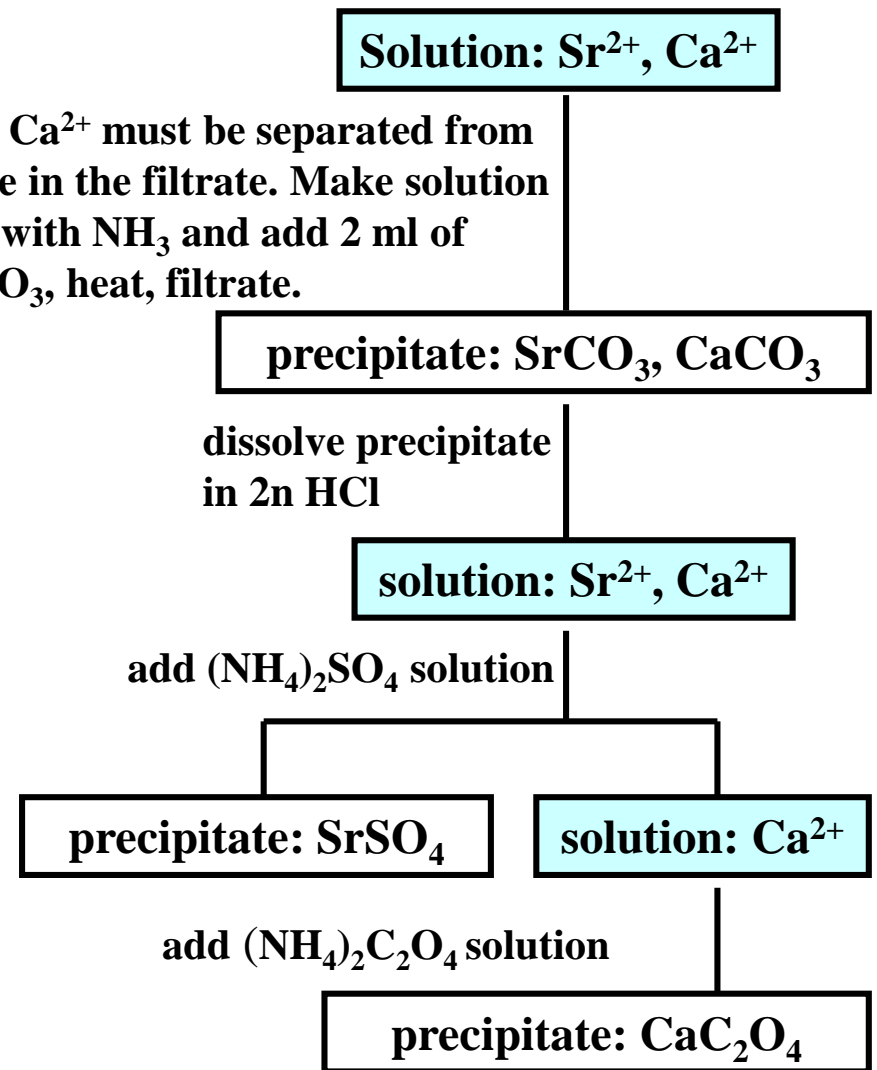
Precipitation as sulphates



Precipitation as oxalates



Sr^{2+} and Ca^{2+} must be separated from chromate in the filtrate. Make solution alkaline with NH_3 and add 2 ml of $(\text{NH}_4)_2\text{CO}_3$, heat, filtrate.



10. Separation Process for Cations

Soluble Group

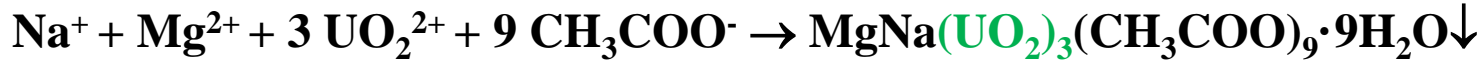
The filtrate of the carbonate group still contains Mg^{2+} , Li^+ , Na^+ , K^+ and NH_4^+ (and Rb^+ , Cs^+)
For these ions, a separation is difficult and not necessary for their detection

NH_4^+ from primary substance \rightarrow blue cross procedure: $\text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3\uparrow + \text{H}_2\text{O}$

Li^+ carmine red colourisation of Bunsen burner flame (670.8 nm)

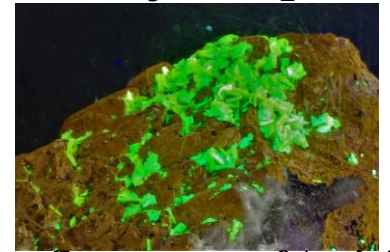
Na^+ yellow colourisation of Bunsen burner flame (589.3 nm)

precipitation with uranylacetate

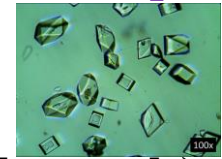


K^+ pale violet colourisation of Bunsen burner flame (Co glass needed, if Na^+ is present)
forms crystals with diluted $\text{HClO}_4 \rightarrow \text{KClO}_4$ (rhombic crystals) \rightarrow

Mg^{2+} addition of NH_3 and $(\text{NH}_4)_2\text{HPO}_4 \rightarrow \text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ (star-shaped crystals)



Green fluorescence of Autinite
 $\text{Ca}[\text{UO}_2]_2(\text{PO}_4)_2 \cdot 11\text{H}_2\text{O}$



11. Digestions

Transformation of poorly soluble Substances into readily soluble Compounds

Compounds, insoluble in acids

Typical digestions

Substance	Colour
Hg ₂ Cl 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 ₂ O ₃	green
Fe ₂ O ₃	red-brown
Al ₂ O ₃	white
SnO ₂	white
SiO ₂	white
TiO ₂	white

Soda-potash digestion	Na ₂ CO ₃ + K ₂ CO ₃	Ca/Sr/BaSO ₄ Al ₂ O ₃ SiO ₂
alkaline digestion	Na ₂ CO ₃ + NaOH	AgX
acidic digestion	KHSO ₄	Fe ₂ O ₃ Al ₂ O ₃ TiO ₂
oxidative digestion	NaNO ₃ + several alkaline metal carbonates	Cr ₂ O ₃ Cr ₂ (SO ₄) ₃
Freiberger digestion	Na ₂ CO ₃ + K ₂ CO ₃ + S ₈	SnO ₂

11. Digestions

Soda-Potash Digestion

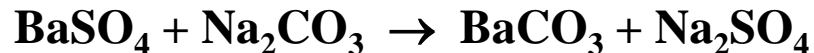
Digestion of

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

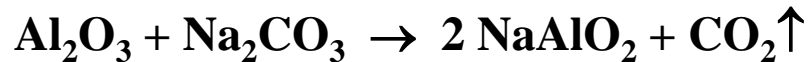
Course of action

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



oxide



silver halide



11. Digestions

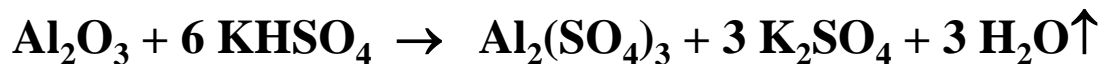
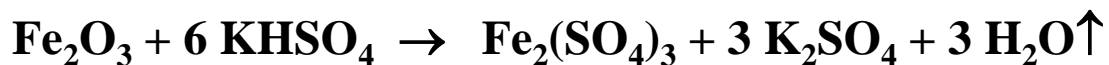
Acidic Digestion

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 .



11. Digestions

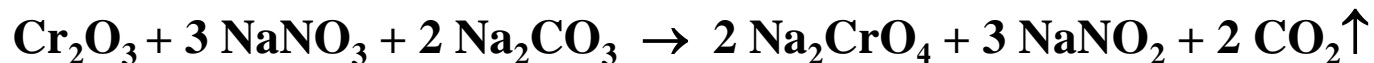
Oxidative Digestion

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)



11. Digestions

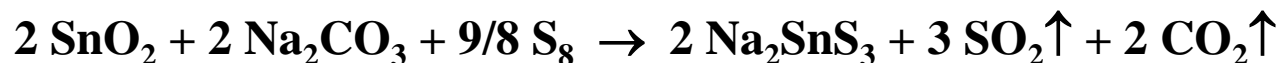
Freiberger Digestion

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



The melt cake is leached with HCl



The SnS_2 precipitated can subsequently be treated in the H_2S group