

---

# GRAVIMETRY

---

# Gravimetry

- Basic method, classical
- Constituent to be determined is transferred from a given, precise amount of a sample into a defined chemical individuum, whose mass determined by weighing is a measure of a content of the constituent in the sample
- Analytical weighing balances (scales) in principle isosceles lever + pendulum
  - sensitivity
  - accuracy



# Weighing

- 1) accuracy – the same length of both scale beams

(Gauss method of double weighing)  $m_x = \sqrt{z_1 \cdot z_2} \cong \frac{z_1 + z_2}{2}$

- Buoyancy force (reduction of weighing at vacuum)

$m_x$  – real mass

$z$  – weight of the weight

$s_x, s_z$  – specific mass of  $m_x, z$

$\sigma$  – specific mass of air

$$m_x = z \left[ 1 + \sigma \left( \frac{1}{s_x} - \frac{1}{s_z} \right) \right]$$

$\Sigma = 0,0012 \text{ g.cm}^{-3}, s_z = 8,4 \text{ g.cm}^{-3}$  (brass)  $\rightarrow$  for  $z = 1$

0,5 g of subst.  $\approx$  buoyancy 0,08 mg

$$k = 1,2 \left( \frac{1}{s_x} - \frac{1}{8} \right) \text{ [mg]}$$

# Weighing

- Other influencing factors:
  - ❑ air humidity: adsorption of H<sub>2</sub>O, time factor
  - ❑ finger prints: tweezers, laboratory tongs
  - ❑ hygroscopic substances: ground-glass weighing bottles
  - ❑ electric charge: powdered non-conductive substances on dry glass
  - ❑ weights (relative calibration – calibration standards)
  - ❑ weighing procedure: to lock balances, opening... no overloading !!!

# Weighing

- 2) sensitivity

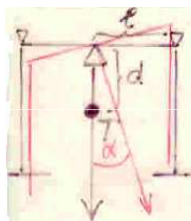
$$c = \frac{\Delta n}{\Delta z}$$

$$c = \frac{l}{G \cdot d}$$

$l$  – scale beam

$G$  – beam weight

$d$  - distance



## Analytical balances

Capacity: The largest weight the balance is capable of weighing

Accuracy: the extent to which a given measurement agrees with the standard value for the measurement. (i.e. given weight is 100.000 g, weighed 100.002 g, accuracy is 2 mg.)

- Calibration: to determine, check or rectify the graduations of balance. It is the comparison between the output of a scale or balance against a standard value.
- Reproducibility: ability of scales to return to the same numeric result with repeated application of the same weight. (hysteresis)

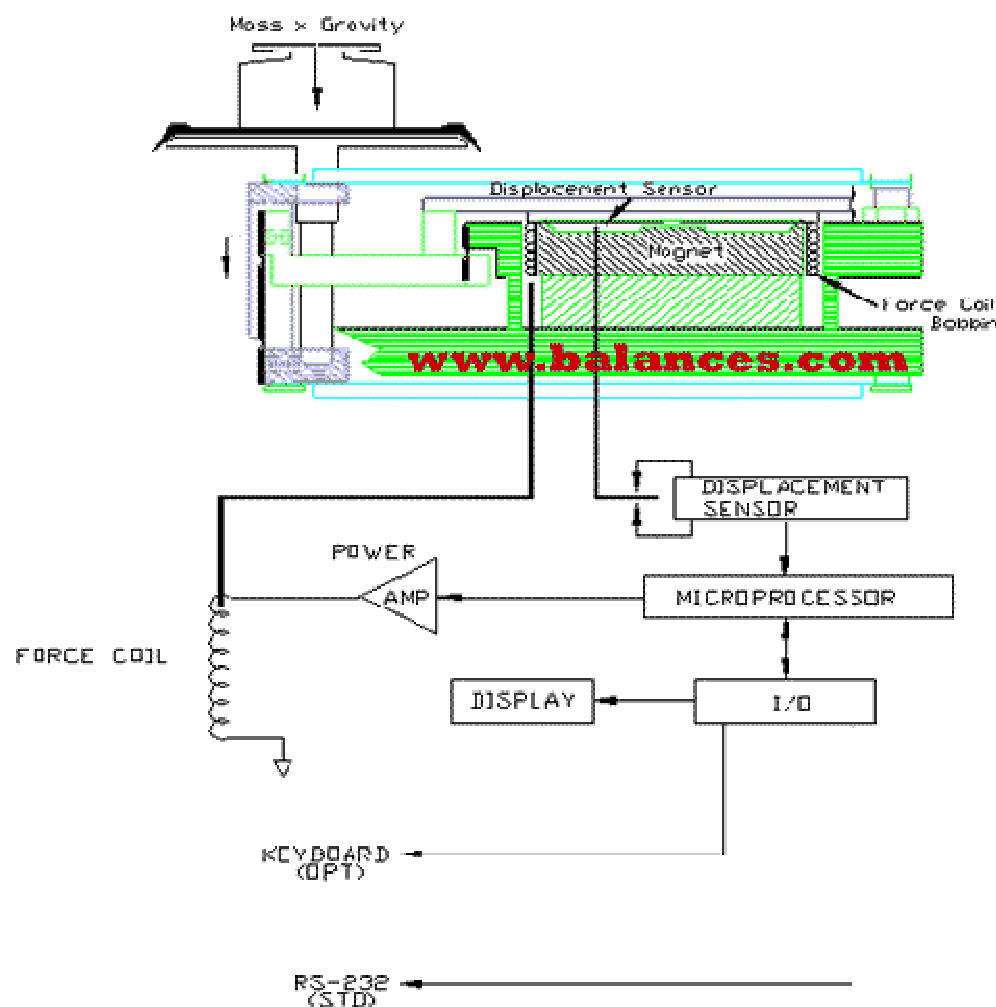
# Weighing

- Hysteresis: property of load cells, and other weighing systems dependant on elastic materials, such as spring balances, resulting in different indication at the same load, depending upon the direction of approach to that load, i.e. whether it is approached by increasing the load or decreasing the load. Hysteresis error refers to the condition of repeatedly weighing the same object, but obtaining different readings on the numeric readout.
- Drift: is a progressive (continuously upward or continuously downward) change in the number displayed on the digital readout. The weight readings does not stabilize, or unstable readings with no weight applied. All analytical balances show some uncertainty.

# Weighing

- Precision: The extent to which a given set of measurements of the same sample agree with their mean. Amount of agreement between repeated measurements of the same quantity. Also known as repeatability. A scale can be extremely precise, but not necessarily be accurate.
- Repeatability: refers to an instrument's ability to consistently deliver the same weight reading for a given object, and to return to a zero reading after each weighing cycle. Test this by repeatedly weighing the same object.
- Count (digit): The smallest increment of weight which the digital display resolves. Also called "division."
- Divisions: The amount of increments a scale offers.

# Weighing



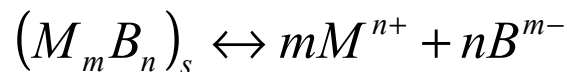
Mechanically the sensor is a simple lever & fulcrum. One end of the lever holds the weighing pan where an unknown weight is placed. On the opposite end of the lever is a FORCE COIL suspended in a magnetic field (much in the same way a speaker operates). The displacement detector, and power amplifier produce an appropriate current to hold the lever balanced in the null position for any weight placed on the pan. The amount of current required to do this is proportional to the weight on the pan.

The MICROPROCESSOR monitors the current produced in response to the applied load to determine the magnitude of the weight. Software contained in memory allows the user through the front panel, keyboard or one of the optional interfaces to perform such tasks as converting units of weight and parts counting. In addition the user can change filter parameters to suit most environments or gather statistical data form groups of weights. Calibration coefficients and user developed constants are stored in a non volatile memory.



# Precipitation

- classical separation technique for gravimetry
- preparation of pure compounds
  - insolubility of precipitate x loss (< 0,1 mg)
  - solubility of precipitate  $\approx$  concentration of saturated solution above the precipitate
  - Low soluble salts  $\approx$  strong electrolytes  $\approx$  complete dissociation



$$K = \frac{a_M^m \cdot a_B^n}{a_{M_m B_n}} \leftarrow \text{unit activity of the solid phase is included in the constant}$$

$$\Rightarrow (K_s)_T = a_M^m \cdot a_B^n = \text{solubility product (thermodynamic value)}$$

$$a_M = [M] \cdot \gamma_M, a_B = [B] \cdot \gamma_B \Rightarrow (K_s)_T = K_s \cdot \gamma_{\pm}^{m+n}$$

$$K_s = [M^{n+}]^m \cdot [B^{m-}]^n$$

# Calculation of solubility of pure compounds

$$c_M < 10^{-3} \text{ mol} \cdot \text{l}^{-1} \Rightarrow \gamma_{\pm}^{m+n} \rightarrow 1 \Rightarrow a \rightarrow c$$

uni-univalent electrolyte

$$c_{MB} = [M] = [B] = c \Rightarrow K_s = [M] \cdot [B] = c^2 \Rightarrow c = \sqrt{K_s}$$

- It is valid in distilled water in the absence of other ions

$$M_m B_n \Rightarrow K_s = [M^{n+}]^m \cdot [B^{m-}]^n = (m \cdot c)^m \cdot (n \cdot c)^n$$

$$\Rightarrow c = \sqrt[m+n]{\frac{K_s}{m^m \cdot n^n}}$$

# Calculation of solubility of pure compounds

- **example:** How many grams of AgCl is contained in 1 l of saturated solution of AgCl,  $M(\text{AgCl}) = 143,32 \text{ g}\cdot\text{mol}^{-1}$



$$K_s = [\text{Ag}^+][\text{Cl}^-] = 1,78 \cdot 10^{-10} \Rightarrow c = \sqrt{K_s} = \sqrt{1,78 \cdot 10^{-10}} = 1,33 \cdot 10^{-5} \text{ mol}\cdot\text{l}^{-1}$$

$$\Rightarrow \text{mass conc.} = 1,33 \cdot 10^{-5} \cdot 143,32 = 1,91 \cdot 10^{-3} \text{ AgCl g}\cdot\text{l}^{-1}$$

- **example:** What is the solubility of  $\text{Ag}_2\text{CrO}_4$  in  $\text{H}_2\text{O}$ ?



$$c = \sqrt[3]{K_s / 4} \Rightarrow c(\text{Ag}_2\text{CrO}_4) = \sqrt[3]{1,12 \cdot 10^{-12} / 4} = 6,6 \cdot 10^{-5} \text{ mol}\cdot\text{l}^{-1}$$

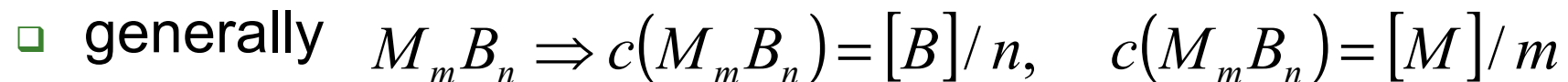
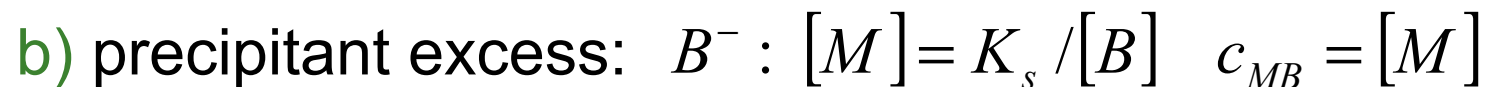
$$[\text{Ag}^+] = 2 \cdot c(\text{Ag}_2\text{CrO}_4) = 1,32 \cdot 10^{-4} \text{ mol}\cdot\text{l}^{-1}$$

# Solubility

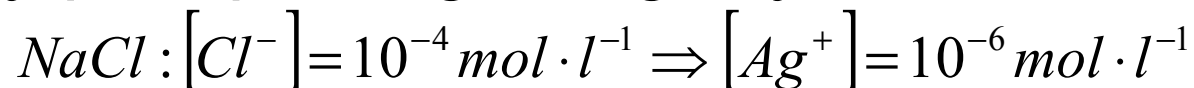
- Factors influencing solubility
  - own ions
  - pH
  - complexation } side reactions
  - temperature
  - solvent
  - particle size
  - ionic strength

# Factors influencing solubility

## ■ 1) influence of own ions – excess of precipitant



by precipitating of  $Ag^+$  by excess of



→ washing the precipitate by diluted solution of precipitant, no water

× large excess → (soluble) complexes formation → dissolution



# Factors influencing solubility

- **example:** calculate concentration of  $SO_4^{2-}$  necessary for quantitative precipitation of  $BaSO_4$   
( $M(BaSO_4) = 233,43 \text{ g} \cdot \text{mol}^{-1}$ ;  $K_s = 1,08 \cdot 10^{-10}$ )
  - Condition:  $m(BaSO_4)$  in solution  $< 10^{-4} \text{ g}$ ;  $V = 300 \text{ cm}^3$

$$c(BaSO_4) = [Ba^{2+}] = \frac{10^{-4}}{233,43} \cdot \frac{1000}{300} = 1,43 \cdot 10^{-6} \text{ M}$$

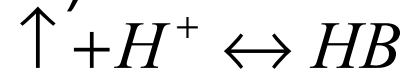
$$[SO_4^{2-}] = K_s / [Ba^{2+}] = 1,08 \cdot 10^{-10} / 1,43 \cdot 10^{-6} = 7,55 \cdot 10^{-5} \approx 10^{-4}$$

$= 10^{-4} \text{ M}$  of solution of  $SO_4^{2-}$

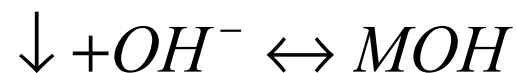
# Factors influencing solubility

## ■ 2) pH and complex formation

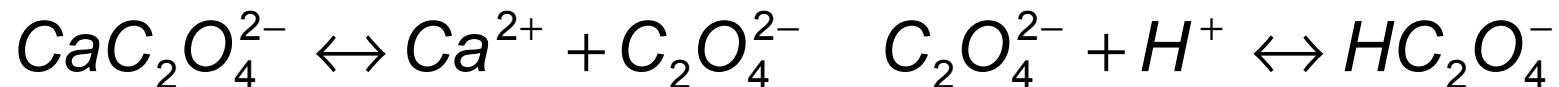
- side equilibria → soluble complexes (hydroxocomplexes of cations, protonization of anions)



- solid phase dissolution  $M^+ + B^- \leftrightarrow MB \downarrow$



- acids and bases increase solubility of precipitate



# Factors influencing solubility

- conditional solubility product

$$K'_s = \frac{c(M) \cdot c(B)}{[M']^m \cdot [B']^n} = [M]^m \cdot \alpha_{M(L)}^m \cdot [B]^n \cdot \alpha_{B(H)}^n = K_s \cdot \alpha_{M(L)}^m \cdot \alpha_{B(H)}^n$$

- $\alpha$  – side reaction coefficient

$$\alpha_{M(L)} = \frac{[M']}{[M]} = \frac{1}{[M]} \{ [M] + [ML] + [ML_2] + \dots \} = 1 + \beta_{ML} [L] + \beta_{ML_2} [L^2] \dots$$

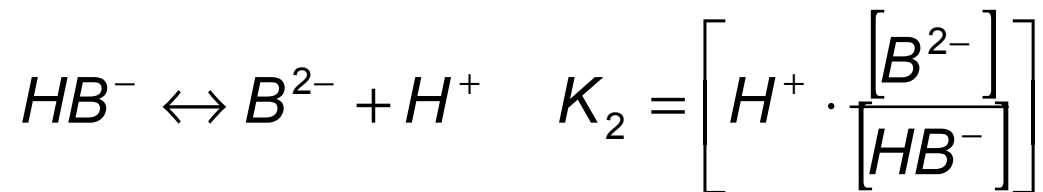
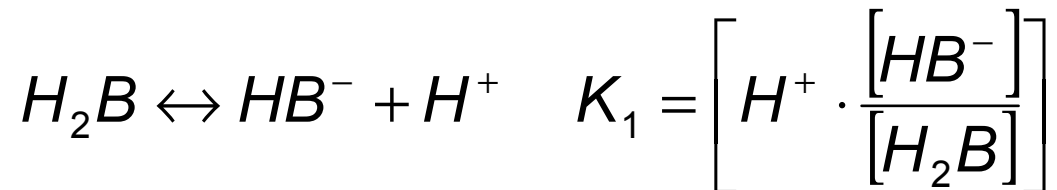
$$\alpha \geq 1$$

$$\beta_{ML} = \frac{[ML]}{[M][L]} \quad \beta_{ML_2} = \frac{[ML_2]}{[M][L]^2} \text{ overall formation constant}$$



# Factors influencing solubility

- **example:** diprotic acid:



$$\begin{aligned} \alpha_{B(H)} &= \frac{1}{[B]} \{ [B] + [HB] + [H_2B] \} = \frac{1}{[B]} \left\{ [B] + [B] \cdot [H] \cdot \frac{1}{K_2} + [HB] \cdot [H] \cdot \frac{1}{K_1} \right\} = \\ &= \frac{1}{[B]} \left\{ [B] + [B] \cdot [H] \cdot \frac{1}{K_2} + [B] \cdot [H]^2 \cdot \frac{1}{K_1 K_2} \right\} = 1 + \frac{[H]}{K_2} + \frac{[H]^2}{K_1 K_2} \end{aligned}$$

# Factors influencing solubility

- **example:** what is solubility of  $\text{CaF}_2$  in 0,01 M – HCl?

$$K_{HF} = 6 \cdot 10^{-4}, K_s(\text{CaF}_2) = 4 \cdot 10^{-11},$$

$$F^- + H^+ \leftrightarrow HF \Rightarrow \alpha_{F^-} = \left\{ 1 + \frac{[H^+]}{K_{HF}} \right\}, \alpha_F = 1 + (6 \cdot 10^{-4})^{-1} \cdot [10^{-2}] \approx$$

$$\approx 8, c(\text{CaF}_2) = \sqrt[3]{K'_s / 4} = \sqrt[3]{K_s \cdot \alpha_F^2 / 4} = \sqrt[3]{K_s / 4} \cdot \sqrt[2]{\alpha_F^2} =$$

$$= 2,15 \cdot 10^{-4} \cdot 312^{1/3} = 2,15 \cdot 10^{-4} \cdot 6,78 = 0,0015 \text{ M}$$

# Factors influencing solubility

- **example:** calculate solubility of AgI v 0,01 M NH<sub>3</sub>

$$K_s(\text{AgI}) = 1,00 \cdot 10^{-16} \quad \beta_1 = \frac{[\text{Ag}(\text{NH}_3)^+]}{[\text{Ag}^+][\text{NH}_3]} = 10^{3,4} \quad (\log \beta_1 = 3,4)$$

$$K_s(\text{AgI}) = [\text{Ag}^+] \cdot [\text{I}^-]$$

$$K_s'(\text{AgI}) = K_s(\text{AgI}) \cdot \alpha_{\text{Ag}} \quad \beta_2 = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2} = 10^{7,2} \quad (\log \beta_2 = 7,2)$$

$$\begin{aligned} c'(\text{AgI}) &= \sqrt{K_s'} = \sqrt{K_s \cdot \alpha_{\text{Ag}}} = \sqrt{K_s} \cdot \left\{ 1 + \beta_1[\text{NH}_3] + \beta_2[\text{NH}_3]^2 \right\}^{\frac{1}{2}} = \\ &= \sqrt{10^{-16}} \cdot \left\{ 1 + 10^{3,4} \cdot 10^{-2} + 10^{7,2} \cdot 10^{-4} \right\}^{\frac{1}{2}} = 4,01 \cdot 10^{-7} \text{ M} \end{aligned}$$

$$c(\text{AgI}) = \sqrt{10^{-16}} = 1 \cdot 10^{-8} \text{ M} \quad \text{Solubility increases 40x.}$$

# Factors influencing solubility

- **example:** calculate molar solubility of  $\text{BaCO}_3$  at  $\text{pH} = 6$  and  $I = 0,1$  ( $\text{pK}_s = 8,09$ ;  $\text{pK}_1 = 6,15$ ;  $\text{pK}_2 = 9,99$ )

$$K_s = [\text{Ba}^{2+}][\text{CO}_3^{2-}]; K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}; K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

$$\begin{aligned}\alpha(\text{CO}_3^{2-}) &= 1 + [\text{H}^+] \cdot K_2^{-1} + [\text{H}^+]^2 \cdot K_1^{-1} \cdot K_2^{-1} = \\ &= 1 + 10^{-6} \cdot 10^{9,99} + 10^{-12} \cdot 10^{6,15} \cdot 10^{9,99} = 1 + 10^{3,99} + 10^{4,14} = 10^{4,37}\end{aligned}$$

$$K_s' = K_s \cdot \alpha(\text{CO}_3^{2-}) = 10^{-8,09} \cdot 10^{4,37} = 10^{-3,72}$$

$$c(\text{BaCO}_3) = \sqrt{K_s'} = 1,38 \cdot 10^{-2} \text{ M}$$

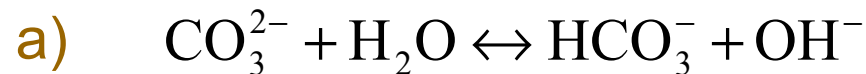
# Factors influencing solubility

- Dissolution of  $\text{BaCO}_3$  in  $\text{H}_2\text{O}$ , influenced pH, iteration

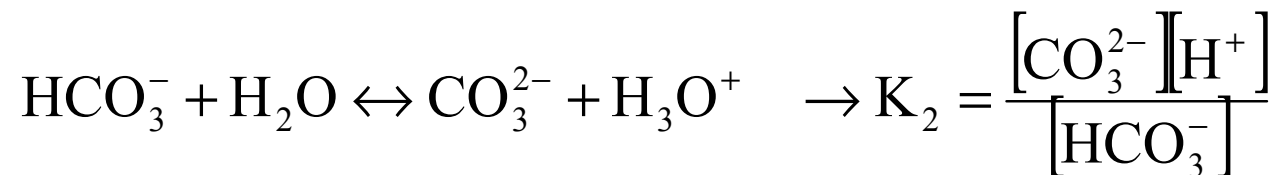
1) hydrolysis neglected  $\rightarrow$

$$c(\text{BaCO}_3) = c(\text{CO}_3^{2-}) = \sqrt{K_s} = \sqrt{10^{-8,09}} = 9,03 \cdot 10^{-5} \text{ M}$$

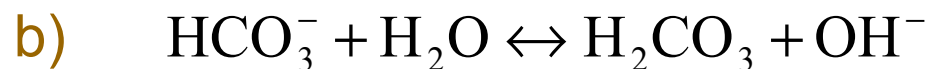
2) we find pH at hydrolysis of  $\text{CO}_3^{2-}$



$$K_{\text{CO}_3^{2-}} = K_{\text{H}_2\text{O}} / K_2 \quad \text{hydrolytic constant}$$



$$K_{\text{CO}_3^{2-}} = 10^{-14} / 10^{-9,99} = 10^{-4,01}$$



we neglect for calculation of pH, because  $K_{\text{HCO}_3^-} = 10^{-7,85} \ll K_{\text{CO}_3^{2-}} = 10^{-4,01}$

# Factors influencing solubility

c) pH of weak acid:  $[H^+]^2 + [H^+] \cdot K_2 - K_2 \cdot c(HCO_3^-) = 0$   
substitute  $\rightarrow [OH^-]^2 + [OH^-] \cdot K_{CO_3^{2-}} - K_{CO_3^{2-}} \cdot c(CO_3^{2-}) = 0$  ←  
 $\rightarrow [OH^-] = 5,82 \cdot 10^{-5} \text{ M} \rightarrow \text{pH} = 9,76$

3) we find cond. solub. product.  $K_s'$  and  $c(\text{BaCO}_3)$

$$\alpha_{CO_3^{2-}} = 1 + [H^+] \cdot K_2^{-1} + [H^+]^2 \cdot K_1^{-1} \cdot K_2^{-1} = 1 + 10^{0,23} + 10^{-3,38} = 2,70 =$$
$$= 10^{0,43} \rightarrow K_s' = K_s \cdot \alpha_{CO_3^{2-}} = 10^{-8,09} \cdot 10^{0,43} = 10^{-7,66}$$
$$c(\text{BaCO}_3) = \sqrt{K_s'} = 1,48 \cdot 10^{-4} \text{ M} \quad \times \quad \sqrt{K_s} = 9,03 \cdot 10^{-5} \text{ M}$$

4) we repeat calc. pH according 2c) with  $c(CO_3^{2-}) = 1,48 \cdot 10^{-4}$   
we get  $\text{pH} = 9,90$ ,  $K_s' = 10^{-7,74}$ ,  $c(\text{BaCO}_3) = 1,35 \cdot 10^{-4} \text{ M}$   
further approximation yields  $c(\text{BaCO}_3) = 1,32 \cdot 10^{-4} \text{ M}$

# Factors influencing solubility

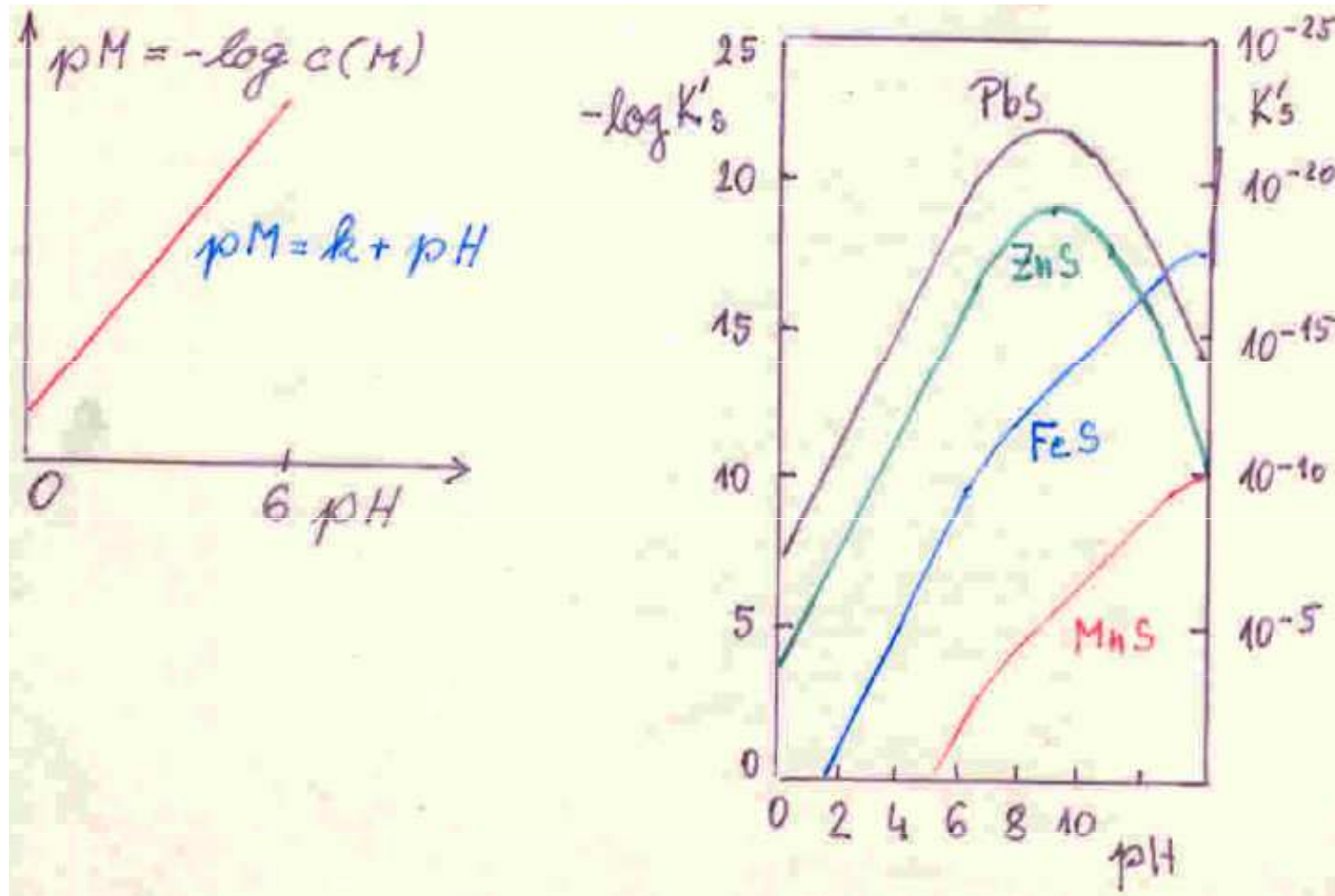
- dependence of solubility of sulfides on pH – principle of „sulfane“ separation of cations
- sulfide MS:  $c(M) = c(MS) = \sqrt{K_s'} = \sqrt{K_s \cdot \alpha(S)}$
- boundary condition:  $\text{pH} \leq 6$  – simplification  $\rightarrow x(S)$  comprises only 1 term:  $\alpha = (K_1 \cdot K_2)^{-1} \cdot [H^+]^2$

$K_1, K_2$  – dissoc. const.  $H_2S$  a  $HS^-$ , hydrolysis of M is neglected

$$c(M) = \sqrt{K_s} \cdot \frac{1}{\sqrt{K_1 \cdot K_2}} \cdot [H^+] \rightarrow -\log c(M) = -\log \left( \frac{K_s}{K_1 \cdot K_2} \right)^{\frac{1}{2}} + \text{pH}$$

$$\underline{\underline{\text{pM} = \frac{1}{2} \text{pK}_s - \frac{1}{2} (\text{pK}_1 + \text{pK}_2) + \text{pH}}}}$$

# Factors influencing solubility



$$K'_s = K_s \cdot \alpha_M \cdot \alpha_s$$



# Factors influencing solubility

- Influence of formation of complexes with own ions

M – cation; B – anion, ligand; MB – weak soluble comp.

$$c(M) = c(MB) = [M] + [(MB)_r] + \underbrace{[MB_2] + \dots + [MB_n]}_{\text{soluble complexes}}$$

$(MB)_r$  – soluble, non-dissociated portion of MB

$$\beta_{MB} \text{ – stability constant} = \frac{[(MB)_r]}{[M][B]} = \frac{[(MB)_r]}{K_s} = \beta_1$$

$$K_s' = c(M) \cdot [B] = K_s \cdot \alpha_M = K_s \{1 + \beta_1[B] + \beta_2[B]^2 + \dots + \beta_n[B]^n\}$$

$$c(M) = c(MB) = K_s \{[B]^{-1} + \beta_1 + \beta_2[B] + \dots + \beta_n[B]^{n-1}\}$$

↑ calculation of solubility MB in excess of precipitant ↑



# Factors influencing solubility

- Dependence of solubility of hydroxides on pH

$$c(\text{M}(\text{OH})_n) = c(\text{M}) = K_s \left\{ [\text{OH}^-]^{-n} + \beta_1^{\text{OH}} [\text{OH}^-]^{(1-n)} + \dots + \beta_N^{\text{OH}} [\text{OH}^-]^{(N-n)} \right\}$$

$\beta_1^{\text{OH}} \dots \beta_N^{\text{OH}}$  – stability constants of hydroxocomplexes

$$\text{e.g. } \beta_1 = \frac{[\text{M}(\text{OH})]}{[\text{M}][\text{OH}]}$$

substitute  $[\text{OH}^-] = K_v / [\text{H}^+] \rightarrow$

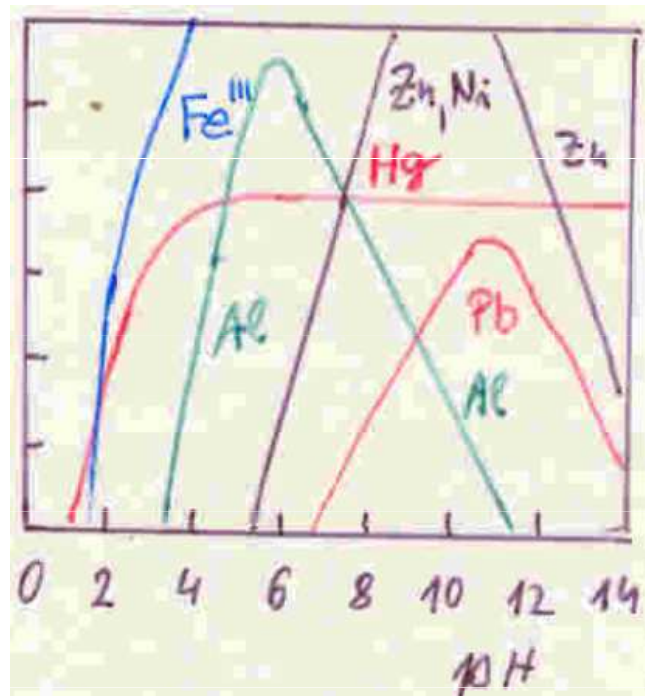
$$\rightarrow c(\text{M}(\text{OH})_n) = c(\text{M}) = K_s \left\{ [\text{H}^+]^n \cdot \frac{1}{K_v^n} + [\text{H}^+]^{n-1} \cdot \frac{\beta_1^{\text{OH}}}{K_v^{n-1}} + [\text{H}^+]^{n-2} \cdot \frac{\beta_2^{\text{OH}}}{K_v^{n-2}} \dots \right\}$$

# Factors influencing solubility

- Hydroxides of trivalent cations are less soluble than hydroxides of divalent ones.

At pH 4,5 to 6:  $\text{Fe}(\text{OH})_3 \downarrow$ ,  $\text{Al}(\text{OH})_3 \downarrow$  quantitatively

Separate from  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$



# Factors influencing solubility

## ■ 3) ionic strength (influence of third ions)

### □ indifferent electrolyte

$$1) \log y_{\pm} = 0,5z_N \cdot z_B \cdot \sqrt{I} / (1 + \sqrt{I})$$

$$2) (K_s)_T = [M^{n+}]^m \cdot [B^{m-}]^n \cdot y_M^m \cdot y_B^n = K_s \cdot y_{\pm}^{m+n}$$

$$3) c = \sqrt[m+n]{\frac{K_s}{m^m \cdot n^n}}$$

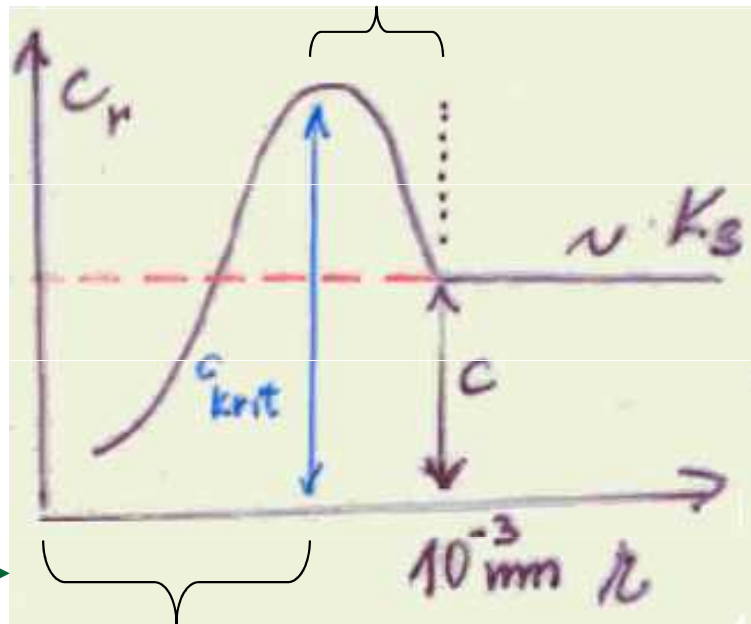
$$1) + 2) + 3) \rightarrow \underline{\log c = \log c_0 + 0,5z_N z_B \sqrt{I}} \quad (c_0 \text{ pro } I \leq 10^{-4})$$

### □ solubility increases with increasing concentration of third ions

# Factors influencing solubility

## ■ 4) particle size of precipitate

influence of surface of crystals



- for  $> 10^{-3}$  mm is valid

$$K_s = [M]^m \cdot [B]^n$$

- solubility increases – crystal edges – weaker attractive forces
- small crystals dissolve – bigger grow

**aging of the precipitate**

**colloid dispersion** – charge of adsorbed ions decreases solubility

$$\ln\left(\frac{c_r}{c}\right) = \frac{a}{r} - \frac{b}{r^4} \quad \parallel \quad \ln\left(\frac{c_2}{c_1}\right) = \frac{2\sigma M}{RT\rho} \left(\frac{1}{r_2} - \frac{1}{r_1}\right) \quad \text{OSTWALD - FREUNDLICH}$$

# Factors influencing solubility

## ■ 5) influence of solvent

- ❑ Organic solvents decrease solubility of inorganic substances
- ❑ example:  $\text{CaSO}_4$  in 50% EtOH quantitatively precipitates  
LiCl soluble in amylalcohol,  
neither KCl a NaCl
- ❑ Influence increases with charge of ions

# Properties of precipitates

- depend on :
  - chemical composition
  - properties and composition of medium in which precipitation occurs
  - method of precipitating
- precipitate types:
  - colloidal (sulfur)
  - gel-like ( $\text{Fe}(\text{OH})_3$ )
  - lumpy ( $\text{AgCl}$ )
  - crystalline (convenient, better filterable, more pure than amorphous):
    - fine ( $\text{BaSO}_4$ )
    - coarse ( $\text{PbCl}_2$ )
- requirements: filterability, easy drying, ignition, defined composition



# Properties of precipitates

- mechanism:
  - 1) formation of oversaturated solution (metastable)
  - 2) formation of crystallization centers (cores, primary)
  - 3) growth of particles (aging)
- big particles grow at the expense of small

a) rate of formation of precipitate (Weimarn)

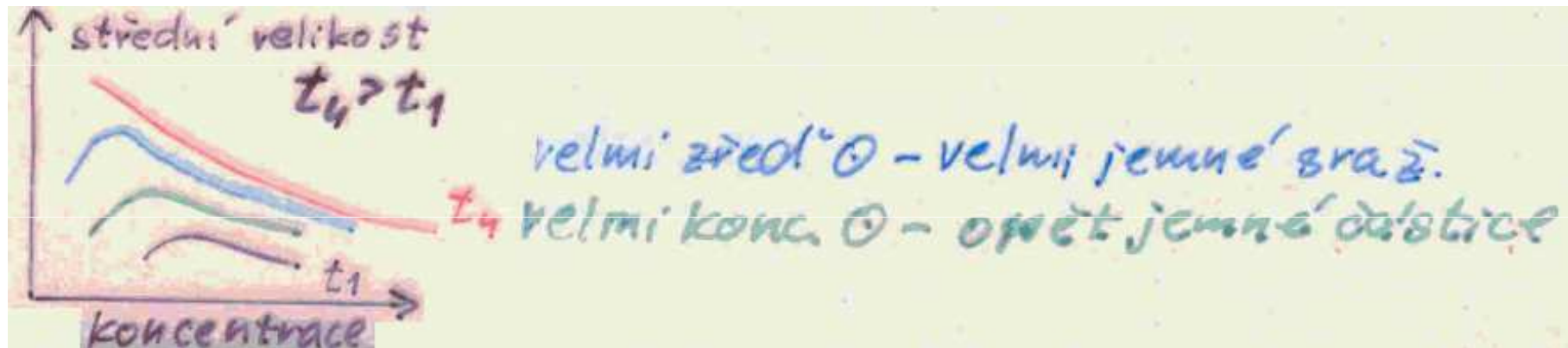
$$v = k \frac{c' - c}{c}$$

$c'$  - instantaneous concentration of oversaturated solution

$c$  - solubility

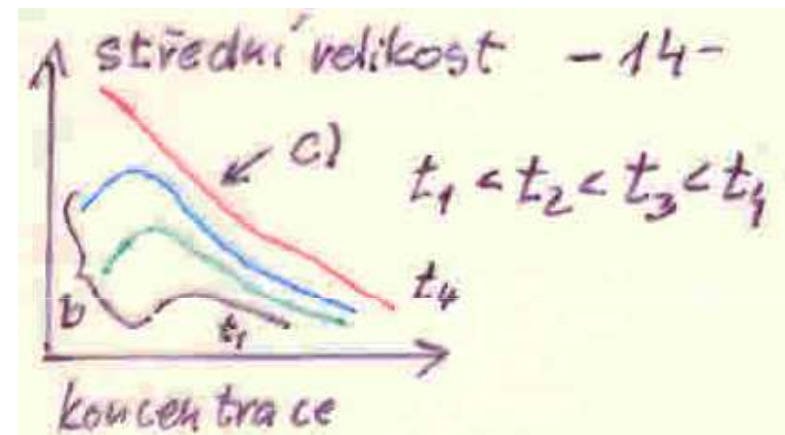
# Properties of precipitates

b) mean particle size depends on original concentration of solution (Weimarn)



- More soluble substances – bigger particles
- $t$  – time – aging

c) mean particle size increases with time of contact of precipitate with original solution.

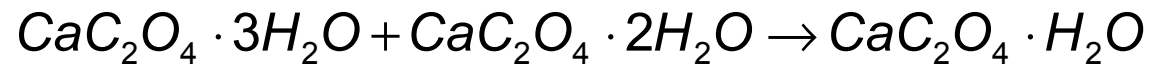


# Properties of precipitates

- aging:

$10^{-1}$	HRUBÉ DISPERZE (EMULZE, SUSPENZE)	FILTROVA- TELNĚ PAR. FILTREM
$10^{-3}$		
$10^{-5}$	KOLOIDNÍ DISPERZE	NEFILTRO- VATELNĚ PAPIROVÝM FILTREM
$10^{-7}$		
$10^{-9}$	PRAVÉ ROZTOKY	FILTREM
[cm]		

- less perfect → more perfect crystals
- Metastable modifications → stable (aragonit → kalcit)
- change of number of crystal water molecules

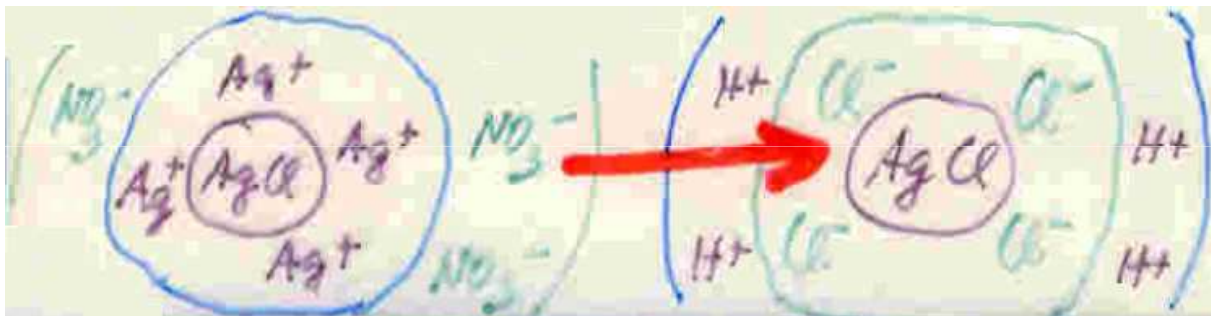


- dehydration (hydrat. oxidy Fe, Ti, Sn, Al, Zr, Th)
- polymeration (CoS, NiS)

# Properties of precipitates

- ❑ Colloidal dispersions ( $10^{-5} - 10^{-7}$  cm): Brown motion  
Tyndall effect
- ❑ RTG → crystalline character
  - large specific surface (S/V)
  - adsorption ability
- ❑ existence of colloidal dispersions: repulsive elastic forces
- ❑ electric double layer → micelles

example:



change of sign of charge in  
isoelectric point x point of  
equivalence

# Properties of precipitates

## ■ coagulation

- ❑ charges of the same sign on micelles **x** coagulation
- ❑ electrolyte excess disturbs a double-layer → micelles coagulate
- ❑ coagulation increases with discharge of salt in washing solution ( $\text{AlCl}_3 \gg \text{NH}_4\text{Cl}$ , 1000 x)

**x** ammonia salts preferred – removable at heating

dispersion stability –  $\text{H}_2\text{O}$  molecules binding →

- lyophobic colloids – unstable ( $\text{As}_2\text{S}_3$ , S, Au, AgX)
- lyophilic colloid – stable (starch, gels, proteins,  $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ ,  $\text{SiO}_2 \cdot x\text{H}_2\text{O}$ )

## ■ peptization – the opposite of coagulation

- ❑ at filtration and washing with water – removing of electrolyte – unwanted effect! – therefore we wash with electrolyte solution

# Contamination of precipitates

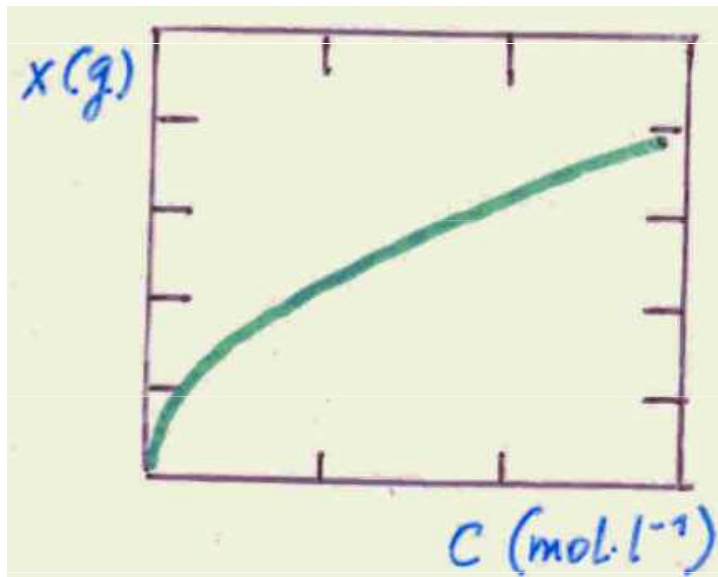
- ❑ co-precipitation
- ❑ post-precipitation (induced precipitation)
- coprecipitation
  - adsorption
  - occlusion
  - inclusion
  - mixed crystals
- a) adsorption: depends on – conc. of adsorbed substances
  - properties of adsorbed substances
  - properties of precipitate
  - **Paneth-Fajans**: most adsorbed own ions and forming low soluble substances

# Coprecipitation

- example:  $\text{BaSO}_4$  in excess of  $\text{Ba}^{2+}$ :  $\text{Br}^- < \text{Cl}^- < \text{ClO}_3^- < \text{NO}_3^-$   
 $\text{BaSO}_4$  in excess of  $\text{SO}_4^{2-}$ :  $\text{Na}^+ < \text{K}^+ < \text{Ca}^{2+} < \text{Pb}^{2+}$
- easier adsorbed ions with higher charge
- Freundlich adsorption isotherm

( $T = \text{const.}$ );  $k, n$  – const.;  $x$  – amount / 1 g precip.

$$x = k \cdot c^{1/n}$$



- relatively highest adsorption of impurities occurs at lowest conc. of impurities
- **contamination of precipitate is proportional to surface** →  
coagulated colloidal dispersion **x**  
coarse crystalline precipitate

# Coprecipitation

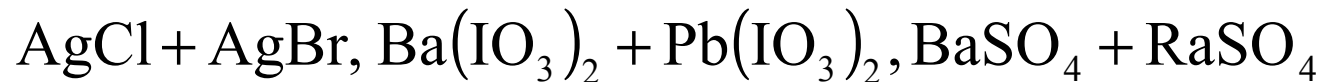
b) occlusion: mechanical stripping of extraneous components of solution at precipitating and growth of crystals around the impurity  $\approx$  concentration of solution and  $\approx$  rate of precipitation

c) inclusion: mechanical closure of parent solution at crystal growth



# Coprecipitation

d) mixed crystals: isomorphic substitution of ions at  $\Delta r_{\text{ion}} < 10-15 \%$  and at the same crystal group = solid solutions preferred ions with the same electric charge numbers



$$D = \frac{(c_1 / c_2)_t}{(c_1 / c_2)_r}$$

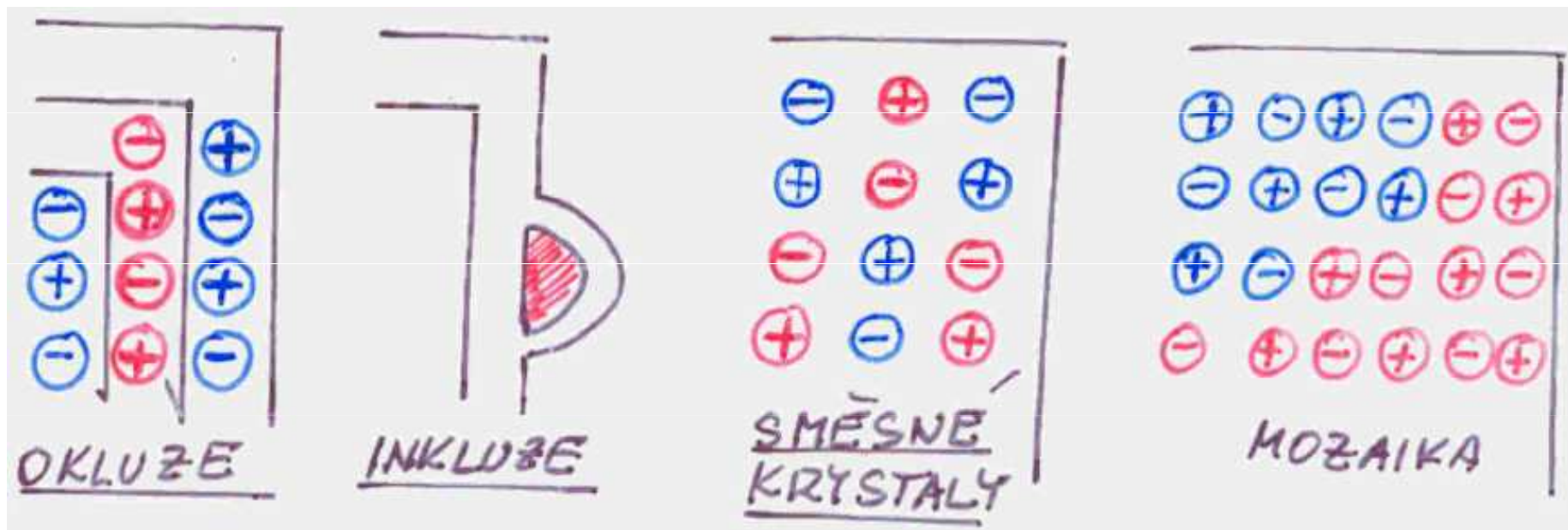
D – partition koef.;  $c_1, c_2$  – koncentration of isomorphic const.; t – precip.; r-solution

it is not possible to purify by repeated precipitating with the same precipitant!!!

D less depends on T(K), precip. rate, conc.

# Coprecipitation

- types of contamination



# Postprecipitation

- postprecipitation– induced
  - 1) originally pure precipitate:  $\text{Ca}^{2+} + \text{Ox} \rightarrow \text{CaOx}$  (Ox – oxalate)
  - 2) after some time from oversaturated solution of MgOx precipitates MgOxit is therefore advisable to keep concentration ratios, and CaOx soon be filtered off, dtto sulfides
- Klathrates:  $[\text{Ni}(\text{NH}_3)_2(\text{CN})_2]$  inside benzen

# Amorphous precipitates

- Amorphous precipitates – by coagulating of colloids → gels
  - large specific surface → significant sorption
  - coagulation by excess of electrolyte – source of contamination
  - filtration – immediately after precip.
  - to wash with electrolyte solution (peptization!!!)
- Minimizing of coprecipitation – by a suitable procedure

# Principles of precipitation

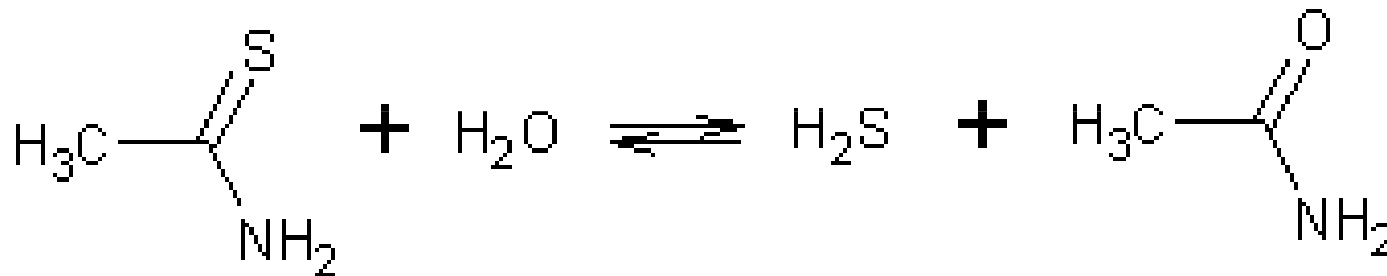
- precipitation from hot solutions – better formation of crystal lattice without third ions – contaminating ions; to cool before filtration in case of more soluble precipitates ( $\text{MgNH}_4\text{PO}_4$ )
- precipitation from sufficiently diluted solutions; repeated precipitation (2x) (hydroxides); diminution of coprecipitation of cations on precip.  $\text{A}^+\text{B}^-$  by precipitating with  $\text{B}^-$  and vice versa
- precipitating agent is added slowly at agitation x local increase of concentration; formation of coarse precipitate with small surface
- allow to settle before filtration– less occlusion x less postprecipitation!
- thorough washing (hot water, electrolyte), colloids!! Too much soluble substances by alcohol

# Precipitation procedure

- 1) solution of substance to be precipitated is adjusted according to instruction (pH, temperature) and precipitated with clear solution of precipitating reagent
- 2) precipitation is carried out in 250-400 ml beakers, sample volume is adjusted to ca 100-200 ml
- 3) precipitation solution is added slowly from burette or pipette + stirring with glass rod
- 4) after the precipitate is settled the test for complete precipitation is performed

# Precipitation procedure

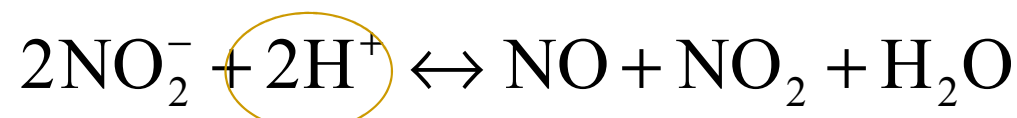
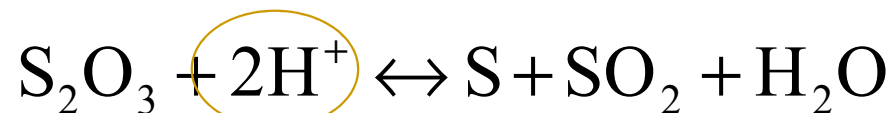
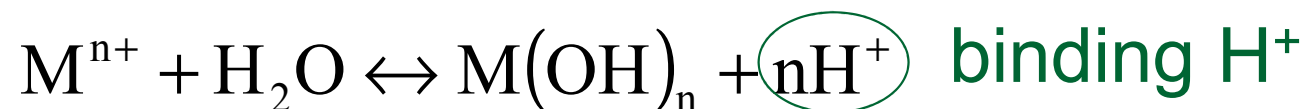
- Precipitating from homogeneous medium:
  - precipitatin reagent occurs gradually and continuously by chemical reaction
  - decomposition, hydrolysis
  - example: precipitation of sulfides by thioacetamide (at hot, hydrolysis)



sulfide precipitates better coagulate and less adsorb

# Precipitation procedure

- example: precipitation of hydroxides ( $M^{3+}$ ,  $M^{4+}$ )  
separation from  $M^{2+}$





# Filtration

- rate of filtration

$$v = \frac{dV}{dt} = k \frac{P \cdot r^2 \cdot (p_1 - p_2)}{l \cdot \eta}$$

P – filtration area

r – pore radius

$p_1 - p_2$  hydrostatic pressure difference between both sides of filtration medium

l – effective length of capillaries

$\eta$  – dynamic viscosity

V – capillary volume

t – time

- filtration acceleration:

- increase P (folded filter, frit)  $p_1 - p_2$  (exhausting, longer filter funnel stem)

- decreased  $\eta$  (by warming)

# Filtration

- besides mechanical effect influenced by:
  - hydration
  - adhesion
  - adsorption
  - elektrokinetic effect
  - character of filtered substance
  
- **hydration** – swelling of lyophilic filtration material  
→ filtration retardation (retained even smaller particles)
  
- **adhesion** – liquid in capillaries flows slower along capillary walls

# Filtration

- ❑ **adsorption** – precipitate particles adhere on capillary walls
- ❑ **elektrokinetic efekct** – potential difference between capillary wall and liquid →
  - negative charge of filtr. paper retains cations and positively charged particles of the precipitate
  - paper retains negative particles after washing with HCl
- ❑ **character of filtered substance** – it creates another filtration layer – different capillarity
  - Gels – filter clogging, therefore larger filter porosity is required and filtration with exhausting is necessary ( $p_1-p_2$ )

# Filtration

- quantitative paper filters (ash-free) pure cellulose, 0,01 mg of ash
- Different colour codes
  - „red ribbon“ – medium fast filtration (amorphous  $\text{Fe}_2\text{O}_3$ )
  - „yellow ribbon“ (colloides, sulfides)
  - „green ribbon“ – slow filtration, fine precipitates
  - „blue ribbon“ – slow filtration, very fine crystalline precipitate,  $\text{BaSO}_4$
  - „black ribbon“ - fast filtration, coarse precipitates
  - „white ribbon“ – medium fast filtration, standard filter for many applications

# Filtration

- > 10% solutions of acids or bases damages paper filters
- paper filters can not be used for filtration of substances that are reduced at ashing
- filtration crucibles
  - crystalline precipitates
  - glass crucibles – only drying (to 200°C)
  - porcelain crucibles – ignition (to 1200°C)

# Washing of precipitate

- removal of residues of parent solution – **decantation** is efficient – washing in beaker after precipitation
  - using smaller volumes more times

$$c_n = c \cdot \left( \frac{V_1}{V_1 + V_2} \right)^n$$

$V_1$  – filtrate volume retained by precipitate

$V_2$  – washing volume

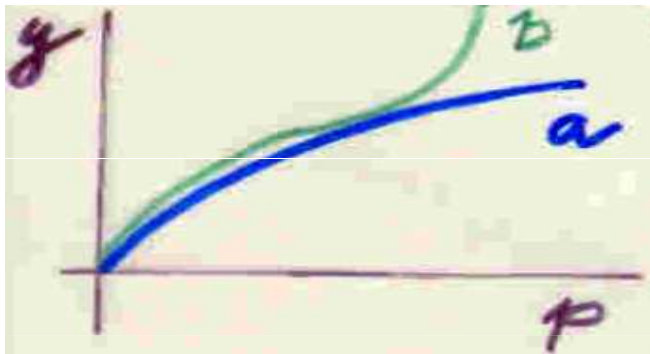
$c_n$  – concentration of third ions after n-times washing

# Washing of precipitate

- precipitate – ionex – it is necessary to substitute third ions by adsorption of ions of a washing solution electrolyte
- crystalline precipitates – washing by solution of salt with common ion with precipitate
- colloidal precipitates – washing by solution of electrolyte protecting from peptisation
- ammonium salts – easily removable by ignition
- water at last, alcohol for more soluble precipitates

# Drying

- a) drying in open atmosphere
- removal of excess moisture until equilibrium with the pressure of water vapor in the air at a given temperature
  - Freundlich adsorption isotherm  $y = a \cdot x^b$  – monomolecular layer of water



a) non-hygroscopic substances

b) hygroscopic substance

(more layers of H<sub>2</sub>O)

ad b) can not be dried in open atmosphere → it is necessary to decrease ambient pressure and increase temp.; vacuum drying

- Water vapor pressure of surface bound water is lower nižší, therefore 105-110°C is needed



# Drying

- b) in dessicator – dessicants

- chemically ( $P_2O_5$ )
- By adsorption (silik.)

mg/l  $H_2O$  in vapor

$P_2O_5$

$2 \cdot 10^{-5}$

$Mg(ClO_4)_2$

$5 \cdot 10^{-4}$  (anhydron) – for elemental analysis

BaO

$7 \cdot 10^{-4}$

KOH

$2 \cdot 10^{-3}$

silica gel

$3 \cdot 10^{-2}$  – retains water vapor up to 40 % of its mass

addition of  $CoCl_2$  – anhydrous blue → wet pink,  
regeneration 180-200°C

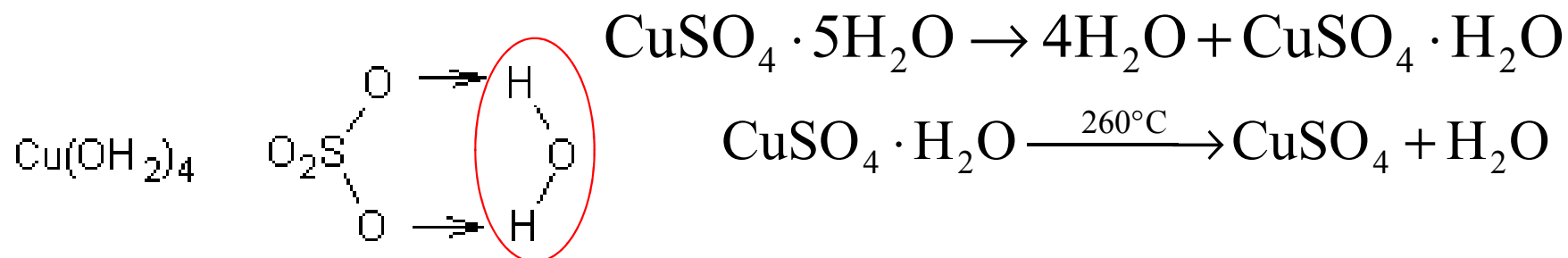
# Drying

- ❑ molecular sieves – silicates Al, Ca, K, Na
- ❑ gas adsorption
  - acid ( $\text{CO}_2$ ,  $\text{SO}_2$ )  $\approx$  CaO, KOH, NaOH
  - alkaline ( $\text{NH}_3$ )  $\approx$   $\text{P}_2\text{O}_5$ ,  $\text{H}_2\text{SO}_4$
- ❑ alcohol vapors  $\approx$   $\text{CaCl}_2$
- ❑ benzene, chloroform, ether  $\approx$  paraffin

# Drying

- c) at elevated temperature

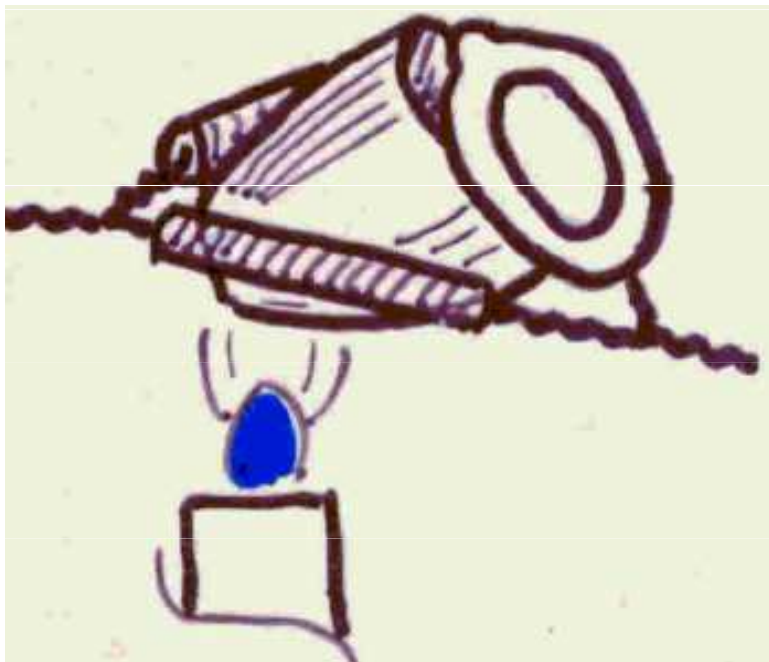
- dryer oven to 180°C, ± 5°C control, 105-110°C, also: loss of crystallization water



- volatilization:  $\text{NH}_3$ ,  $\text{CO}_2$ ,  $\text{SO}_2$ , ammonium salts at 150°C, volatile chlorides
- filtration paper can withstand 150°C
- drying to **constant weight**– if a precipitate is dried directly to the form suitable for weighing – repeat the drying and weighing until the weight change (0,2 mg)

# Ignition

- transfer of precipitate to ignited state
- porcelain crucible + triangle with ceramic rollers (Pt-crucible)



temperatures:

**Bunsen burner** - porcel. 700-800°C

- Pt 850-1000°C

**Teclu** + 100°C x Buns.

**Mecker** + 200°C x Buns.

# Principles and procedures of ignition

- 1) drying and ignition of empty crucible to constant weight slowly (non-luminous flame), tongs
- 2) filter into the crucible:
  - a) to dry at 70°C in drying oven or over burner
  - b) to incinerate (charring, air, no fire!!!)
- 3) ignition (500-1000°C) – burner, muffle furnace; after cooling down to 100-200°C → into dessicator; to constant weight ( $\pm 0,2$  mg)

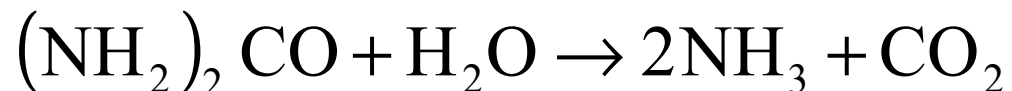
# Types of gravimetric determinations

- a) without precipitation reagent – salts ignition, heavy metal salts with anions of volatile acids ( $\text{NO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ )  $\rightarrow$   $\text{CuO}$ ,  $\text{ZnO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{Sb}_2\text{O}_3$ ,  $\text{SnO}_2$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ )
- b) addition of precip. reagent :  $\text{H}_2\text{S}$ ,  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{NH}_4\text{OH}$ ,  $\text{Na}_2\text{HPO}_4$ ,  $\text{AgNO}_3$ ,  $\text{BaCl}_2$  organic reagents : 8-hydroxyquinoline, anthranilic acid, oxalic acid

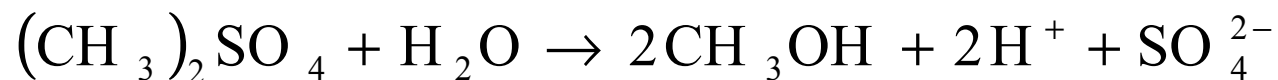
# Types of gravimetric determinations

## c) precipitation from homogeneous solution

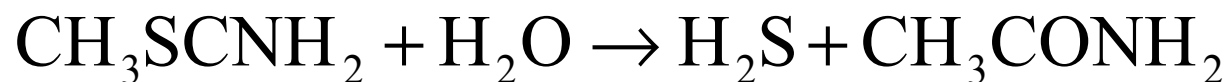
for precipitation of hydroxides (urea, carbonyldiamide, carbamide, diaminmethanal):



for precipitation of oxalates, phosphates and sulphates – hydrolysis of esters:



for precipitation of sulphides:



thioacetamide

acetamide

# Overview of gravimetric methods

ion	precipitating reagent	form: precipitated/weighted	temperature dry./ign. °C
Ag <sup>+</sup>	HCl	AgCl	130
Al <sup>3+</sup>	NH <sub>4</sub> OH 8-quinolinol	Al(OH) <sub>3</sub> / Al <sub>2</sub> O <sub>3</sub>	1000
		Al(C <sub>9</sub> H <sub>6</sub> ON) <sub>3</sub>	130
Ba <sup>2+</sup>	H <sub>2</sub> SO <sub>4</sub> (NH <sub>4</sub> ) <sub>2</sub> CrO <sub>4</sub>	BaSO <sub>4</sub>	700
		BaCrO <sub>4</sub>	550
Bi <sup>3+</sup>	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> 8-quinolinol	BiPO <sub>4</sub>	800
		Bi(C <sub>9</sub> H <sub>6</sub> ON) <sub>3</sub> ·H <sub>2</sub> O / Bi(C <sub>9</sub> H <sub>6</sub> ON) <sub>3</sub>	130
Ca <sup>2+</sup>	(NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	Ca C <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O	105
Cu <sup>2+</sup>	benzoin oxime	Cu(C <sub>14</sub> H <sub>11</sub> O <sub>2</sub> N)	110
Fe <sup>3+</sup>	NH <sub>4</sub> OH 8-quinolinol	Fe(OH) <sub>3</sub>	1000
		Fe(C <sub>9</sub> H <sub>6</sub> ON) <sub>3</sub>	120
Hg <sup>2+</sup>	H <sub>2</sub> S	HgS	110



# Overview of gravimetric methods

ion	precipitating reagent	form: precipitated/weighted	temperature dry./ign. °C
Mg <sup>2+</sup>	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	NH <sub>4</sub> MgPO <sub>4</sub> ·6H <sub>2</sub> O/Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	1100
Ni <sup>2+</sup>	2,3-butandion-dioxim	Ni(C <sub>4</sub> H <sub>7</sub> O <sub>2</sub> N <sub>2</sub> ) <sub>2</sub>	120
Pb <sup>2+</sup>	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> anthranilic acid	PbCrO <sub>4</sub>	140
		Pb(C <sub>7</sub> H <sub>6</sub> O <sub>2</sub> N) <sub>2</sub>	110
Zn <sup>2+</sup>	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> 8-quinolinol	NH <sub>4</sub> ZnPO <sub>4</sub> / Zn <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	900
		Zn(C <sub>9</sub> H <sub>6</sub> ON) <sub>2</sub> ·2H <sub>2</sub> O/Zn(C <sub>9</sub> H <sub>6</sub> ON) <sub>2</sub>	130
AsO <sub>4</sub> <sup>3-</sup>	MgCl <sub>2</sub> , NH <sub>4</sub> Cl	NH <sub>4</sub> MgAsO <sub>4</sub> ·6H <sub>2</sub> O/Mg <sub>2</sub> As <sub>2</sub> O <sub>7</sub>	900
Br <sup>-</sup> , Cl <sup>-</sup> , I <sup>-</sup>	AgNO <sub>3</sub>	AgCl, AgBr, AgI	130

# Overview of gravimetric methods

ion	precipitating reagent	form: precipitated/weighted	temperature dry./ign. °C
$\text{CrO}_4^{2-}$	$\text{BaCl}_2$	$\text{BaCrO}_4$	500
$\text{PO}_4^{3-}$	$\text{MgCl}_2, \text{NH}_4\text{Cl}$	$\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O} / \text{Mg}_2\text{P}_2\text{O}_7$	1100
$\text{SO}_4^{2-}$	$\text{BaCl}_2$	$\text{BaSO}_4$	700

# Calculation of gravimetric analysis

- **gravimetric factor**– what is  $\leq 1$ , the error is smaller
  - ex. **a** (g) sample  $\rightarrow$  **b** (g) AgCl, chlorides content is

$$x = \frac{A(\text{Cl})}{M(\text{AgCl})} \cdot b$$

# Calculation of gravimetric analysis

- indirect determination of  $K^+$  and  $Na^+$  - mixture of chlorides

KCl            NaCl

$x$     +     $y$     =  $a$      $\approx$  total mass of chlorides K, Na

$m \cdot x$  +  $n \cdot y$  =  $b$      $\approx$  total mass of chlorides in weighted AgCl

$$m = \frac{A_r(\text{Cl}^-)}{M_r(\text{KCl})} = 0,4756$$

$$n = \frac{A_r(\text{Cl}^-)}{M_r(\text{NaCl})} = 0,6066$$

$$\underline{x = \frac{1}{m - n} \cdot a - \frac{n}{m - n} \cdot b}$$

$$\underline{y = a - x}$$