



13th Practise: Chemical equilibrium. Mean ionic activity coefficient. Debye Hückel law.

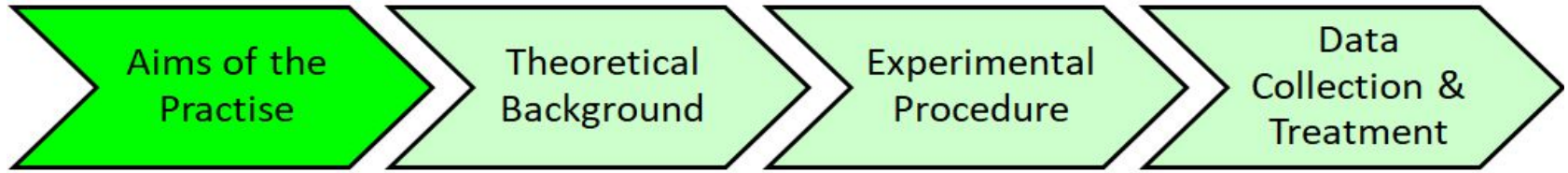
Degree in Chemistry 2nd grade,
Experimentation in Physical Chemistry

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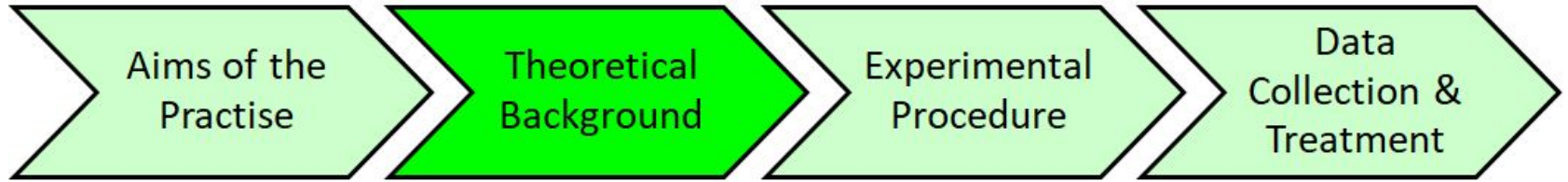
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1. Aims of the practise

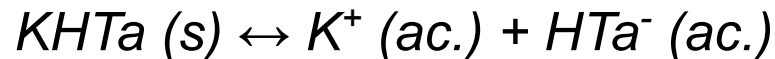


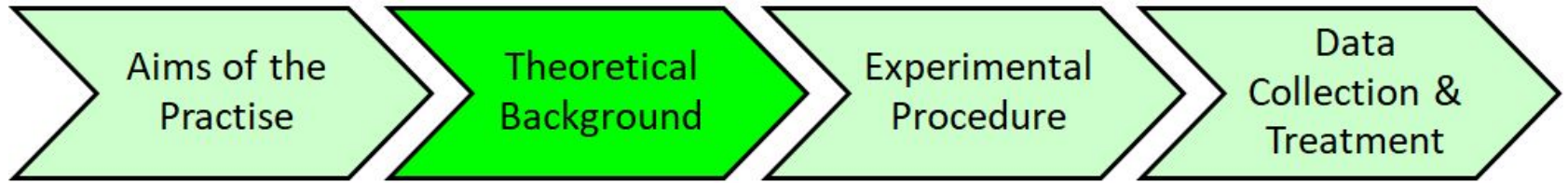
- Analyse the ionic medium's effect on the degree of dissociation of a weak electrolyte
- Prove the validity of the Debye-Hückel limiting law

2. Theoretical Background



- Electrolytes are solutes that can be dissolved in water
 - Dissociated completely → Strong electrolyte
 - Dissociated partially → Weak electrolyte
- Activity and concentration are different between them
- Potassium bitartrate (KHTa)
 - Weak electrolyte with small solubility
 - Dissociates giving potassium and bitartrate ions (K^+ and HTa^-)
 - HTa^- → Weak acid that dissociates in tartrate and hydrogen ions (ignored)





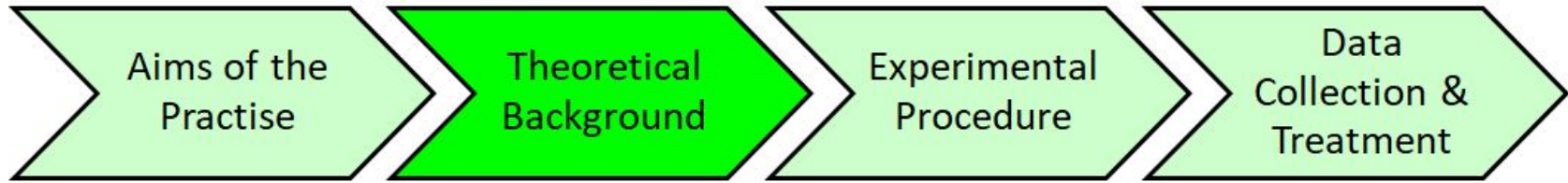
- The solubility product constant is equal to the ions' activity

$$K_{sp} = a_+^{(1)} \times a_-^{(1)} = a_{\pm}^2$$

- a_{\pm} : mean ionic activity
- $K_{sp} \rightarrow$ thermodynamic constant \rightarrow changed only with T
- γ_{\pm} : mean ionic activity coefficient

$$a_{\pm} = \gamma_{\pm} \times c_{\pm}$$

- c_{\pm} : mean ionic concentration



- In this case $\rightarrow c_{\pm} = s$ (salt's solubility)

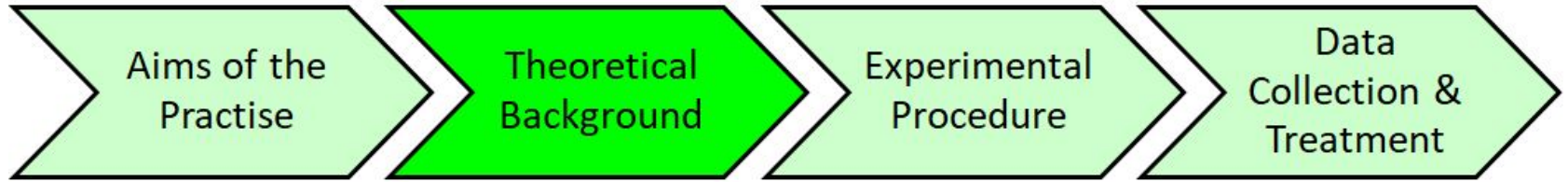
$$a_{K^+} = \gamma_{K^+} \times s \quad \text{and} \quad a_{HTa^-} = \gamma_{HTa^-} \times s$$

- Taking this into account to calculate K_{sp} :

$$K_{sp} = a_{K^+} \times a_{HTa^-} = \gamma_{K^+} \times \gamma_{HTa^-} \times s^2 = \gamma_{\pm}^2 \times s^2$$

- s can be changed after the effect of other salts
 - Lewis and Randall innovated measuring solubilities \rightarrow A linear dependency with I^2 has been observed ⁽¹⁾

(1): S.Glasstone, *An Introduction of Electrochemistry*, D.Van Nostrand Co., Inc. 1942, 175)

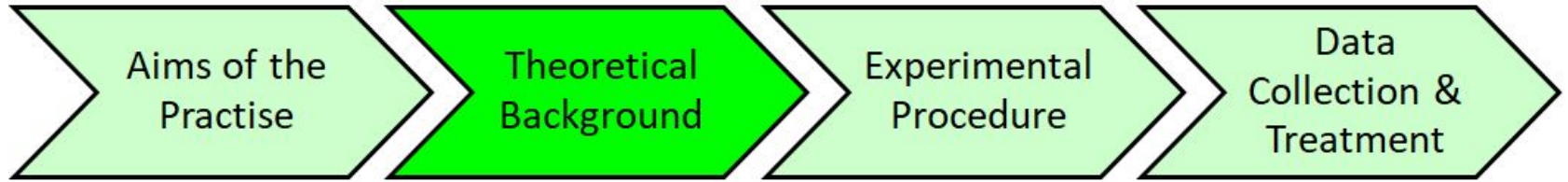


- I : Ionic strength

- The contribution of electrostatic forces from all the ions of the solution

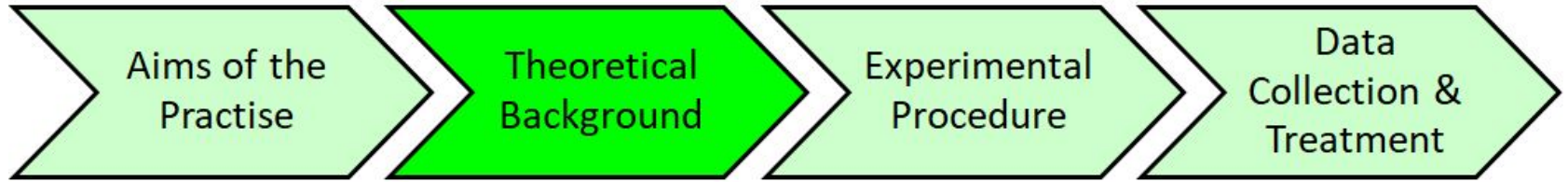
$$I = \frac{1}{2} \sum_i c_i Z_i^2$$

- c_i : concentration (mol/L)
- Z_i : electric charge of the ions



- If the solution is put in conditions where $I = 0 \rightarrow S_0$
 - S_0 : Solubility when there aren't interactions between ions
 - In this conditions $\rightarrow a=c \rightarrow \gamma=1$
 - So, knowing S_0 :

$$\gamma_{\pm} = \frac{S_0}{S}$$



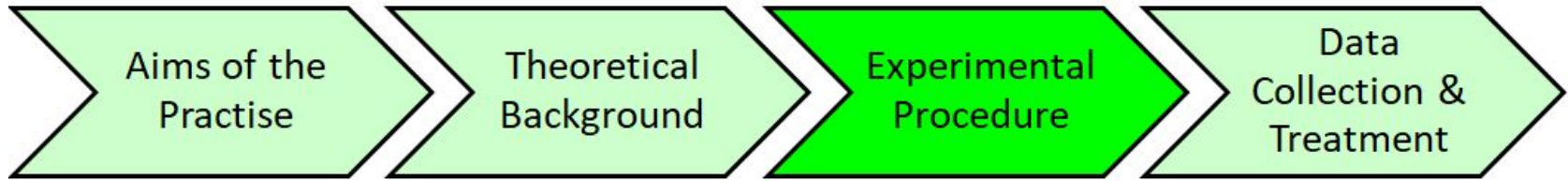
- γ_{\pm} is connected with $I \rightarrow$ When a solution is diluted ($m < 0,01$):

$$\log \gamma_{\pm} = -A \times z_{+} \times z_{-} \times \sqrt{I}$$

(Debye-Hückel limiting law)

- A : a constant depended by the temperature and dielectric constant of the medium (in water $T=25^{\circ}\text{C} \rightarrow 0,509$)
- z_{+} and z_{-} : positive/negative charge of the electrolyte

3. Experimental Procedure



1. Prepare these NaCl solutions:

a. 250mL 0,4M

i. 100mL 0,15M

ii. 100mL 0,10M

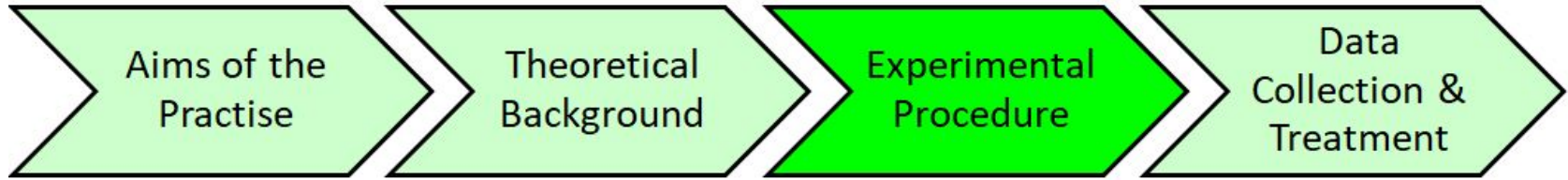
iii. 100mL 0,05M

iv. 100mL 0,04M

v. 100mL 0,02M

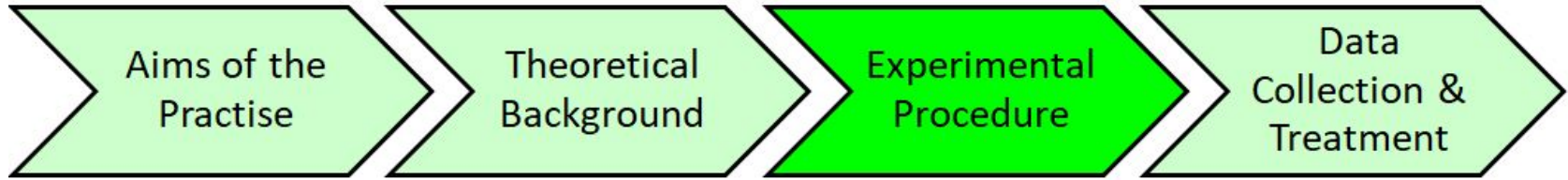
vi. 100mL 0,01M

(Label the concentration in each solution)



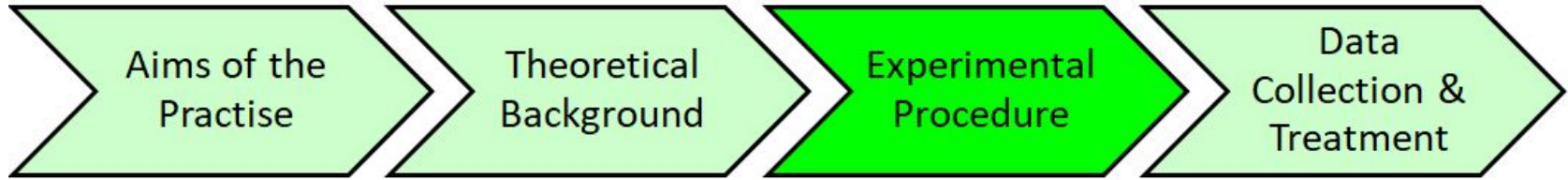
2.

- ❖ Put 50mL of each solution in 6 test tubes and label them properly (50mL water in the 7th tube)
- ❖ Add 0,5g KHTa in each tube
- ❖ Deposit the tubes in a 1L beaker with water and place it in a water bath for 20 minutes at 40°C (until the solutions are transparent)
- ❖ Leave the solutions to cool down 30 minutes so the solid can precipitate



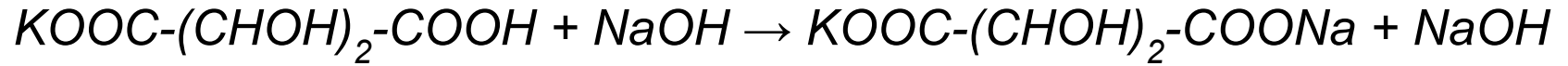
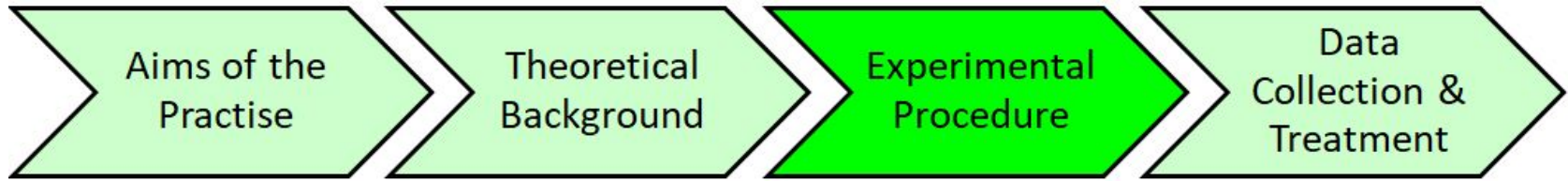
3.

- ❖ Prepare 250mL 5×10^{-2} M NaOH and 500mL 1×10^{-2} M HCl
- ❖ Normalise the solutions with phenolphthalein as an indicator



4.

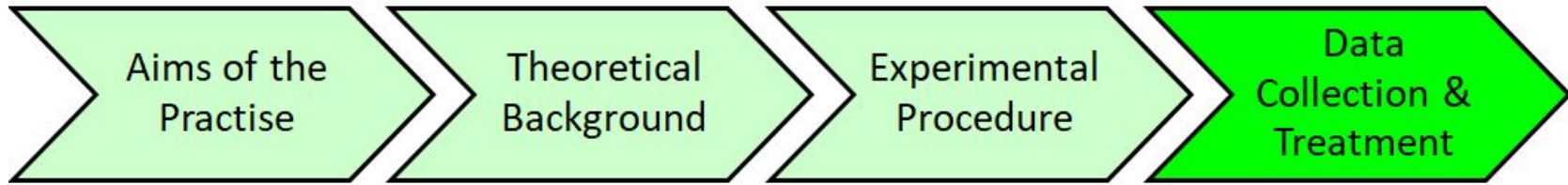
- ❖ Measure out 10mL of the solutions with a pipette (without any solid)
- ❖ Titrate the KHTa using back-titration
 - Pour 10mL KHTa to 10mL 5×10^{-2} M NaOH in a 100mL erlenmeyer flask
 - Titrate the remaining solid (NaOH) with 1×10^{-2} M HCl
 - Titrate the 7th tube with NaOH 5×10^{-2} M



$$10 \times 10^{-3} \times 5 \times 10^{-2} = 10 \times 10^{-3} \times s + V_{HCl} \times 10^{-2}$$

- s : [KHTa]
- V_{HCl} : The V of HCl used to neutralise the NaOh excess

4. Data Collection and Treatment



- Calculate s with the last equation and do a table with the values of V_{HCl} , c_1 , s , l and \sqrt{l}
- Observe the tartrate's solubility change in presence of NaCl at different concentrations (s_{KHTa} vs $[NaCl]$)
- Calculate S_0 for KHTa
- Calculate γ_{\pm} of all the solutions using S_0
- Calculate K_{sp} and compare it with the values of the books



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