Applied thermodynamics of solutions

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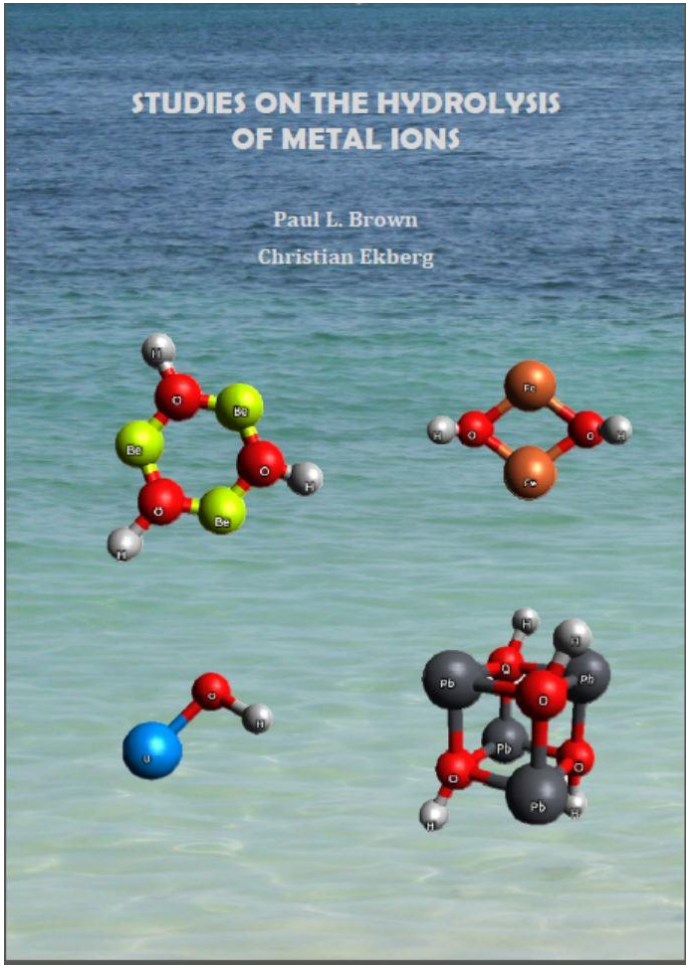
Commercial


STUDIES ON THE HYDROLYSIS
OF METAL IONS
Paul L. Brown
Christian Ekberg

Outline

Basic complexations chemistry

Determination of stability constants

Uncertainties in stability constants

Chemical activity coefficients

Example using BaOH formation

Eaxmple using pH measurements

Basic complex formation reactions

$$Th^{4+} + OH^- \Leftrightarrow ThOH^{3+} \qquad \beta_1^{'} = \frac{\left[ThOH^{3+}\right]}{\left[Th^{4+}\right]\left[OH^-\right]}$$

$$Th^{4+} + 2OH^- \Leftrightarrow Th(OH)_2^{2+} \qquad \beta_2^{'} = \frac{\left[Th(OH)_2^{2+}\right]}{\left[Th^{4+}\right]\left[OH^-\right]^2}$$

$$Th^{4+} + 3OH^- \Leftrightarrow Th(OH)_3^{+} \qquad \beta_2^{'} = \frac{\left[Th(OH)_3^{+}\right]}{\left[Th^{4+}\right]\left[OH^-\right]^3}$$

$$Th^{4+} + 4OH^- \Leftrightarrow Th(OH)_4 \qquad \beta_2^{'} = \frac{\left[Th(OH)_4\right]}{\left[Th^{4+}\right]\left[OH^-\right]^4}$$

$$Th(OH)_4(s) \Leftrightarrow Th^{4+} + 4OH^- \qquad Ks = \left[Th^{4+}\right]\left[OH^-\right]^4$$

Determination of stability constants

1. Several methods for determining stability constants exists

2. They all have different pros and cons but also different validity regions

3. In principle it is possible to apriori select the optimal method using a fishbone structure for uncertainty analysis.

4. The impact of uncertainties in hydrolysis constants have an important effect on speciation diagrams.

Determination of stability constants

- Potentiometric titrations
- Solubility
- Ion exchange
- Spectrophotometry
- Solvent extraction

Potentiometric titrations

Rationale:

As hydrolysis progresses, hydrogen ions are released. By titrating the solution with and without metal, the difference in the hydrogen ion concentration at different hydroxide additions permits calculation of the hydrolysis constants by fitting.

Pros

Rather sensitive
Simple to perform
Cheap instrumentation
Indication of ratios e.g. using Bjerrum's method

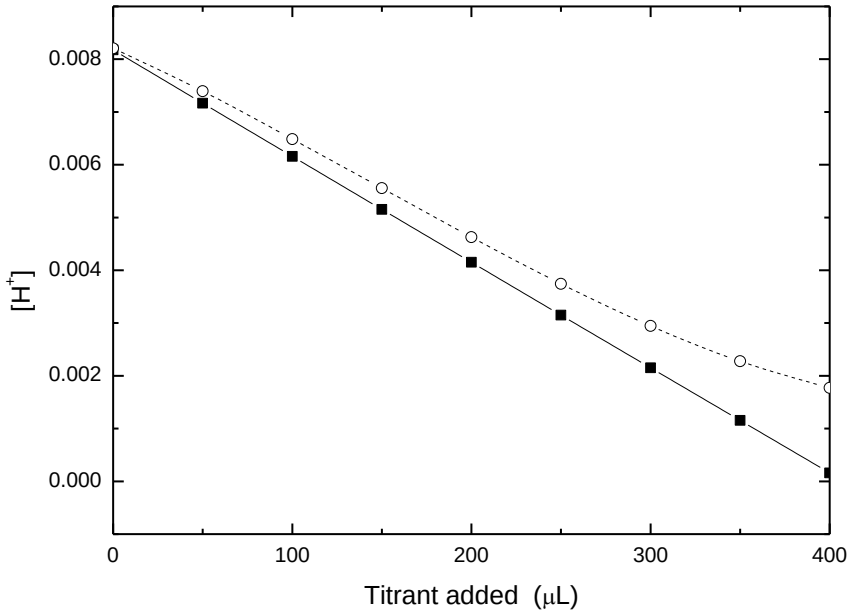
Cons

Difficult for highly hydrolyzing metals
Only the first couple of constants obtainable using simple methodologies
Sensitive to model input
No identification of species
High metal concentrations may be needed

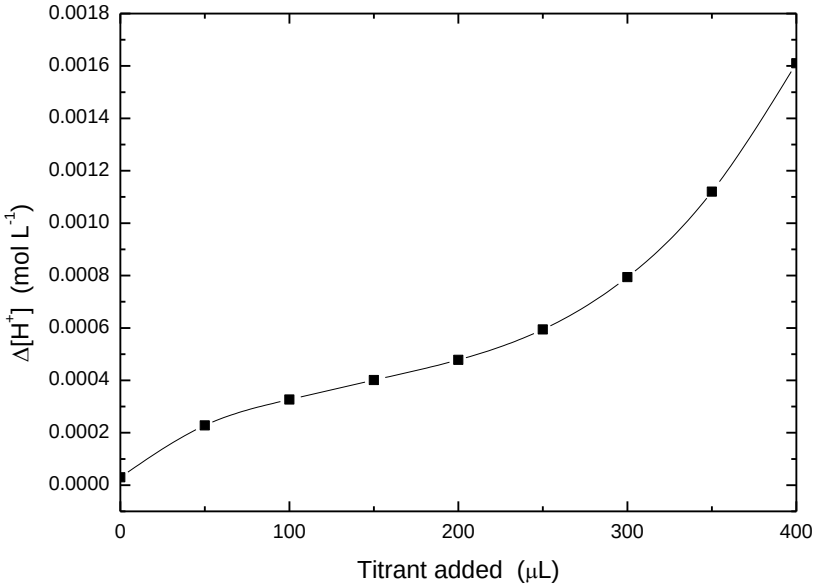
Potentiometric titrations

$$[H^+] = [H^+]_0 - [OH^-]_{tit} + [MOH^{z-1}] + 2[M(OH)_2^{z-2}] + \ldots$$

$$[H^+] - \left([H^+]_0 - [OH^-]_{tit}\right) = \beta_1[M^{z+}][OH^-] + 2\beta_2[M^{z+}][OH^-]^2 + \ldots$$



The hydrogen concentration of a solution in absence of metal (squares) and the hydrogen ion concentration in the presence of metal (rings) plotted against the amount of titrant added.



The difference between the free hydrogen ion concentration in a titrated solution without metal and the free hydrogen ion concentration in a solution containing metal as a function of titrant added

Solubility

Rationale:
The total dissolved metal concentration is measured as a function of hydrogen ion concentration. The set of hydrolysis constants are then fitted to the solubility curve.

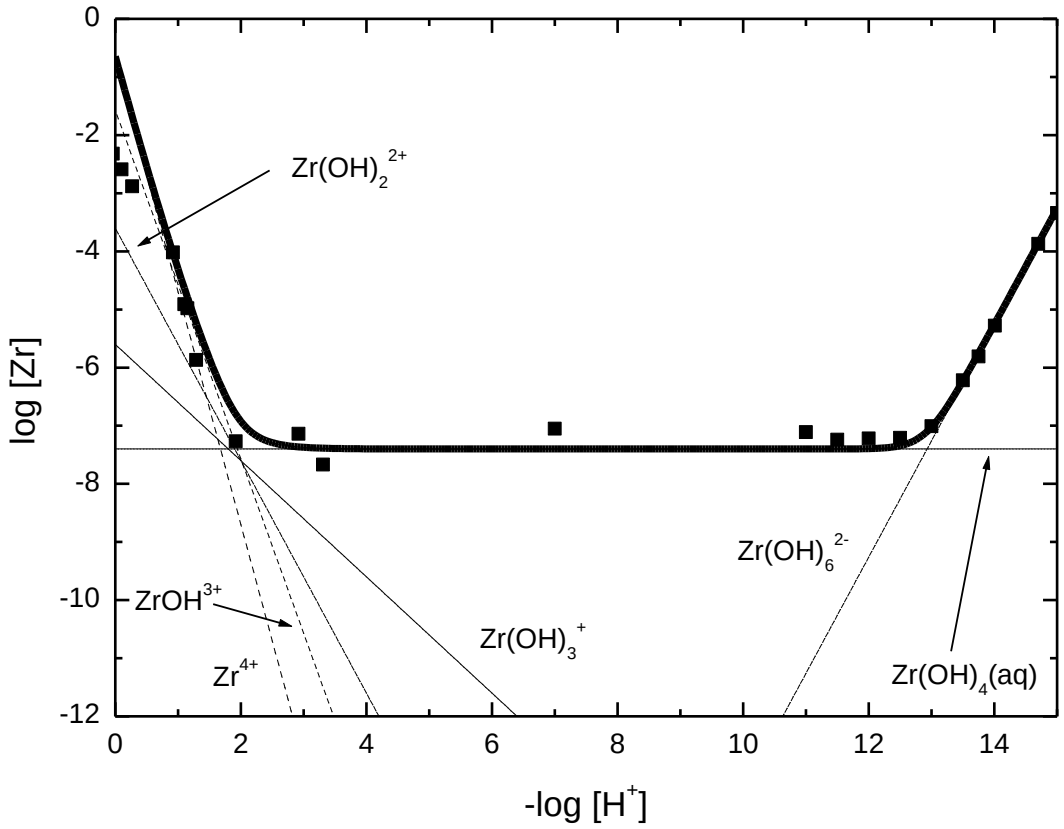
Pros	**Cons**
Simple to perform	Imprecise
Solubility slope gives and indication of the dominating species	Sensitive to model input
	No identification of species

Solubility

$$[M]_{tot} = [M] + \sum_q [M(OH)_q] + \sum_r [ML_r] + \ldots\ldots$$

$$*K_{s10} = [M^{z+}] / [H^+]^z$$

$$[M]_{tot} = \frac{K_{s10}}{[OH^-]^z}\left(1 + \sum_q \beta_q [OH]^q\right)$$



Ion exchange

Rationale:
The distribution between an aqueous solution and an ion exchange resin is measured as a function of hydrogen ion concentration. Constants obtained by fitting.

Pros
Simple to perform using radioactivity
All constants may be obtained

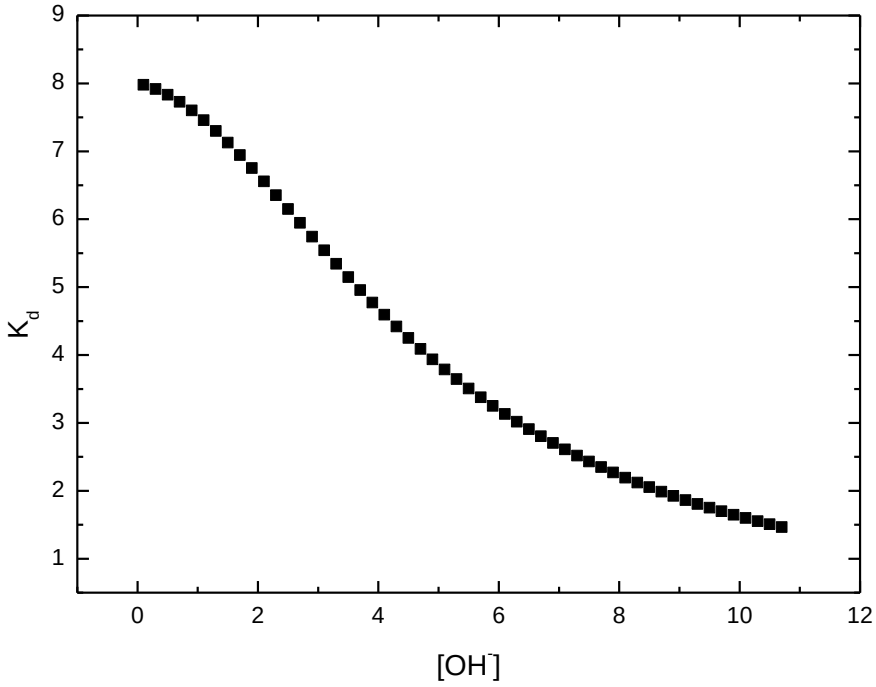
Cons
Distribution can be tricky to obtain
Radioactive tracers are preferred
Many parameters to fit
Sensitive to model input
No identification of species

Ion exchange

$$\mathrm{M}^{\nu+}(aq) \leftrightarrow \mathrm{M}^{\nu+}(ex) \qquad \mathrm{k}_{\nu} = \frac{\left\{\mathrm{M}^{\nu+}(ex)\right\}}{\left\{\mathrm{M}^{\nu+}(aq)\right\}}$$

$$D = \frac{\left\{M^{\nu+}(ex)\right\} + \left\{MOH^{\nu-1}(ex)\right\} + ..}{\left\{M^{\nu+}(ex)\right\} + \left\{MOH^{\nu-1}(ex)\right\} + ..}$$

$$D = \frac{k_{\nu}\left\{M^{\nu+}(aq)\right\} + k_{\nu-1}\left\{MOH^{\nu-1}(aq)\right\} + ...}{\left\{M^{\nu+}(aq)\right\} + \left\{MOH^{\nu-1}(aq)\right\} + ...}$$



Spectrophotometry

Rationale:
The shift in a spectrum is measured as a function of hydrogen ion concentration.
Constants obtained by fitting.

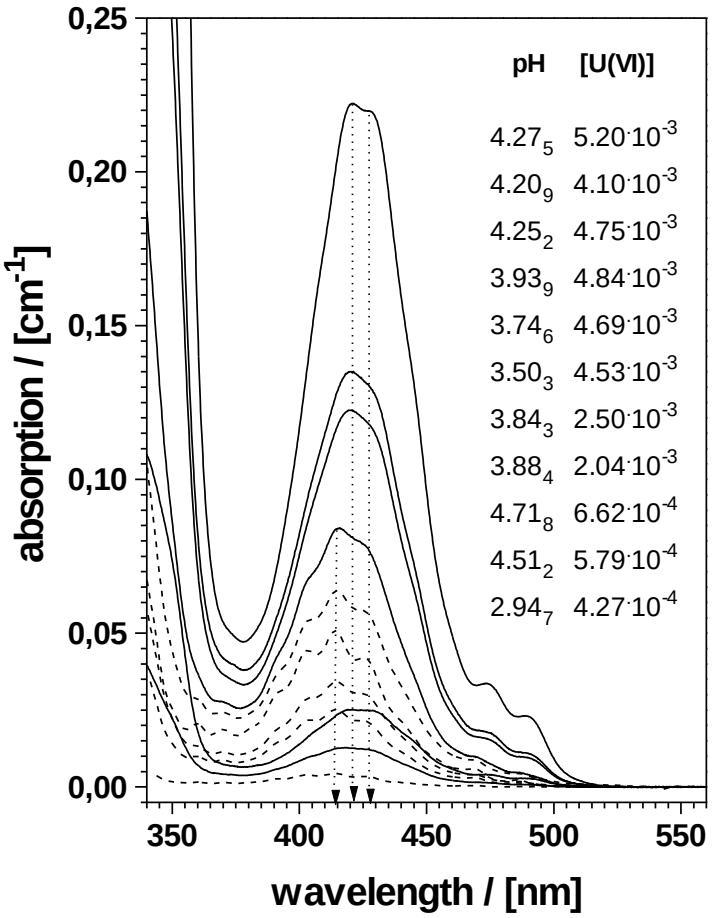
Pros
Possible identification of species
All constants may be obtained
Shifts may be pre-calculated

Cons
Slightly tricky to perform
High metal concentration needed

Spectrophotometry

$A = \varepsilon c l$

$\%A = 100\ A/A_0$



Solvent extraction

Rationale:
The distribution between an aqueous and organic solution is measured as a function of hydrogen ion concentration. Constants obtained by fitting.

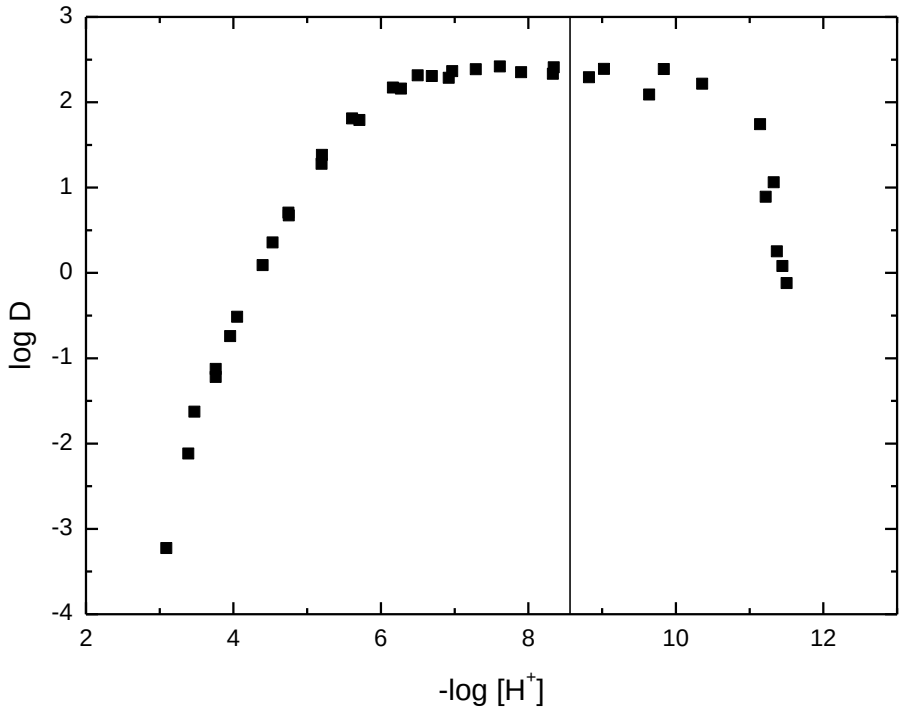
Pros
Simple to perform using radioactivity
Indication of dominating species from slope
All constants may be obtained

Cons
Distribution can be tricky to obtain
Radioactive tracers are preferred
Sensitive to model input
No identification of species

Solvent extraction

$$D = \frac{[M]_{T(org)}}{[M]_{T(aq)}} = \frac{\text{Total concentration of metal in the organic phase}}{\text{Total concentration of metal in the aqueous phase}}$$

$$D = \frac{[MA]_{org}}{[M] + \sum_i [MA_i] + \sum_j [MY_j]} = \frac{\lambda_z \beta_{z,A} [A]^z}{1 + \sum_i \beta_{i,A} [A]^i + \sum_j \beta_{j,Y} [Y]^j}$$



Multiple Methodologies

Rationale:
Allows the pros of the different methodologies to be combined. The cons of certain methods can be eliminated by using another methodology.

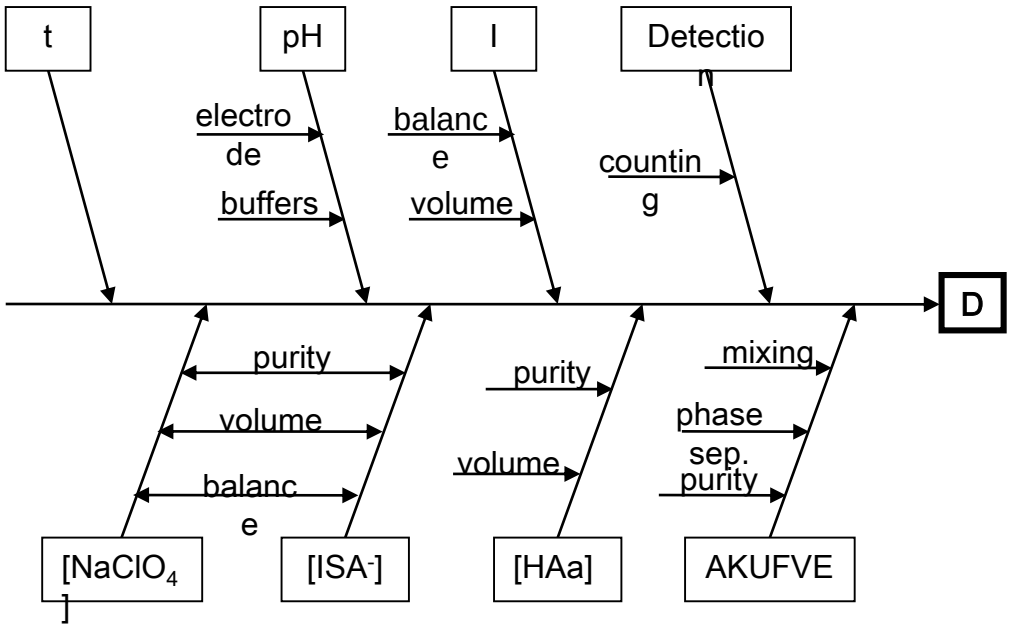
Pros
Different methods can be used to identify different species
Multiple methods can decrease uncertainty in constants
All constants may be obtained by careful selection of methodologies

Cons
Few methodologies identify species leading to uncertainty
Large amount of data is needed to adequately define all species
May still be sensitive to model input

Uncertainty analysis

Fishbone structure:

Allows the user to identify the contributors to the uncertainty. It also helps future reader to reevaluate the uncertainty in the experiment.



Contributor	Description	Uncertainty
t		< 0.5 %
pH	Electrode, buffers	Negligible
I	Balance, volume	Negligible
$[NaClO_4]$	Purity, volume, balance	< 1 %
[HAa]	Purity, volume	< 1 %
$[ISA^-]$	Purity, volume, balance	< 1 %
AKUFVE	Mixing, phase separation Sample volume	< 1 % each Negligible
Detection	Counting	< 1 %

Uncertainty analysis

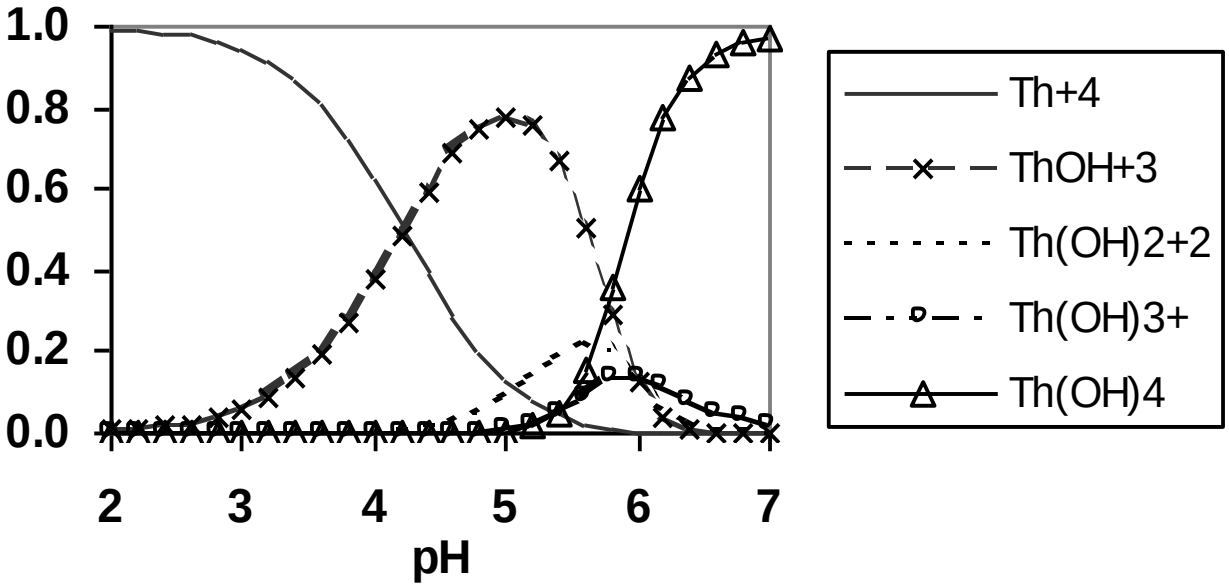
Statistical methods:

Several different ones exist. A simple one called the Chi-square method is recommended

How to do:

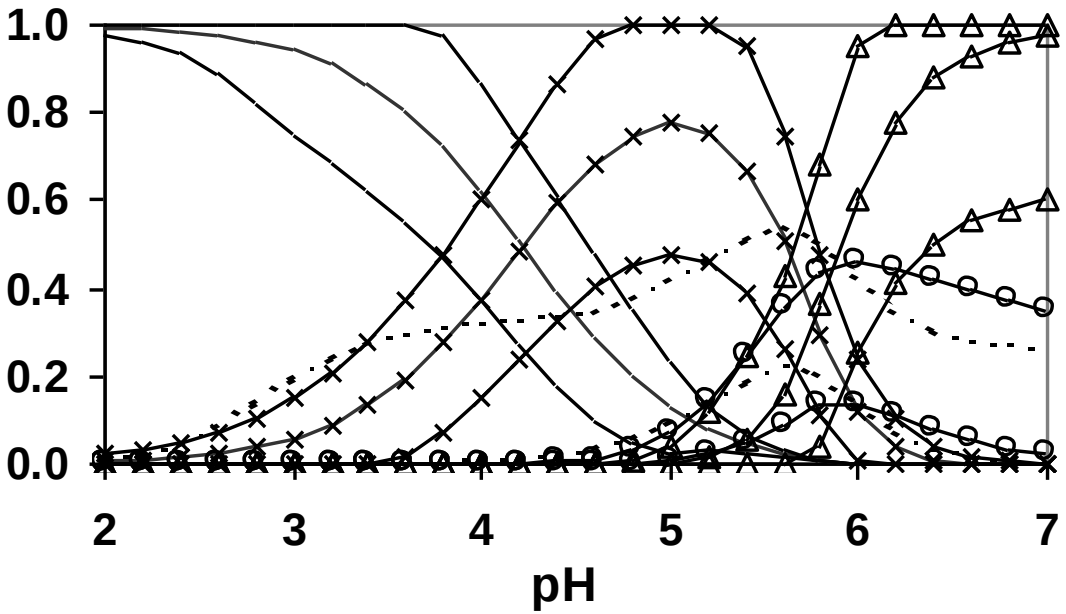
1. Fit your parameters using e.g. the sum of least squares as the minimization function
2. Change one of them up so the sum of least squares increase by 1.41 (SQRT(2)
3. Change the same one down until the sum of least squares increase by 1.41
4. Repeat for all fitted parameters
5. Now one standard deviation is obtained for each fitted

Uncertainty analysis



Species	$\log(\beta^*)$
$ThOH^{3+}$	-3.3±0.2
$Th(OH)_2^{2+}$	-8.6±0.1
$Th(OH)_3^{+}$	-14.3[a]
$Th(OH)_4$	-19.4±0.5

Uncertainty analysis



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$Th(OH)_3^{+}$	-14.3[a]
$Th(OH)_4$	-19.4±0.5

Activity coefficients: introduction

It is important to **keep ionic strength constant** when determining stability constant.

$$I = 0.5 \cdot \sum_{1}^{n} c_i \cdot z_i^2$$

Background inert electrolyte is usually used ($NaClO_4$, NaCl etc)

Stability constants are usually determined at specific ionic strengths, it means that determined constant is valid only for specific ionic strengths and only for specific electrolyte.

Why?

Activity coefficients: introduction

Strong electrolyte – substance which exists in solution only as free ions (completely dissociated)
Weak electrolyte – substance which exist in solution both in ionic (as free ions) and molecular forms (partly dissociated)

In *ideal solutions* ions and molecules are assumed as point particles (without size, shape etc).
In real solutions particles have size, volume, charge etc and move in solutions. In case of neutral species Van der Waals and dipole-dipole interactions becomes important in concentrated solutions (no chemical bond is formed). Ions can be attracted to each other or repulsed due to electrostatic Coulomb forces *even in dilute solutions* (long-range interactions).

Activity coefficients: definition

To be able to use equations and laws for ideal solutions for description of real thermodynamic system properties we need to include long-range electrostatic interactions. This can be done by introducing *activities* and *activity coefficients*:

$$A = c \cdot \gamma$$

Thus we can describe chemical equilibrium of real thermodynamic systems using activities instead of concentrations:

$$Na^+ + SO_4^{2-} \rightarrow NaSO_4^-$$

$$K_{NaSO_4^-} = \frac{A_{NaSO_4^-}}{A_{Na^+} \cdot A_{SO_4^{2-}}} = \frac{c_{NaSO_4^-} \cdot \gamma_{NaSO_4^-}}{c_{Na^+} \cdot \gamma_{Na^+} \cdot c_{SO_4^{2-}} \cdot \gamma_{SO_4^{2-}}}$$

Experimental determination of activity coefficients

Practically it is impossible to determine activity coefficient of an ion, but activity coefficients of solute and solvent depend on each other. Thus, it is possible to measure change of solvent activity (at different concentrations and with or without solute) and derive mean activity coefficient of solute.

1. Vapor pressure decrease (measurements of vapor pressure of pure solvent and with solute)
2. Boiling point increase (measurements of boiling point of pure solvent and with solute)
3. Freezing point decrease (measurements of freezing point of pure solvent and with solute)
4. Osmotic pressure measurements (osmotic pressure of real solution is higher than osmotic pressure of ideal solution, this pressure difference can be measured. Thus osmotic coefficient has the same meaning as activity coefficient - deviation from ideality. Activity coefficient can be calculate from osmotic coefficient and vice versa using Gibbs-Duhem equation)
5. EMF measurements (lead to experimental values of mean activity coefficient)
6. Solubility measurements (Measurements of solubility of sparingly soluble salts in dilute solutions when activity coefficients are almost 1 and in concentrated solutions)

Expressions for activity coefficients

Law	Equation	Applicability, Ionic strengths, M
Debye - Hückel	$\log(\gamma_i) = -A \cdot z_i^2 \cdot \sqrt{I}$	~0,001
Extended Debye - Hückel	$\log(\gamma_i) = -\frac{A \cdot z_i^2 \cdot \sqrt{I}}{1 + B \cdot a \cdot \sqrt{I}}$	~0,1
Davies	$\log(\gamma_i) = -\frac{A \cdot z_i^2 \cdot \sqrt{I}}{1 + B \cdot a \cdot \sqrt{I}} - 0.2 \cdot I$	~0,3

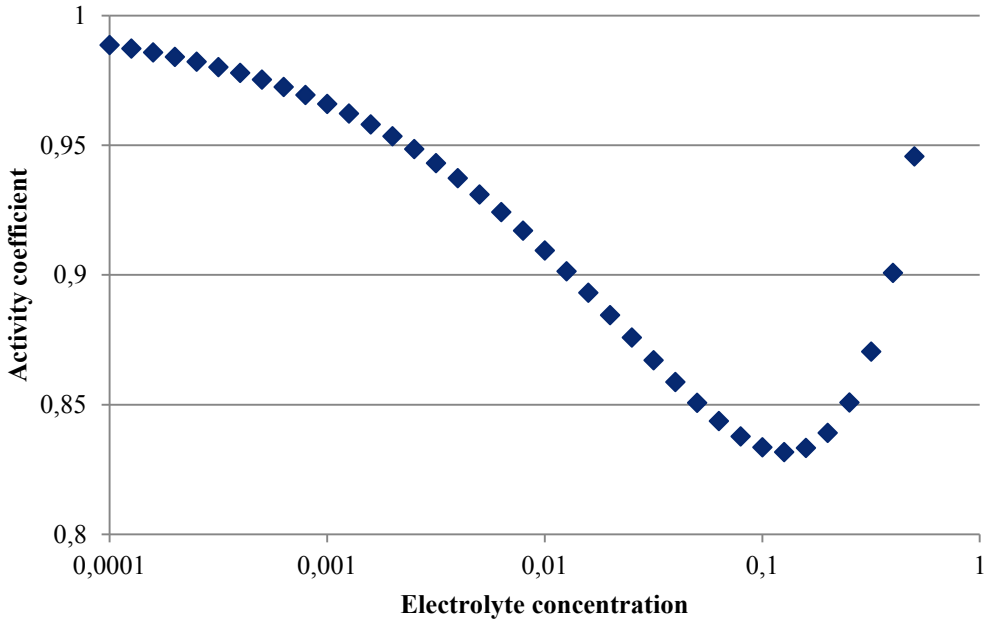
A and B are temperature/pressure dependent constants
a is “distance of closest approach” . Normally at 25 deg C we use A = 0.5085 and B = 0.3281. Often the term Ba = 1.5

$$a \geq r_+ + r_-$$

Stumm, W., & Morgan, J. J. (2012). *Aquatic chemistry: chemical equilibria and rates in natural waters* (Vol. 126). John Wiley & Sons.

Expressions for activity coefficients

The long range interactions described by the Davies equations will affect the activity coefficient like this:



The Davies equations does not take the specific shorter range interactions into account so further corrections have to be made

Stumm, W., & Morgan, J. J. (2012). *Aquatic chemistry: chemica equilibria and rates in natural waters* (Vol. 126). John Wiley & Sons.

Specific Ion Interaction Theory (SIT)

$$\log(\gamma_i) = -\frac{A \cdot z_i^2 \cdot \sqrt{I}}{1 + B \cdot a \cdot \sqrt{I}} + \sum \varepsilon(i-k) \cdot I$$

Where ε is interaction coefficient between two ions of opposite charge.
Let's take the following reaction in 1M NaCl media:

$$Na^+ + SO_4^{2-} \rightarrow NaSO_4^-$$

Stability constant for this reaction at *constant ionic strengths*:

$$K_{NaSO_4^-} = \frac{c_{NaSO_4^-} \cdot \gamma_{NaSO_4^-}}{c_{Na^+} \cdot \gamma_{Na^+} \cdot c_{SO_4^{2-}} \cdot \gamma_{SO_4^{2-}}} = K^0_{NaSO_4^-} \cdot \frac{\gamma_{NaSO_4^-}}{\gamma_{Na^+} \cdot \gamma_{SO_4^{2-}}}$$

$$\log(K_{NaSO_4^-}) = \log(K^0_{NaSO_4^-}) + \log(\gamma_{NaSO_4^-}) - \log(\gamma_{Na^+}) - \log(\gamma_{SO_4^{2-}})$$

$$\log(K_{NaSO_4^-}) = \log(K^0_{NaSO_4^-}) + \frac{4 \cdot A \cdot \sqrt{I}}{1 + B \cdot a \cdot \sqrt{I}} + (\varepsilon_{NaSO_4^- - Na^+} - \varepsilon_{Na^+ - Cl^-} - \varepsilon_{SO_4^{2-} - Na^+}) \cdot I$$

Extended Specific Ion Interaction Theory

$$\log(\gamma_i) = -\frac{A \cdot z_i^2 \cdot \sqrt{I}}{1 + B \cdot a \cdot \sqrt{I}} + \sum \varepsilon(i-k) \cdot I$$

$-\frac{A \cdot z_i^2 \cdot \sqrt{I}}{1 + B \cdot a \cdot \sqrt{I}}$ - Debye Hückel term

$$\varepsilon = \varepsilon_1 + \varepsilon_2 \cdot \log(I)$$

In this model second ion interaction coefficient is added. This makes possible to describe thermodynamic systems at higher temperatures and ionic strengths.
However, according to this equation:

$$\varepsilon \to -\infty \quad \text{when} \quad I \to 0$$

Grenthe, I., & Wanner, H. (2000). Guidelines for the extrapolation to zero ionic strength.

Pitzer formalism

$$\ln(\gamma_{\pm}) = 4 \cdot f^{\varphi} + m \cdot B^{\phi}_{MX} + m^2 \cdot C^{\phi}_{MX}$$

Can be compared with equation for real gasses:

$$p \cdot V = R \cdot T + p \cdot B + \cdot p \cdot C^2 ...$$

$$f^{\varphi} = -A_{\varphi} \cdot \left(\frac{\sqrt{I}}{1 + b \cdot \sqrt{I}} + \frac{2}{b} \cdot \ln(1 + b \cdot \sqrt{I}) \right)$$ - Debye Hückel term

$$B = 2 \cdot \beta^0 + \frac{2 \cdot \beta^1}{\alpha_1^2 \cdot I} \cdot \left(1 - \exp(-\alpha_1 \cdot \sqrt{I})(1 + \alpha_1 \cdot \sqrt{I} - 0.5 \cdot \alpha_1^2 \cdot I \right)$$

K. S. Pitzer, Thermodynamics 3rd ed., McGraw-Hill, New York, 1995
Pitzer, K. S. (1991). *Activity coefficients in electrolyte solutions*. CRC press.

Determination of weak complex formation

$$Na^+ + SO_4^{2-} \rightarrow NaSO_4^-$$

Stability constant for this reaction at *constant ionic strengths*:

$$\log(K_{NaSO_4^-}) = \log(K^0_{NaSO_4^-}) + \frac{4 \cdot A \cdot \sqrt{I}}{1 + B \cdot a \cdot \sqrt{I}} + (\varepsilon_{NaSO_4^- - Na^+} - \varepsilon_{Na^+ - Cl^-} - \varepsilon_{SO_4^{2-} - Na^+}) \cdot I$$

This equation is valid if ionic strengths was kept constant (background inert electrolyte NaCl, NaClO4), only in this case activity coefficients or long range electrostatic interactions are constant.

In case of weak complex formation it is necessary to introduce large quantities of ligand (2 mole/L) and thus, substitute more than 10% of background electrolyte. It means that it is necessary to separate two effects: weak complex formation (short range) and activity coefficient change (long range).

Direct methods for weak complex formation determination

- Direct experimental determination of activity coefficients (vapor pressure, boiling point, freezing point, osmotic coefficient, emf, solubility)
- Conductivity measurements of electrolyte solutions (change in conductivity due to neutral species formation)
- Spectroscopic measurements: UV, IR, Raman, NMR (additional lines in spectrum can indicate complex formation)
- Relaxation methods (direct relaxation spectroscopy)

Marcus, Y., & Hefter, G. (2006). Ion pairing. *Chemical reviews*, *106*(11), 4585-4621.

Barium hydrolysis: ion interaction model

- $Ba^{2+} + 2 \cdot NaR^{solid} \rightarrow BaR_2^{solid} + 2 \cdot Na$

$$[BaR_2]_{solid} = \frac{\lambda \cdot [Ba^{2+}] \cdot \gamma_{[Ba^{2+}]}}{\gamma^2_{[Na^+]}}$$

$$D = \frac{[BaR_2]_{solid}}{[Ba^{2+}]} = \frac{\lambda \cdot [Ba^{2+}] \cdot \gamma_{[Ba^{2+}]}}{\gamma^2_{[Na^+]}} \cdot \frac{1}{[Ba^{2+}]} = \frac{\lambda \cdot \gamma_{[Ba^{2+}]}}{\gamma^2_{[Na^+]}}$$

$$\lg \gamma_{Na^+} = -DH + \varepsilon_{Na-OH} \cdot [OH^-] + \varepsilon_{Na-ClO_4} \cdot [ClO_4^-] = -DH + \varepsilon_{Na-OH} \cdot [OH^-] + \varepsilon_{Na-ClO_4} \cdot (I - [OH^-]) =$$
$$= -DH + \varepsilon_{Na-OH} \cdot [OH^-] + \varepsilon_{Na-ClO_4} \cdot I - \varepsilon_{Na-ClO_4} \cdot [OH^-]$$

$$\lg \gamma_{Ba^{2+}} = -4 \cdot DH + \varepsilon_{Ba-OH} \cdot [OH^-] + \varepsilon_{Ba-ClO_4} \cdot [ClO_4^-] = -4 \cdot DH + \varepsilon_{Ba-OH} \cdot [OH^-] + \varepsilon_{Ba-ClO_4} \cdot (I - [OH^-]) =$$
$$= -4 \cdot DH + \varepsilon_{Ba-OH} \cdot [OH^-] + \varepsilon_{Ba-ClO_4} \cdot I - \varepsilon_{Ba-ClO_4} \cdot [OH^-]$$

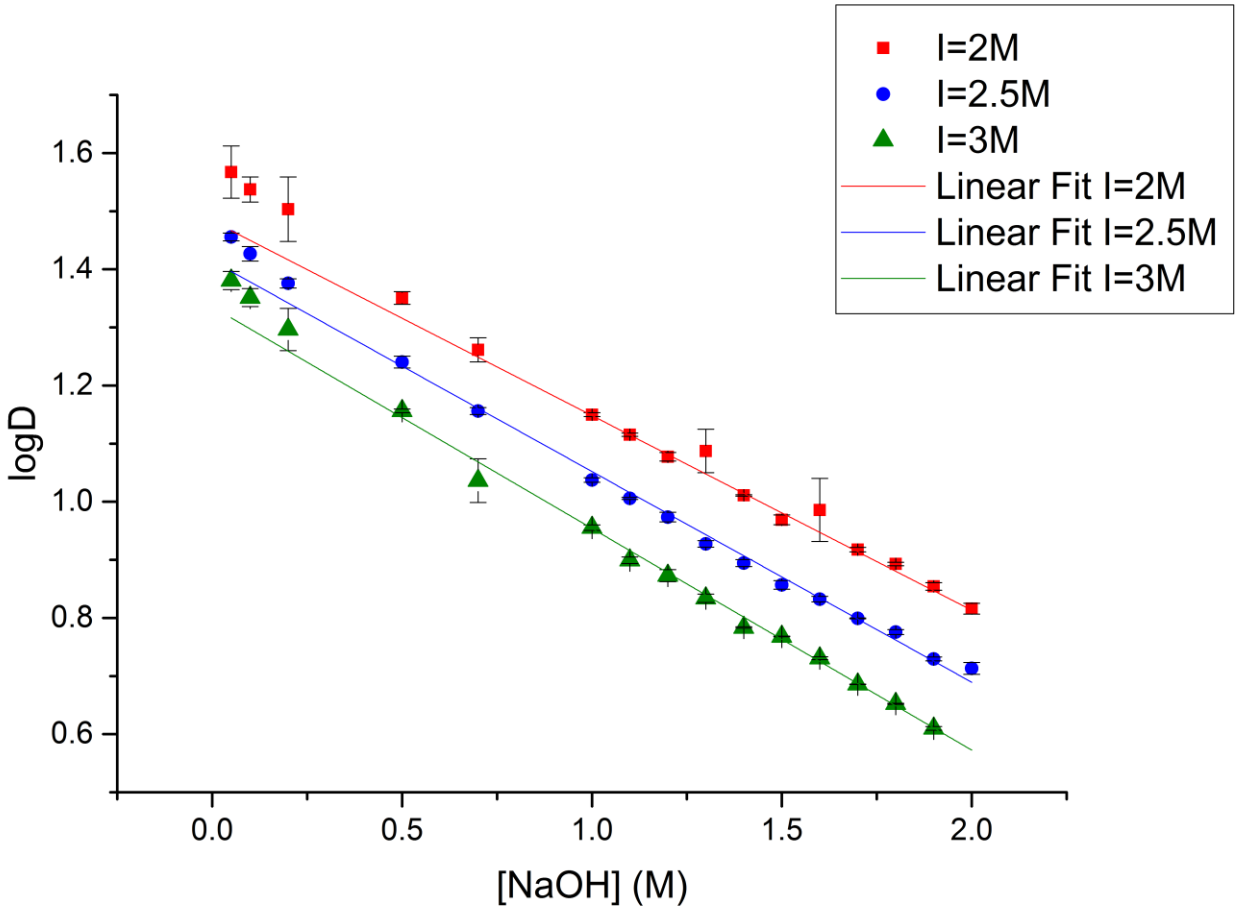
$$D = \lambda \cdot 10^{-2 \cdot DH + I \cdot \varepsilon_{Ba-ClO_4} - 2 \cdot I \cdot \varepsilon_{Na-ClO_4} + [OH^-] \cdot (\varepsilon_{Ba-OH} - \varepsilon_{Ba-ClO_4} - 2 \cdot \varepsilon_{Na-OH} + 2 \cdot \varepsilon_{Na-ClO_4})}$$

$$D = \lambda \cdot 10^{a + b \cdot [OH^-]} \qquad \lg(D) = \lg(\lambda) + a + b \cdot [OH^-]$$

Spahiu, K., & Puigdomenech, I. (1998). On weak complex formation: re-interpretation of literature data on the Np and Pu nitrate complexation.*Radiochimca Acta*, *82*(Supplement), 413-420.

Barium hydrolysis: ion interaction model

$$\lg(D) = \lg(\lambda) + a + b \cdot [OH^-]$$



Barium hydrolysis: ion association model

$$[Na]^{total}_{aqueous} = [Na^+] + [NaOH] + [NaClO_4] = [Na^+] + K_{NaOH} \cdot [Na^+] \cdot [OH^-] + K_{NaClO_4} \cdot [Na^+] \cdot [ClO_4^-]$$

$$[Na]^{total}_{aqueous} - [Na^+] \cdot (1 + K_{NaOH} \cdot [OH^-] + K_{NaClO_4} \cdot [ClO_4^-]) = 0$$

$$[ClO_4]^{total}_{aqueous} = [ClO_4^-] + [NaClO_4] = [ClO_4^-] + K_{NaClO_4} \cdot [Na^+] \cdot [ClO_4^-]$$

$$[ClO_4]^{total}_{aqueous} - [ClO_4^-] \cdot (1 + K_{NaClO_4} \cdot [Na^+]) = 0$$

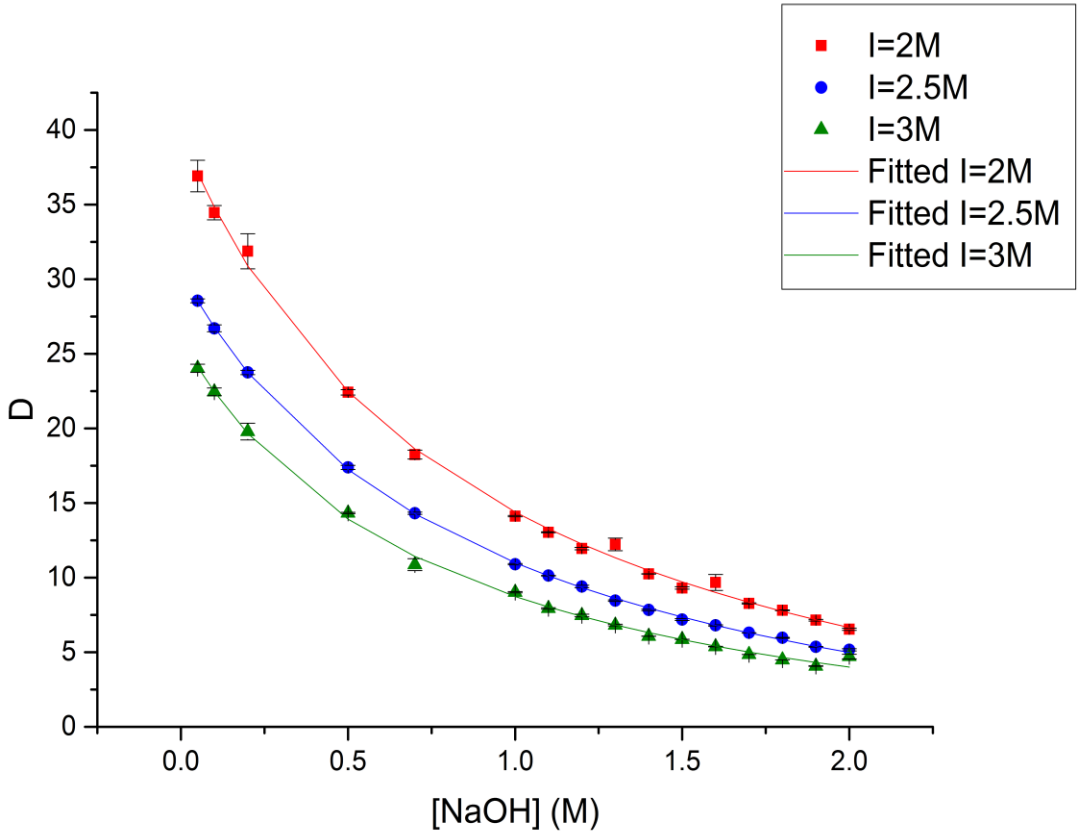
$$[OH]^{total}_{aqueous} = [OH^-] + [NaOH] = [OH^-] + K_{NaOH} \cdot [Na^+] \cdot [OH^-]$$

$$[OH]^{total}_{aqueous} - [OH^-] \cdot (1 + K_{NaOH} \cdot [Na^+]) = 0$$

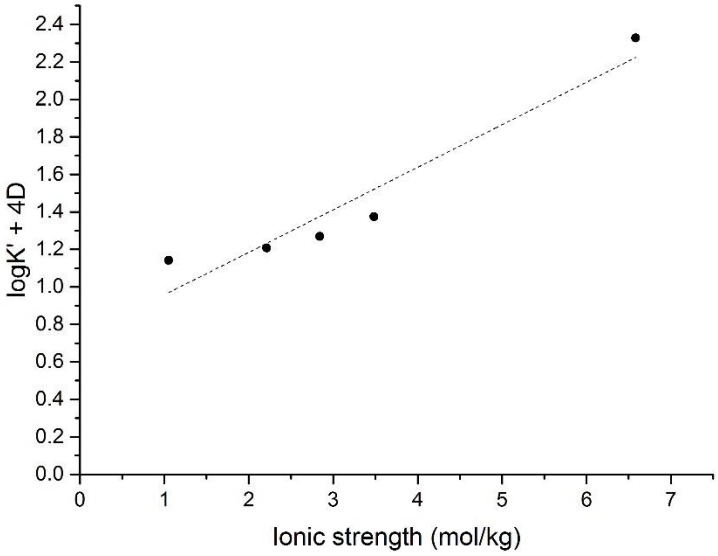
$$D = \frac{\lambda_0 + \lambda_1 \cdot [ClO_4^-]^{total}_{aqueous}}{1 + K_1^{BaOH^+} \cdot \left(\frac{1}{1 + K^{NaOH} \cdot [Na^+]^{total}_{aqueous}}\right) \cdot [OH^-]^{total}_{aqueous}}$$

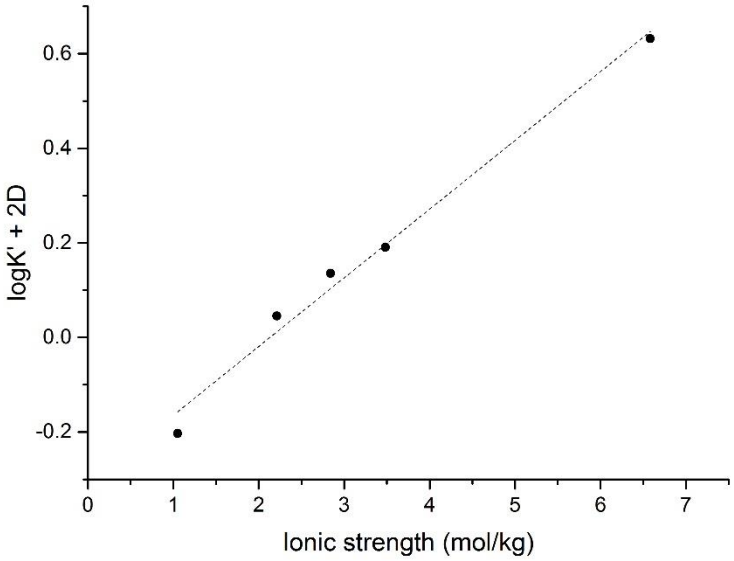
Barium hydrolysis: ion association model fit

$$D = \frac{\lambda_0 + \lambda_1 \cdot [ClO_4^-]^{total}_{aqueous}}{1 + K_1^{BaOH^+} \cdot \left(\frac{1}{1 + K^{NaOH} \cdot [Na^+]^{total}_{aqueous}}\right) \cdot [OH^-]^{total}_{aqueous}}$$



Barium hydrolysis: extrapolation to zero ionic strength





According to the plots logarithms of stability constants of NaOH and BaOH+ complexes at zero ionic strength are 0,31 and 0,73 which is in agreement with literature data (-0.4 ± 0.2 for NaOH and 0.68 ± 0.07 for BaOH+)

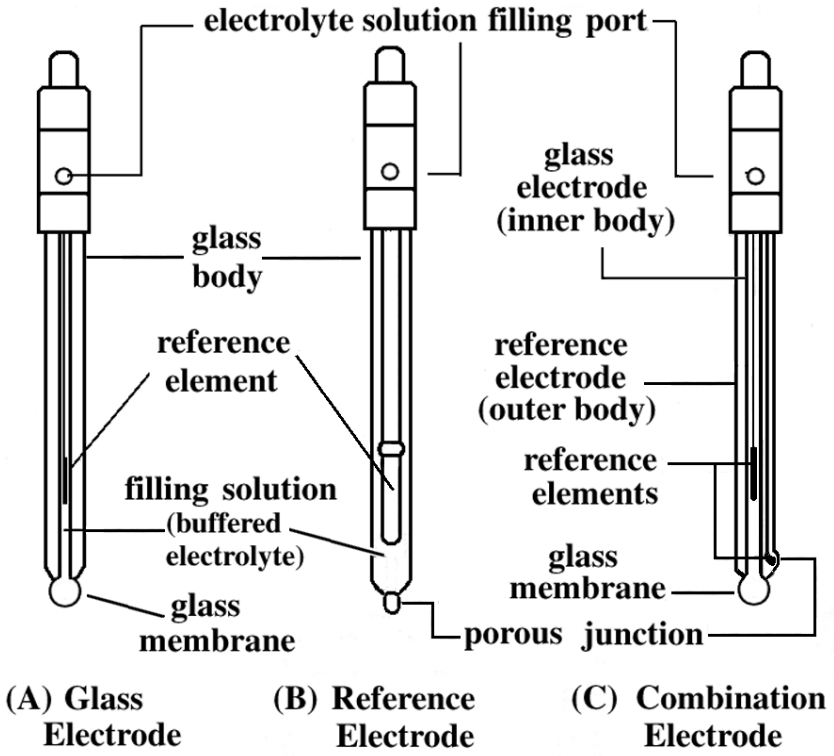
"The chief criterion for [classifying] an electrolyte [as nonassociated] is the absence of valid evidence for any form of association. Since the validity of such evidence can be a matter of personal opinion...there can be no general agreement." – Robinson and Strokes

"However, if K<2 [logK<0,3], the mere existence of the ion pair may be questioned"

[EKB15] Ekberg, C. and Brown, P. (2015). Studies on the Hydrolysis of metal ions
[MAR06] Marcus, Y., & Hefter, G. (2006). Ion pairing. *Chemical reviews*, *106*(11), 4585-4621.

BASIC ELECTRODE KNOWLEDGE

”What you need to know when measuring pH”



Basic electrochemistry (light thermodynamics)

Consider the reaction: $aA + bB \rightleftarrows cC + dD$

With the disequilibrium factor : $Q = \frac{\{C\}^c\{D\}^d}{\{A\}^a\{B\}^b}$ and

stability constant: $K = \frac{\{C\}^c\{D\}^d}{\{A\}^a\{B\}^b}$

where {A} denotes the chemical activity of species A.

At equilibrium the activities reach a state in order to satisfy Q=K

Basic electrochemistry (light thermodynamics)

Consider the reaction: $aA + bB \rightleftarrows cC + dD$

The Gibbs energy of a reaction is a function of the temperature, pressure and composition (expressed in moles).
For a small change in any of these entities:

$$dG = -SdT + VdP + \sum_x \mu_x dn_x$$

where S is the entropy and μ the partial molar free energy or chemical potential according to:

$$\mu_x = \left(\frac{\partial G}{\partial nx}\right)_{T,P,n}$$

Basic electrochemistry (light thermodynamics)

Consider the reaction: $aA + bB \rightleftarrows cC + dD$

A standard state can always be selected arbitrarily and then the thermodynamic values are related to that standard state.
Typically this is: 25 °C, 1 bar and 1 M solution for a solute.
This has led to a definition of the chemical activity:

$$\mu_x - \mu_x^o = RTln\{A\}$$

and thus the change in Gibbs energy is:

$$\Delta G = c\mu_C + d\mu_D - a\mu_A - b\mu_B$$

Basic electrochemistry (light)

Consider the reaction: $aA + bB \rightleftarrows cC + dD$

We also know that Gibbs energy is an equation of state which can be related to other equations of state like the enthalpy and entropy according to: $\Delta G = \Delta H - T\Delta S$.

The energy change (possibility) during a reaction is given by how far it is from its equilbrium at standard state:

$\Delta G = \Delta G^o + RT\ln Q = -RT\ln K + RT\ln Q$

Thus, at equilibrium at standard state the change in Gibbs energy is zero

Basic electrochemistry: a side track

Consider the reaction: $aA + bB \rightleftarrows cC + dD$

Following from the reaction that $\Delta G^o = \Delta H^o - T\,\Delta S^o$ and $\Delta G^o = -RT\ln K$ we get a possibility to estimate the enthalpy and entropy of a reaction by determining the stability constant (or standard EMF) at different temperatures:

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{R}\frac{1}{T}$$

by plotting the inverse temperature versus the determined lnK

Basic electrochemistry (light thermodynamics)

Consider the reaction: $aA + bB \rightleftarrows cC + dD$

The free energy can also be related to the maximum electromotive force (EMF) that can be achieved by a reaction through:

$\Delta G = -nFE$

where F is the Faraday constant and n the number of moles of electron transfer needed for the reaction.
In analogy with the Gibbs energy we can now write:

$$\Delta E = \Delta E^o - \frac{RT}{nF} lnQ$$

Basic electrochemistry (cells)

Anode

Always oxidation
Electrons donated
Anions accepted
Minus (GALVANIC CELL)

A galvanic cell is goverened by a spontanous reaction while an electrolytic cell requires electric w

Cathode

Always reduction
Electrons accepted
Cations accepted
Plus (GALVANIC CELL)

Basic electrochemistry (cells)

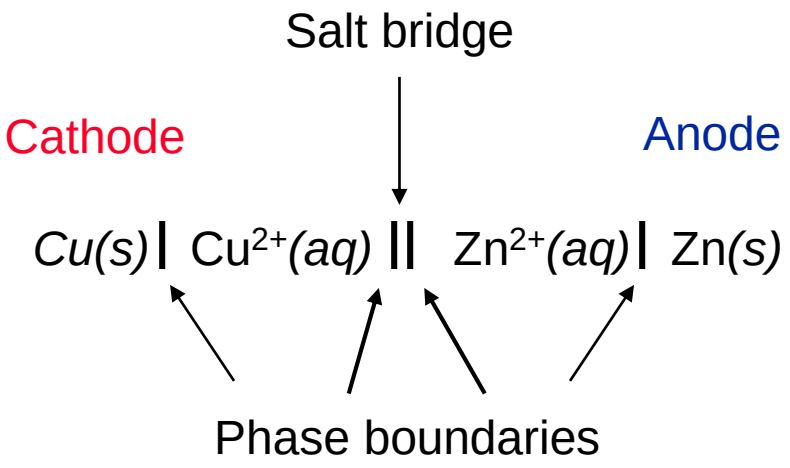
Consider the reaction: $Zn(s) + Cu^{2+} \longrightarrow Zn^{2+} + Cu(s)$

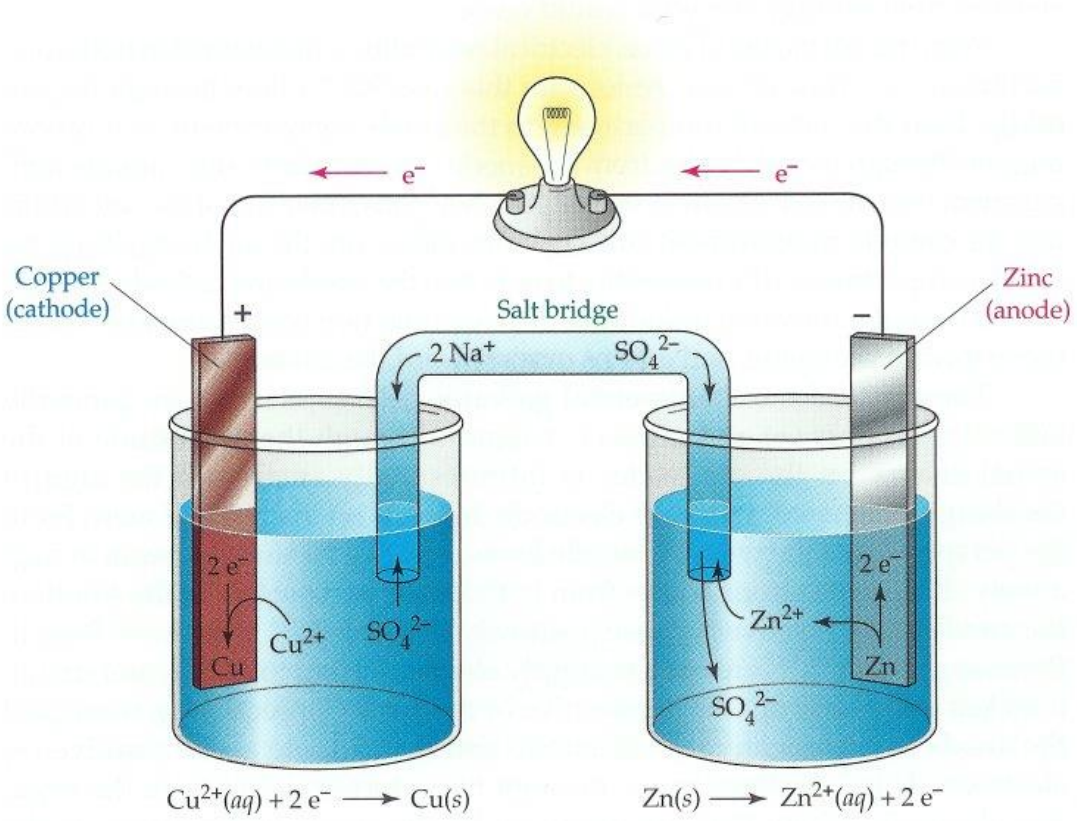
This reaction ca be divided into an oxidation and a reduction reaction:

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$	(Oxidation)	Anode
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	(Reduktion)	Cathode
$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$		Cell

Basic electrochemistry (cells)

If the contact between the reactants are limited we can build a cell





Basic electrochemistry (cells)

Consider the reactions: $Zn(s) + Cu^{2+} \longrightarrow Zn^{2+} + Cu(s)$ at standard state

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$	(Oxidation)	Anode	$E_a^o = -0.76$ V
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	(Reduction)	Cathode	$E_c^o = 0.34$ V
$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$		Cell	$E^o = E_c^o - E_a^o = 1.1$ V

Please note the clear inconsistency here: The potentials are not added when the reactions are added. The reason for this is that by convention it is **ALWAYS** the reduction potential that is used. The oxidation potential has a reversed sign and then the basic rules of thermodynamics would apply (like that the Gibbs energy of two added reactions is the addition ofthe respective Gibbs energies)

Basic electrochemistry (cells)

Consider the cell: $Zn(s) + Cu^{2+} \longrightarrow Zn^{2+} + Cu(s$

The voltage over the cell when both solutions are at standard states is 1.100V.

Let us now consider the case when we measure a potential of 1.2 V over a cell governed by the same reaction but where only the concentration (activity) of the Zn^{2+} solution is known (1.000(M)). Then:

$$1.2 = 1.1 - \frac{RT}{nF} ln \frac{\{Zn^{2+}\}}{\{Cu^{2+}\}}$$

We can now calculate the activity of the Cu^{2+} solution to be: 1.169 M

Basic electrochemistry (hydogen electrode)

It is all about comparison.....

Consider the cell: $Pt \mid H_2, H^+ \mid \mid KCl(sat), Hg_2Cl_2(s) \mid Hg(l)$

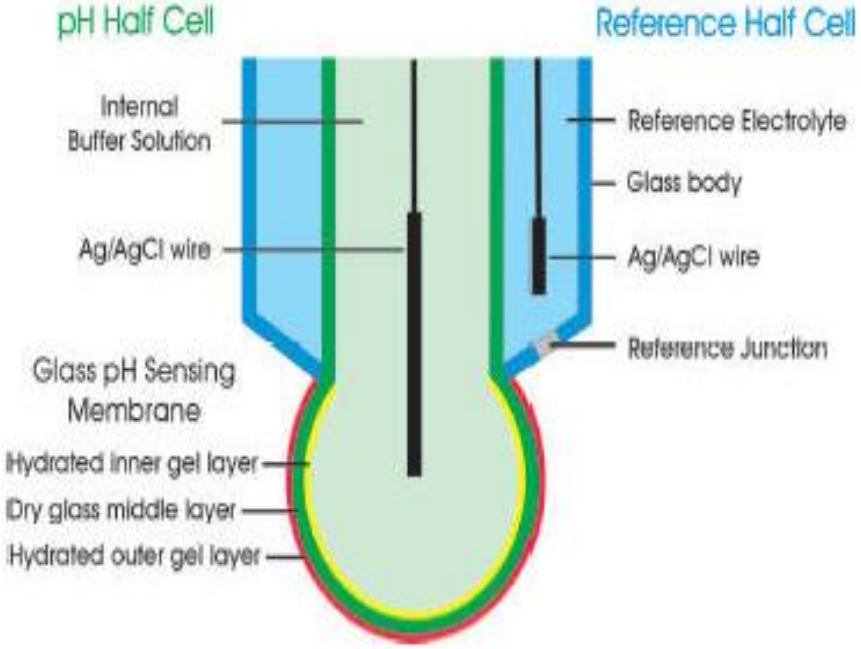
By keeping the hydogen pressure at 1 atm and the proton activity at 1 M and define that under these conditions the reduction potential for that half cell reaction =0 we can also define the potential of the other half cell.
Now we can immerse a platinum wire (and bubble H_2) in a solution which is in contact with the reference by electric conduction and a ”salt bridge” and any H^+ activity can be measured.

VIOLA We have built a pH electode!!

Basic electrochemistry (modernising)

Over the years both the hydogen and the calomel electrodes were abandoned for the glass electrode and the Ag/AgCl electrode. The principles are the same but the exact working of the glass electrode is still a mystery. However, its properties are well investigated.

It is today rather unusual to have separate refernce electrodes and glass electrodes. Typically the refernce electrode is within the combined electrode while only the glass electride is in contact with the solution.



Ag(*s*) | AgCl(*s*) | KCl(*aq*) || 1×10^{-7}M H^{+} solution || glass membrane || Test Solution || ceramic junction || KCl(*aq*) | AgCl(*s*) | Ag(*s*)

Basic electrochemistry (getting complicated)

So far everything has been rather straight forward (except the working of the glass electrode). Matters get complicated when it is time to consider which partial potentials actually build up the measured potential. So far we have only considered the chemical potential (ideally).

The most important additional potential is the liquid junction potential. To maintain electrical contact between the reference electrode and the pH electrode, there must be a relatively free diffusion of ions between the reference fill solution and the process solution. Essentially we need the negative and positive ions to be equitransferent which means that they move (diffuse) equally fast through the solution and membrane. If this is not the case we will have a charge imbalance over the membranes which will add to the measured potential.

Basic electrochemistry (getting complicated)

Evidently we can not use a filling solution which will form a solid when in contact with the measured solution. A typical example is using a KCl electrode when measuring in a ClO_4^- based solution. $KClO_4$ will then precipitate in the glass frit and destroy the electrode.

Please note that an electrode measures the H^+ ACTIVITY and NOT concentration. To get the concentration from a measurement either calibrate using well determined concentration standards (in the same ionic strength and medium) or calculate the activity coefficient for the hydogen ion.
Remember that all reactions are temperature dependent. So are also buffers and the auto-protolysis of water. Keep track of the temperature!

Most pH sensors are designed to produce a 0 mV signal at pH 7.0, with a (theoretically ideal) slope (sensitivity) of -59.16 mV / pH at 25 °C.

Basic electrochemistry (final words)

Probably some items and important issues have been forgotten. By considering the content of this lecture you are ready to make ”working” pH determinations. For more precise determinations and evaluations other aspects have to be taken into account.

During this leacture only pH electrodes have been considered. However, as you understand from the theory, almost any ions activity can be measured this way by (home made) electrodes.

Measuring pH is an art and should be regarded with the respect it deserves. Any detector can produce a value but what does the value actually say?

This is the field of science!