STABILITY OF COORDINATION COMPOUNDS

Stability constants

For the mononuclear complex ML_n with up to til N of the same (mono-, di -, tri- .....dentate) ligands coordinated to a metal ion M, we may define the *over all* (in Danish: *brutto) stability constant* β_n as

$$[ML_n] = \beta_n \cdot [M] \cdot [L]^n$$

n has a value between 0 and N, the maximum coordination number; for 0 and N we have β_0 (the value of which is 1) and β_N.
The total concentration (also called the formal or stoichiometric concentration) of the metal ion C_M may be rewritten as

$$C_M = [M] + [ML] + [ML_2] + \ldots\ldots\ldots\ldots + [ML_N]$$

or

$$C_M = \beta_0[M] + \beta_1[M]\cdot[L] + \beta_2[M]\cdot[L]^2 + \ldots\ldots\ldots\ldots + \beta_N[M]\cdot[L]^N \quad \text{or}$$

$$C_M = [M]\sum_{n=0}^{N} \beta_n \cdot [L]^n \quad (1)$$

Correspondingly, we may express the total concentration (the formal or stoichiometric concentration) of the ligand C_L as

$$C_L = [L] + [ML] + 2[ML_2] + \ldots\ldots\ldots\ldots + N[ML_N]$$

or

$$C_L = [L] + \beta_1[M]\cdot[L] + 2\beta_2[M]\cdot[L]^2 + \ldots\ldots\ldots\ldots + N\beta_N[M]\cdot[L]^N \quad \text{or}$$

$$C_L = [L] + [M]\sum_{n=0}^{N} n\beta_n \cdot [L]^n \quad (2)$$

In this case it is assumed that the ligand in the medium used has no relevant acid base properties (i.e. is a very weak base). If the ligand is not a very weak base C_L should be replaced by $C_L - ([LH^+] + [LH_2^{2+}] + \ldots)$ elaborate on that question when relevant.
In a given solution with the total concentrations C_M and C_L an equilibrium will exist between the different components L, M, ML, ML_2 , ...and ML_N. The concentration of the components is determined by C_M and C_L and the values of the N β_n's. With the values of these N+2 entities it is possible to calculate the N+2 concentrations through the N+2 equations.
To do so, the N β_n's has to be determined..
It is relevant to define the *mean ligand number* or **the degree of formation of the system** (in Danish*: middelligandtallet* også kaldet **systemets dannelsesgrad***),* $\bar{n}$ (udtales n-middel), as the concentration of ligands, which are bound to the metal ion divided by the concentration of metal ions:

$$\bar{n} = \frac{C_L - [L]}{C_M} \tag{3}$$

Equation (1) and (2) are inserted to give

$$\bar{n} = \frac{\sum n\beta_n \cdot [L]^n}{\sum \beta_n \cdot [L]^n} \tag{4}$$

There are a number of experimental procedures for the determination of the stability of metal complexes. The different methods are in all cases base don the determination of some or more of the actual concentrations [L], [M], [ML],..... directly or indirectly, depending on what is fast, convenient, accurate, or possible at all.

The ligand.

L is often a base and may be determined indirectly from a measurement of pH via

$$[L] = K_{LH^+} \cdot \frac{[LH^+]}{[H^+]}$$

as long as the other entities in the acidity constant equation are known. A principle which has been used successfully has been to conduct the experiments in a solution with a high and constant, known concentration of a soluble salt of LH^+ (e.g. of NH_4NO_3, where the ligand is ammonia).

From equation (4) it is seen that $\bar{n}$ is independent of the concentration of the metal ion, and that $\bar{n}$ can be determined by equation (3), if [L] - thee free ligand concentration can be measured in the prepared solution, (where C_M and C_L are known)

Now, if N different solutions (with an appropriate variation in C_M and C_L) are prepared, and the [L] can be determined in each of these solutions, there are sufficient information to determine the N values of β_n from the N equations with med N parameters:

$$\bar{n}_1 = \frac{\sum n \cdot \beta_n [L]_1^n}{\sum \beta_n \cdot [L]_1^n}$$

$$\bar{n}_2 = \frac{\sum n \cdot \beta_n [L]_2^n}{\sum \beta_n \cdot [L]_2^n}$$

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$$\bar{n}_N = \frac{\sum n \cdot \beta_n [L]_N^n}{\sum \beta_n \cdot [L]_N^n}$$

It may be convenient to approach the C_L and C_M of the solutions in such a way as to give $\bar{n} = n+½$. In this case $[ML_n]$ is almost equal to $[ML_{n+1}]$, and accordingly

$$K_{n+1} = \left(\frac{1}{[L]}\right)_{\bar{n}=n+½}$$

The central ion

In some cases it is possible to measure the free metal ion concentration [M] electrochemically by using a rod of the metal as electrodes in the following reversible concentration cell

$$\bar{M}|C_L, C_M \| C_M|\overset{+}{M}$$

Here the two half cells are only different in concentration of ligand, which is zero in the right half cell. The complex formation in the left half cell gives a lower free metal ion concentration. This is the entity measured in this electrochemical set up. The lower metal ion concentration in the left cell gives a lower half cell potential according to the Nernst equation

$$E = E^0 + \frac{RT}{nF} \cdot \ln[M]$$

For the above concentration cell the potential difference measured is given by

$$\Delta \mathbf{E} = \frac{59.16}{\mathbf{n}} \cdot \log \frac{\mathbf{C_M}}{[\mathbf{M}]} \qquad \text{(in mV at 25 } ^0\text{C)} \qquad (5)$$

Equation 5 gives immediately $\alpha_0 = \frac{[M]}{C_M}$, which is the proportion of metal ions to which exactly 0 ligands are bound. Correspondingly *the degree of formation* (in Danish *dannelsesgraden)* α_n are defined for all the complexes ML_n, as $\alpha_n = \frac{[ML_n]}{C_M}$.

α_n is a convenient entity when the relative distribution of species are plotted, using the estimated β_n 's..

Example: Cadmium ions form complexes with ammonia as the ligand with up to 6 ligands coordinated. $\log\beta_n$ values are 2.66, 4.76, 6.18, 7.11, 6.84, 4.4, respectively. The numbers reveal that the last two ligands have only a very little affinity to Cd^{2+}. A plot of α_0 , α_1 α_2 and α_4 as a function of pH in a solution with C_M = 1 mM and C_L = 1 M, gives the following:

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Complex ions

In some case it is possible to determine the concentration of one of the complex ions ML_n, so that α_n is available. It could be the measurement of solubility, of partition equilibrium (uncharged complexes with anionic ligands) and the measurement of spectra (at a wavelength where only one complex species absorb light).
If Beer's law is valid for all ML_n complexes and if the absorption by the ligand is negligible in an interval, the absorbance for a mixture of complexes may be expressed as the sum of the absorbance from all the complexes in the mixture:

$$\mathbf{A}_{\mathbf{mixture}} = \mathbf{A}_{\mathbf{M}} + \mathbf{A}_{\mathbf{ML}} + \mathbf{A}_{\mathbf{ML_2}} + ...\mathbf{A}_{\mathbf{ML_N}}$$

or (divide by C_M and the length of the cuvette, l)

$$\varepsilon_{\text{blanding}} = \alpha_0 \cdot \varepsilon_M + \alpha_1 \cdot \varepsilon_{ML} + \alpha_2 \cdot \varepsilon_{ML_2} + ... + \alpha_N \cdot \varepsilon_{ML_N} \qquad (7)$$

It might happen that the absorbance divided by C_M in different solutions (different C_M and C_L and different ratios between C_M and C_L) in this wavelength interval is equal. According to equation 7 this implies, that the distribution of complexes in these solutions is also equal. In such cases the solutions are said to be *corresponding*. This experimental situation could be aimed at, because one could benefit from

The principle of corresponding solutions.

In two or more corresponding solutions, the distribution of complexes is the same, i.e. the degree of formation α_n of each single complex is the same in the corresponding solutions. If it it shown by some measurement, that one of the complexes has the same degree of formation α_n in two solutions, it can be shown, that all the α_n's are the same in the two solutions. If the degree of formation in the two solutions are $\alpha_n(1)$ and $\alpha_n(2)$, respectively, the expression for the n'th consecutive constant K_n as

$$K_n = \frac{\alpha_n(1)}{\alpha_{n-1}(1)\cdot[L]_1} = \frac{\alpha_n(2)}{\alpha_{n-1}(2)\cdot[L]_2}.$$

Since the numerators are equal, the denominator is also equal, and two possibilities arises:

1) either $\alpha_{n-1}(1) = \alpha_{n-1}(2)$ and $[L]_1 = [L]_2$
2) or $\alpha_{n-1}(1) \neq \alpha_{n-1}(2)$ and $[L]_1 \neq [L]_2$

It can be shown that only the first solution is possible. In turn this means that concentrations of free ligand [L] in two (or more) corresponding solutions are identical. From equation 4 (for $\bar{n}$) it is seen, that also values of $\bar{n}$ are equal for corresponding solutions. It is also obvious, that values of $\bar{n}$ are the same in corresponding solutions, because the degree of formation α_n of each single complex is the same in the corresponding solutions:

$$\bar{n} = \frac{[ML] + 2[ML_2] + ...+ N[ML_N]}{C_M} = \sum_{n=0}^{N} n \cdot \alpha_n$$

The combination of these two facts [L] and $\bar{n}$ can be calculated, because the stoikiometric concentrations $C_L(1)$, $C_L(2)$, $C_M(1)$, and $C_M(2)$ are known:

$$\bar{n} = \frac{C_L(1) - [L]}{C_M(1)} = \frac{C_L(2) - [L]}{C_M(2)}, \qquad \text{which gives}$$

$$[L] = \frac{C_L(1) \cdot C_M(2) - C_L(2) \cdot C_M(1)}{C_M(2) - C_M(1)}$$

Corresponding solutions: A summary.

- Two or more solutions are corresponding, if the distribution of complexes in the solutions are the same, i.e. $\alpha_n(1)=\alpha_n(2)=\alpha_n(3)$..... for all n.
- The solutions are corresponding, when it is measured, that at least one of the components ML_n has the same relative concentration. In that case all the other complexes have the same relative concentrations in the solutions.

  -By electrochemical experiments it is measurable if $\alpha_0(1)=\alpha_0(2)$ (EMF is the same in concentration cells)

  -It is possible to find if $\alpha_n(1) = \alpha_n(2)$ by the measurement of absorption spectra at a wavelength(s) where only ML_n absorbs (strongly): ($\varepsilon_{solution.1} = \varepsilon_{solution.2}$)
- In two (or more) corresponding solutions the degree of formation of the system are the same: ($\bar{n}_{opløsning.1} = \bar{n}_{opløsning.2}$)
- In two (or more) corresponding solutions the concentration of the free ligand is the same in all solutions:

$$[L] = \frac{C_L(1) \cdot C_M(2) - C_L(2) \cdot C_M(1)}{C_M(2) - C_M(1)}$$