

# Generalization of the Principle of Corresponding Solutions

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Dedicated to Jannik Bjerrum on the occasion of his 70th birthday

The principle of corresponding solutions is extended to the study of protonated and mixed ligand complexes. The experimentally accessible minimum and maximum values of stability constants in the case of stepwise complex formation are given. It is pointed out that difference spectrophotometry is the best technique to select pairs of corresponding solutions; an experimental procedure and a computation technique are suggested.

An elementary analysis of the stepwise complex formation equilibria shows that for the formation of mononuclear binary complexes, the distribution of the different species is determined by the free ligand concentration only. Solutions in which the total concentrations of the metal ion ( $C_M$ ) and the ligand ( $C_L$ ) are different, but the free ligand concentrations are the same, were named by Jannik Bjerrum,<sup>1</sup> corresponding solutions. For two corresponding solutions the eqns. (1)–(2) hold:

$$\bar{n} = \frac{C'_L - C_L}{C'_M - C_M} \quad (1)$$

$$[L] = \frac{C'_M C_L - C_M C'_L}{C'_M - C_M} \quad (2)$$

so that the values of the complex formation function can be determined. Bjerrum demonstrated the applicability of the principle of corresponding solutions (PCS) by obtaining some stability constants based on spectrophotometric measurements.<sup>1</sup> However, in the last three decades this method was applied only in a few cases<sup>2–5</sup> in spite of its potential possibilities. The main reasons for the neglect of this most promising principle are that its applica-

tion requires a more careful design of experiments than those of the analogous mole ratio and continuous variation methods and that its theory is not elaborated. In this paper we would like to point out that the range of applicability of PCS is broader than has been formerly realized. Further, quite simple experiments can provide the necessary sets of data to evaluate stability constants in such cases where the application of the widely used methods is awkward and results in less precise constants.

## THE BASIC ADVANTAGE OF THE PRINCIPLE OF CORRESPONDING SOLUTIONS

The measurement of any property of a solution in which the concentrations of the species are reflected can provide the basic data for the evaluation of the constants. The different methods can be classified into three groups depending on the contribution of the different species to the measured property ( $Y$ ).

In the case of the colligative properties given in eqn. (3) each species contributes equally to the

$$Y = x \sum_i c_i \quad (3)$$

measured property. ( $x$  is an intensive parameter,  $c_i$  is the concentration of the  $i$ 'th species).

In the case of additive properties

$$Y = \sum_i x_i c_i \quad (4)$$

expressing that the concentrations are weighted with the intensive parameters.

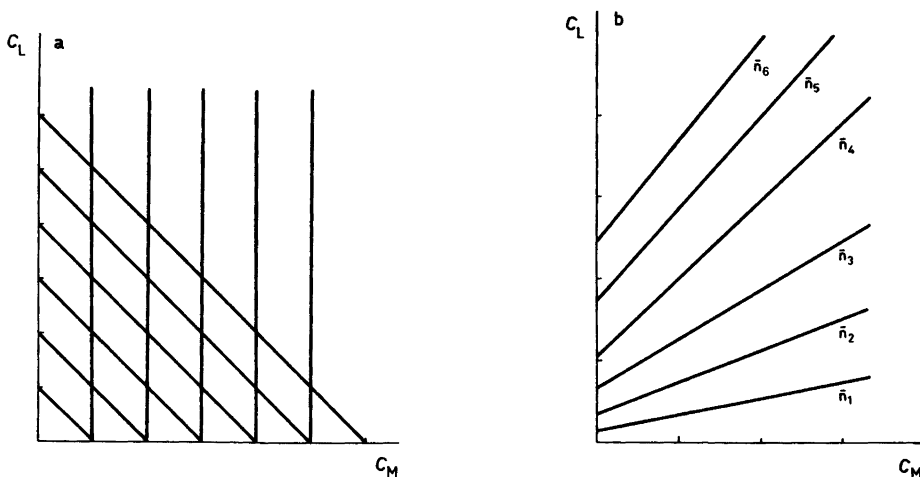


Fig. 1. The differences in the three approaches. (Reproduced with permission from Analytical Chemistry, Essays in Memory of Anders Ringbom, edited by E. Wänninen, Pergamon, Oxford 1977, p. 74). (a). The possibilities for the variation of total concentrations in the study of complex equilibria. Vertical lines represent the mole ratio method, diagonals represent the composition in a continuous variation study. (b). A concentration plane representation of PCS in which each straight line can be expressed by the equation  $C_L = \bar{n}C_M + [L]$ .

In certain cases the measured property is determined exclusively by the concentration of a single species:

$$Y = x_k c_k \quad (5)$$

All the three basic approaches, mole ratio, continuous variation and corresponding solutions, can be applied when one of the additive properties (absorbancy, optical rotatory power, heat of reaction, chemical shift of NMR or EPR signal, etc.) is measured. Fig. 1 illustrates the differences in the three approaches.<sup>6</sup> Note that the vertical lines and the diagonals in the  $C_L - C_M$  concentration plane can be arbitrarily selected, but the straight lines in Fig. 1b referring to corresponding solutions are determined by the equilibrium behaviour of the system investigated.

In the case of successive formation of  $N$  complex species, the number of equilibrium constants to be determined is also  $N$ . In applying, however, either the mole ratio or the continuous variation approach, the calculation of the intensive parameters of the different species is also required, *i.e.*, the number of the unknown constants is at least doubled. When spectrophotometric measurements are made at  $l$  different wavelengths the number of the unknown

constants is  $(l+1)N$ . The difficulties of the evaluation of the constants, including the computing time increase exponentially with the number of constants to be evaluated. Applying PCS there is no need to know the intensive parameters, these can be obtained after calculation of the distribution of the complexes.

Although any experimental method providing a possibility to measure an additive property can be applied, spectrophotometry is the most versatile and best-suited technique, and the following treatment will be restricted to this approach.

#### CRITERIA FOR SELECTION OF CORRESPONDING SOLUTIONS

The absorbance of ligand is zero

In many cases the molar absorbance of each of the complexes is much higher than that of the uncomplexed ligand. In such cases the absorbance of the solution is as given in eqn. (6),  $d$  being the

$$A = d \sum_i \varepsilon_i [ML_i] \quad (6)$$

length of the cell. Considering the mass balances

$$C_L = [L] + [M] \sum_i i \beta_i [L]^i \quad (7)$$

$$C_M = [M] \left( 1 + \sum_i \beta_i [L]^i \right) \quad (8)$$

and the stability products

$$\beta_i = \frac{[ML_i]}{[M][L]^i} \quad (9)$$

one gets the following equation

$$\frac{A}{dC_M} = \frac{\sum_i \varepsilon_i \beta_i [L]^i}{1 + \sum_i \beta_i [L]^i} \quad (10)$$

In the case of corresponding solutions  $[L]$  is the same, *i.e.* the right side of (10) is constant. This means that for corresponding solutions  $A/d C_M$  is constant. Choosing a pair of corresponding solutions in such a way that the product of the cell length and the total metal concentration be equal

$$dC_M = d'C_M \quad (11)$$

the measured absorbance of the corresponding solutions is the same  $A = A'$ . This is independent of the wavelength, *i.e.* the spectral identity of the solutions is the criterion of correspondence.

The absorbance of ligand is non-zero

When the contribution of the ligand to the measured property cannot be neglected eqn. (10) should be written as

$$\frac{A/d - \varepsilon_L [L]}{C_M} = \frac{\sum_i \varepsilon_i \beta_i [L]^i}{1 + \sum_i \beta_i [L]^i} \quad (12)$$

For a pair of corresponding solutions the following equation holds:

$$\frac{A'/d' - \varepsilon_L [L]}{C'_M} = \frac{A/d - \varepsilon_L [L]}{C_M} \quad (13)$$

If the conditions of eqn. (11) are fulfilled, it follows then that

$$A' - A = \varepsilon_L [L] (d' - d) \quad (14)$$

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It can be concluded that when the absorbance of the ligand in the measured spectrum range is not negligible, the difference of the spectra of two corresponding solutions is identical with the spectrum of the free ligand.

#### EXTENSION OF THE PCS TO THE FORMATION OF PROTONATED COMPLEXES

When the ligand is a weak base, in addition to complex formation reactions the protonation of the ligand has to be considered, too. Taking into account the concentration of the non-complexed ligand by the  $\alpha_H$  coefficient

$$\alpha_H = \sum_j \beta_j [H]^j \quad (15)$$

where  $\beta_j$  is the protonation product of the ligand

$$\beta_j = \frac{[LH_j]}{[L][H]^j} \quad (16)$$

For a pair of corresponding solutions the following equation holds:

$$\bar{n} = \frac{C'_L - [L]\alpha'_H}{C'_M} = \frac{C_L - [L]\alpha_H}{C_M} \quad (17)$$

Therefore in this case  $\bar{n}$  and  $[L]$  are given by

$$\bar{n} = \frac{\alpha_H C'_L - C_L \alpha'_H}{\alpha_H C'_M - C_M \alpha'_H} \quad (18)$$

and

$$[L] = \frac{C_L C'_M - C_M C'_L}{\alpha_H C'_M - C_M \alpha'_H} \quad (19)$$

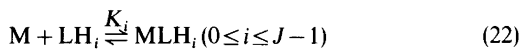
Since  $\alpha_H$  depends on hydrogen activity only, in the case of weak base ligands the corresponding solutions can be prepared in two ways: either at varying or at constant pH. For constant pH, (18) and (19) are simplified to

$$\bar{n} = \frac{C'_L - C_L}{C'_M - C_M} \quad (20)$$

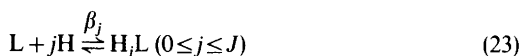
and

$$[L] = \frac{C_L C'_M - C_M C'_L}{(C'_M - C_M) \alpha_H} \quad (21)$$

When stepwise complex formation and successive protonation of the ligand and the complexes take place simultaneously, the system seems to be too complicated for a spectrophotometric study. However, when a multidentate ligand forms a 1:1 complex with the metal ion and the protonation of the free ligand and this complex has to be taken into consideration, the evaluation of the measurements of additive properties is feasible and the application of the PCS is advantageous. Such a system can be characterized by the following equilibria



and



considering the equilibrium constants

$$K_i = [MLH_i]/[M][LH_i] \quad (24)$$

and

$$\beta_j = [LH_j]/[L][H]^j \quad (25)$$

and the mass balances, the complex formation function can be written as

$$\bar{n} = \frac{C_L - [L] \sum_{j=0}^J \beta_j [H]^j}{C_M} = \frac{[L] \sum_{i=0}^{J-1} K_i \beta_i [H]^i}{1 + [L] \sum_{i=0}^{J-1} K_i \beta_i [H]^i} \quad (26)$$

For  $\bar{n}$  and  $[L]$  the same equations are obtained as (20) and (21). Knowing the protonation constants of the ligand, the analysis of the complex formation function either graphically or by computers provides the stability constants of the complexes. The study of the iron(III)–ethylenediaminetetraacetate–HClO<sub>4</sub> system demonstrated the applicability and even superiority of PCS.<sup>7</sup>

#### EXTENSION OF THE PCS TO THE STUDY OF MIXED LIGAND COMPLEXES

The fully general stepwise formation of mixed ligand complexes of the MX<sub>n</sub>Y<sub>j</sub> type where the following conditions are met

$$0 \leq i \leq N, \quad 0 \leq j \leq N, \quad 0 \leq i+j \leq N \quad (27)$$

is far too complicated for a spectrophotometric study. However, there are many systems much less complicated and these are well suited for the application of PCS.

The simplest case is when the mixed ligand complexes are formed from a binary complex MX<sub>n</sub> by expansion of the coordination sphere. The equilibria can then be treated in the same way as for the stepwise formation of binary complexes, the MX<sub>n</sub> unit being now equivalent to the free metal ion.

When the formation of the MX<sub>n</sub>Y<sub>j</sub> complexes are characterized by the following conditions

$$0 \leq i \leq N, \quad 0 \leq j \leq N, \quad i+j=N \quad (28)$$

the system can be described by a set of stability products

$$\beta_i = \frac{[MX_{N-i}Y_i][X]^i}{[MX_N][Y]^i} \quad (29)$$

and the average ligand numbers for X and Y are not independent of each other:

$$\bar{n}_Y = N - \bar{n}_X \quad (30)$$

By expressing  $\bar{n}_Y$  with the stability products

$$\bar{n}_Y = \frac{C_Y - [Y]}{C_M} = \frac{\sum_{i=1}^N i \beta_i ([Y]/[X])^i}{1 + \sum_{i=1}^N \beta_i ([Y]/[X])^i} \quad (31)$$

It appears that the complex formation function depends solely on the ratio  $[Y]/[X]$ . Solutions in which the total concentrations of the metal and the two ligands are different, but the ratio of the free ligand concentrations is the same, are corresponding. If the absorbances of the ligands are negligible, the spectral identity of the solutions is the criterion of correspondence. For a pair of corresponding solutions the following equations are valid

$$\bar{n}_Y = \frac{N(C_Y C'_M - C_M C'_Y) + C'_Y C_X - C_Y C'_X}{C_Y C'_M - C_M C'_Y + C'_M C_X - C_M C'_X} \quad (32)$$

and

$$\frac{[Y]}{[X]} = \frac{C_Y C'_M - C_M C'_Y}{C_X C'_M - C_M C'_X} \quad (33)$$

An analysis of the  $\bar{n}_Y = f([X]/[Y])$  function by either graphical or algebraic methods provides the values of the stability constants. The experimental study of the  $\text{PdCl}_i\text{Br}_j$  ( $i+j=4$ ) system demonstrated the applicability of the PCS.<sup>8</sup>

### PCS IN FORMATION OF POLYNUCLEAR COMPLEXES

It is easy to realize that PCS cannot be applied to formation of polynuclear complexes as illustrated below for the formation of a set of complexes of type  $\text{M}_p\text{L}_q$ . The average coordination number for two corresponding solutions can be written as follows:

$$\bar{n} = \frac{\sum_{p,q} \beta_{pq} [\text{M}]^p [\text{L}]^q}{C_M} = \frac{\sum_{p,q} \beta'_{pq} [\text{M}]^p [\text{L}]^q}{C'_M} \quad (34)$$

Therefore  $C_M$  and  $C'_M$  are necessarily equal, *i.e.*, in the case of polynuclear complex formation correspondence means identity.

### THE MINIMUM AND MAXIMUM VALUES OF THE ACCESSIBLE EQUILIBRIUM CONSTANTS

The basic criterion of the evaluation of stability constants from additive properties is that the concentrations of the two species in equilibrium be of the same order of magnitude. Person<sup>9</sup> formulated this statement by the following condition

$$0.1C_M < [\text{ML}] < 0.9C_M \quad (35)$$

Assuming that the maximum value of  $C_L$  cannot exceed 1 M, one obtains the minimum value of  $K$  as  $K_{\min} = 0.1 \text{ M}^{-1}$ .

For the estimation of  $K_{\max}$  the difference of molar absorbances of the species at equilibrium must be taken into account. The more stable the ML complex, the more dilute the solutions which can be used. The measured absorbance should be bigger than 0.1, *i.e.*

$$A_{\max} = \varepsilon_{\text{ML}} [\text{ML}] d = 0.1 \quad (36)$$

If 90% of the metal is present as ML, and the total concentrations of the metal and the ligand are

approximately the same, the maximum values of the accessible stability constant

$$K_{\max} = 810 \varepsilon_{\text{ML}} \quad (37)$$

In favourable cases the stability constant of rather stable complexes can be spectrophotometrically determined.

In judging the feasibility of the evaluation of successive stability constants three cases should be distinguished.

(1) If  $K_i/K_{i+1} > 100$ , the formation of the two complexes are more or less separated and the former considerations should be taken into account concerning the limiting values of each constant.

(2) When all the intermediate complexes are much less stable than the  $N$ th one, only  $\beta_N$  can be determined. Based on the former considerations one gets for  $\beta_{N,\max}$

$$\beta_{N,\max} = \frac{9 \times 90^N \times \varepsilon_N^N}{N^N} \quad (38)$$

(3) When  $1 \leq K_i/K_{i+1} \leq 100$ , the complex formation occurs in overlapping steps. For the evaluation of the  $N$ th constant it is necessary that the average coordination number should reach the value  $N - 0.9$ . The values of  $K_{i,\min}$  depend on the ratio of successive complexes, *e.g.* assuming the statistical case, for  $N=2$  the following minimum values can be obtained:  $K_{i,\min} = 2.48$ ,  $K_{2,\min} = 0.62$ . The values of the lower limit of the constants increase with increase both in  $N$  and in the ratio of the successive constants.

The values of the upper limit of the constants depend on the absolute and relative values of the molar absorbances of complexes in question. Following the same reasoning as in the case of ML and assuming statistical ratios for both  $K_1/K_2$  and  $\varepsilon_1/\varepsilon_2$ , the upper limits are  $K_{1,\max} = 200\varepsilon_2$  and  $K_{2,\max} = 50\varepsilon_2$ .

The errors in the constants increase exponentially beyond the limiting values. Elementary error calculations show that the precision of the constants obtained by the PCS approach depends on the range of total concentrations of the metal ion and the ligand. As it appears from Fig. 2 it is advantageous to perform the experiments in as broad a range of concentrations as possible. However, different technical limitations generally cannot permit extension of the measurements beyond one order of magnitude change of the total concentrations.

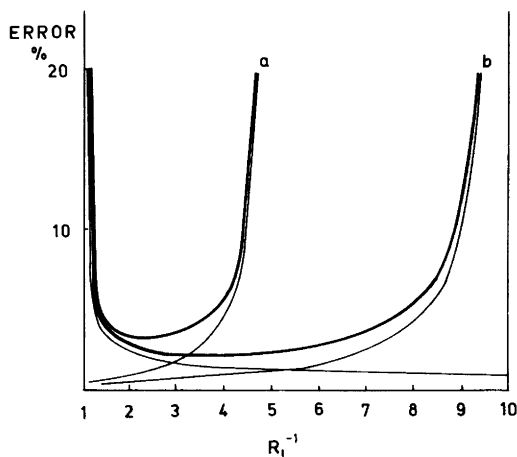


Fig. 2. Dependence of the error of the selection of the corresponding solution on the ratio of total concentrations of the metal ( $R_M = C_M/C'_M$ ) and of the ligand ( $R_L = C_L/C'_L$ ) assuming 1% error in the determination of total concentrations. Thin lines refer to the error of  $\bar{n}$

$$\pm \left( \frac{1}{(1-R_M)^2} + \frac{1}{(1-R_L)^2} \right)^{1/2}$$

and [L]

$$\pm \left( \frac{1+(1-R_M)^2}{(1-R_M)^2} \frac{(1-R_M)^2+(1-R_L)^2}{(R_L-R_M)^2} \right)^{1/2}$$

resp., while thick lines represent the sum of these quantities. In the case of curves *a*  $R_M=0.2$ , while for curves *b*  $R_M=0.1$ . For these two metal ion concentration ratios the difference in the error curves referring to  $\bar{n}$  is too small to be seen on the figure.

#### DETERMINATION OF THE CORRESPONDENCE OF SOLUTIONS BY DIFFERENCE SPECTROPHOTOMETRIC TITRATION

In previous applications of PCS the mole ratio method was used and the corresponding solutions were selected by interpolation. We think that the rather high error of this approach is one of the main reasons for the neglect of the practical application of PCS. On the other hand, precise difference spectrophotometry is convenient for the detection of pairs of corresponding solutions. The following procedure has been elaborated and applied in a number of cases.

We consider a solution in which the total concentrations are  $C'_M$  and  $C'_L$  contained in one of the cells of a double beam spectrophotometer. It is advantageous if the light path length of the cell can be changed so that the condition  $dC_M = d'C'_M$  is met over a broad concentration range. In the titration vessel the total concentration of the metal is kept at a constant value  $C_M$ , arbitrarily fixed and based on the aforementioned condition. The task is then to determine the corresponding  $C_L$ . The solution is continuously circulated through the other cell by a peristaltic pump and the difference spectrum is recorded. The initial total ligand concentration is

$$c = \frac{C'_L}{2} \left( 1 + \frac{C_M}{C'_M} \right)$$

In the case of correspondence the difference spectrum is identical with the base line of the spectrophotometer, in which case  $c$  should be equal to  $C_L$ . In practice the first approximation leads to either positive or negative deviation from  $C_L$ , and consequently from the base line. For the titration three solutions are used. The medium (swamping salt) is the same for each solution. In Solution I the concentration of metal ion is  $2C_M$ , in Solution II the concentration of the ligand is  $C'_L$ , while Solution III contains only the medium. If the total concentration of the ligand is bigger than that in the "corresponding" solution, i.e., the solution is over-titrated, equal volumes of Solutions I and III are added. In the opposite case, equal volumes of Solutions I and II are added. Repeating this procedure the value of  $C_L$  is found in about ten trials even in the most unfavourable case. However, usually it is enough to make four or five trials. This procedure permits the determination of the corresponding concentrations with an 0.1% error factor.

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