On the Method of Continuous Variations

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The implications and the validity of the assumptions made in the theory and in the application of the method of continuous variations as used in complex chemistry have been examined, and the results of such applications from numerous references (22 of which are given in the article) have been compiled and compared to results obtained by different methods where possible. On the basis of this it appears that the method can in general not be considered very reliable and that results obtained by the method must in general be considered as indications rather than solutions. In particular, most of the complexity constants so obtained must be considered erroneous in cases where the ligand number exceeds one. The method of continuous variations is compared to J. Bjerrum's method of corresponding solutions, the latter being superior in that it, for systems to which it is applicable, furnishes quantitative results.

Since the invention of the method of continuous variations (in the following referred to as c.v.) and especially since the work of Vosburgh and Cooper [1] this method has been extensively used in investigations of complex compound formation in solution. Furthermore c.v. has been adopted by standard works on physico-chemical methods for the investigation of reactions in solution [2,3]. It has therefore been of interest to compile some of the data obtained by means of c.v. for a critical review of the implications and the validity of the method.

The invention of c.v. is usually ascribed to P. Job [4,5]. It deserves mentioning that the principles of the method were already outlined by Denison [6] in 1912.

We shall have to consider two different applications of the method:

1) The application to cases in which the reactants, M and A, form only one complex, whereby it is possible not only to establish the stoichiometric composition of the complex but also to calculate its formation constant.

2) The application to cases in which M and A form several complexes, whereby only the composition of (some of) the complexes can be determined.

In the following discussion C denotes total concentrations, [A] the actual concentration of species A and x the "mole fraction" $\dfrac{C_A}{C_M + C_A}$.

FORMATION OF ONE COMPLEX ACCORDING TO

$$mM + nA \rightleftharpoons M_mA_n$$
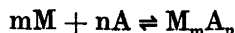
Briefly resuming the theory (for details see Ref.[5]) we shall consider the systems formed by mixing $(1-x)$ volumes of a solution of M ($C_M = C_o$) with x volumes of a solution of A ($C_A = rC_o$), x varying from 0 to 1 (volume changes being neglected). Assuming constant activity coefficients so that the law of mass action is valid in terms of concentrations, the systems, in which the equilibrium $mM + nA \rightleftharpoons M_mA_n$ is supposed to be established, are governed by the equations:

$$K \cdot [M]^m \cdot [A]^n = [M_mA_n];$$
$$C_o(1-x) = [M] + m[M_mA_n];$$
$$rC_ox = [A] + n[M_mA_n];$$

where K denotes the formation constant of M_mA_n. Differentiation of these with respect to x, setting $\dfrac{d[M_mA_n]}{dx}$ equal to zero and elimination of [M], [A] and [M_mA_n] yield:

$$K \cdot C_o^{m+n-1} \cdot r^{n-1} \cdot m^{1-n} \cdot n^{1-m} \cdot ((n+mr)x_{max} - n)^{m+n} = (r-1)^{m+n-1} \cdot (n-(n+m)x_{max}) \quad (1)$$

where x_{max} denotes the value of x which renders $[M_mA_n]$ maximum. The necessary and sufficient condition for x_{max} to be independent of C_o is:

$$((n + mr)x_{max} - n) = (n - (n + m)x_{max}) = 0$$

from which one obtains:

$$x_{max} = \frac{n}{n+m}; \text{ and } C_M = C_A;$$

This means that on mixing equimolar solutions of M and A the concentration of the complex M_mA_n will reach its maximum value at $x_{max} = \dfrac{n}{n+m}$, while on mixing non-equimolar solutions x_{max} will depend on C_o, r and K. Therefore, if x_{max} can be determined experimentally it is possible

(I) to determine the stoichiometric ratio of M and A in the complex from experiments with equimolar solutions, and

(II) to calculate the value of K from experiments with non-equimolar solutions.

It is to be noticed that from the first type of experiments we do not obtain the values of m and n but only their ratio. Their actual values can be obtained from the second type of experiments by trial and error, since only insertion of correct values in (1) will lead to a constant value of K.

The value of x_{max} can be determined experimentally from measurements of the value, P, of a particular physical property of the solutions if, and only if P is of the form:

$$P = s_1 [M] + s_2 [A] + f([M_mA_n]);$$

where s_1 and s_2 are constants. The procedure is to evaluate the difference, Y, between the measured value of P and the value of P calculated under the

assumption of no complex formation. The function $Y = Y(x)$ will show an extremum at $x = x_{max}$. In order to verify this let us evaluate dY/dx:

$$\frac{dY}{dx} = \frac{d[M_mA_n]}{dx} \cdot \left[\frac{df([M_mA_n])}{d[M_mA_n]} - (s_1m + s_2n) \right]$$

It is seen that for well-behaved functions $f([M_mA_n])$

(I) Y will have an extremum at $x = x_{max}$ (except in the trivial case where $Y = 0$ for all x),

(II) if Y has more extrema than the one at $x = x_{max}$, the x values at which these other extrema are found will vary with C_o in the equimolar experiments.

In particular, if $f([M_mA_n]) = k[M_mA_n]$, Y can have only one extremum.

The assumptions made in the above mathematical treatment are the following:

1) Each of the reactants corresponds to one particular formula, $i.\,e.$, the reactants do not partake in equilibria ($e.\,g.$ association, protolysis) other than the one in question;

2) The law of mass action is valid in terms of concentrations;

3) The reactants form only one complex.

Assumption No. 1 will often be justified. In case that an equilibrium of the type $A + bB \rightleftharpoons AB_b$ ($e.\,g.$ A being a base taking up protons) is involved, the treatment will still be valid provided special precautions regarding concentrations are taken [7] (in the example chosen pH must be kept constant).

In order to fulfil condition No. 2 the experiments must be carried out at constant ionic strength or better in a constant salt medium of relatively high concentration. This imposes certain restrictions on the choice of property to be measured, excluding for instance such properties as freezing-point depression and other colligative properties, Faraday-effect, conductivity $etc.$ rendering the accuracy obtainable by these methods too low. Results of early investigations utilizing such properties and neglecting the fulfilment of condition No. 2 must be considered unreliable (experimental proof of this has been given recently [8]). Recent investigations for the most part have been based on measurements of optical density, this being generally considered the most — and probably the only — satisfactory property. Exceptions are Refs.[9,10].

By far the most important limitation is introduced by assumption No. 3, especially since cases where only one complex is formed seem to be rare exceptions *. Failure to meet this requirement is the reason why most of the complexity constants determined by c.v. must be considered erroneous. In order to detect whether the assumption of only one complex is justified in a particular system Job [5] recommended the application of c.v. to the system utilizing the largest possible intervals of C_o and r. It is obvious that the formation of several complexes generally will influence the experimental values of x_{max} in such a way that the calculations will not lead to a constant value of K. If a constant value of K is obtained this therefore according to Job can be taken as a criterion for the justification of the assumption. An example will show how

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* This and the following discussion do, of course, not apply to systems in which the highest complex formed is MA. In such cases the application of c.v. has sometimes proved successful [11].
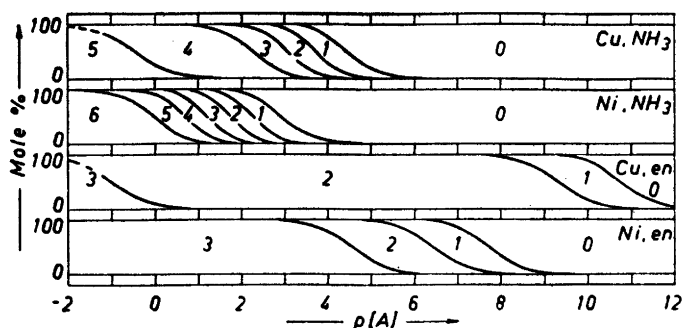
Fig. 1. Ranges of existence for the systems Cu^{++}, NH_3; Ni^{++}, NH_3; Cu^{++}, *en; and*
Ni^{++}, *en.*

The constants for Cu^{++}, en have been taken from Bjerrum and Nielsen[24], the others from Bjerrum[12]. The symbols 0,1,...6 designate the species M,MA...MA$_6$. The abscissa is p[A] = —log [A] and for concentrations higher than $\sim$ 1 M an activity function of the free amine (see Refs.[12, 24]).

this procedure in some cases has led to erroneous conclusions due to the fact that the largest experimentally available intervals in C_0 and r were not sufficiently large or were not employed.

Job[5] applied c.v. to the system cupric nitrate-ammonia measuring the optical density of the mixtures at 615 mμ. Experiments with equimolar solutions were carried out at C_0 values between 0.05 and 0.20 mole/l, yielding x_{max} = 0.80. Consideration of the ranges of existence for the consecutive cupric ammine complexes (Fig. 1) indicates that in the equimolar experiments almost the total content of cupric ions was employed in the complex $Cu(NH_3)_4^{++}$ at x = 0.81—0.82 this complex having a concentration of 0.18—0.19 C_0, while for instance at x = 0.50 the cupric ions were distributed approximately as follows: 0.12 C_0 Cu^{++}, 0.25 C_0 $Cu(NH_3)^{++}$ and 0.12 C_0 $Cu(NH_3)_2^{++}$, the total concentration of complexes being approximately 0.37 C_0. Since the lower complexes have considerably smaller extinction coefficients at 615 mμ than the cupric tetrammine ion, it is to be expected that the maximum in Y will occur close to x = 0.80 indicating the formation of this complex only.

If lower values of C_0 had been used, deviations would have been found. Performing experiments at C_0 = 0.00102 mole/l in order to check this, the present author has found a little pronounced maximum in the Y curve at x = 0.67 (see Fig. 2, curve I).

In the experiments with non-equimolar solutions Job varied C_{NH_3} between 0.2 and 1.0 mole/l and r between 5.4 and 102. Under these circumstances the position of the maximum in Y will essentially be determined by the formation of the cupric tetrammine ion yielding satisfactorily constant, but quite erroneous values of K (log K = 9.3, correct value log K = 13.4, extrapolated from data in Refs.[12, 13]).

If values of r smaller than 4 and low values of C_0 had been employed, deviations would certainly have been found. Fig. 2 shows two experiments by the present author. Curve II represents measurements in which C_0 = 0.0102
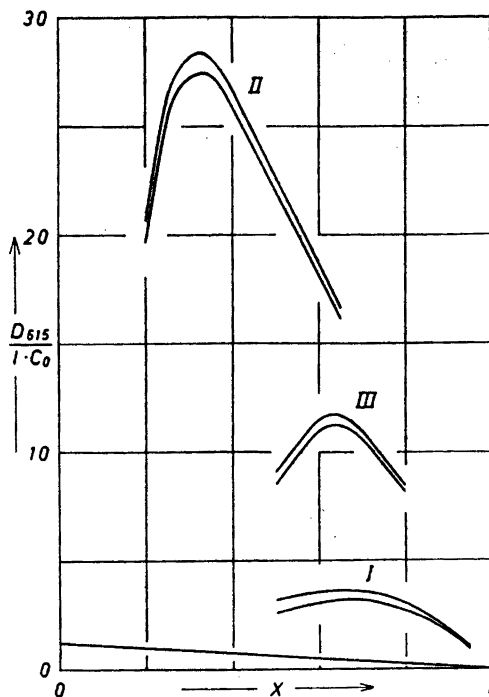
Fig. 2. Continuous variation experiments on the system Cu^{++}, NH_3 in 2 M NH_4NO_3.

The ordinate is the optical density of the solutions at 615 mμ divided by the cell length, l, in cm and by the molar concentration of the Cu^{++} stock solution, C_0. The straight line represents the extinction due to the cupric ions under the assumption of no complex formation. In each pair of curves the upper curve connects the experimental points while the lower curve is the Y-curve.

	C_0	r	l	x_{max}
I	0.00102	1	10	0.67
II	0.0102	10.3	2	0.33
III	0.0102	2	5	0.64

The measurements were carried out by means of a Beckman DU spectrophotometer with photomultiplier attachment which was kindly put at my disposal by Professor M. Kilpatrick at Illinois Institute of Technology.

mole/l, r = 10.3, whereby x_{max} = 0.33 and log K = 9.89 which is still in fairly good agreement with Job's value. When decreasing values of r are employed the maximum of the curve moves towards higher x values and should, if the assumption of only one complex were correct, reach $x = 0.8$ at r = 1. However, at C_0 = 0.01 mole/l the lower complexes become more important so that the maximum is found at an increasing distance to the left of the expected position as r → 1. As a result of this the term $((n+mr)x_{max} - n)$ in (1) decreases so as to reach zero at a value of r greater than one and then becomes negative.

Curve III represents measurements at $C_o = 0.0102$ mole/l, $r = 2$ whereby $x_{max} = 0.64$ which renders the meaningless value of $K = -8.8 \cdot 10^{10}$.

While thus the procedure actually can give the information that the assumption of one complex only is not justified in this case, it is seen that the variations in C_o and r employed by Job were not sufficiently large to reveal this. Similar criticism may be directed towards several c.v. investigations, e. g. Refs.[14, 17].

The uncertainty always present as to whether condition No. 3 is fulfilled is a very serious weakness of this application of c.v. which renders the results so obtained quite inconclusive. Different methods for the calculation of the complexity constant have been suggested [2, 6, 10, 11, 18]. None of these, however, remedies the difficulty elucidated in the above example.

FORMATION OF CONSECUTIVE COMPLEXES ACCORDING TO

$$M + nA \rightleftharpoons MA_n; \qquad MA_n + pA \rightleftharpoons MA_{n+p}; \qquad MA_{n+p} + qA \rightleftharpoons MA_{n+p+q};$$

C.v. was first applied to cases of this kind by Vosburgh and Cooper [1], and the most general treatment has been given by Katzin and Gebert [19] who confining themselves to the measurements of optical densities (or any other property depending linearly on the concentrations of M and the complexes) derived the conditional equation:

$$\frac{x_{max}}{1-x_{max}} = n + \frac{p[(e_2 - e_o)c_2 + (e_3 - e_o)c_3] + q(e_3 - e_o)c_3}{(e_1 - e_o)c_1 + (e_2 - e_o)c_2 + (e_3 - e_o)c_3} \cdot \left[1 + \right.$$
$$\left. \frac{n(c_1 + c_2 + c_3) + p(c_2 + c_3) + qc_3}{C_o(1-x_{max})} \right] - \frac{p(p+n)(c_2+c_3)+q(q+n+2p)c_3}{C_o(1-x_{max})} \qquad (2)$$

in which x_{max} indicates such values of x for which the Y function has extrema, $e_o,...e_3$ indicate the molar extinction coefficients of M and the complexes MA_n, MA_{n+p} and MA_{n+p+q}, and c_1, c_2, c_3 the molar concentrations of the same complexes, while C_o is the concentration of the equimolar solutions of M and A being mixed.

From (2) the conditions for the x values rendering c_1, c_2 and c_3 maximum are obtained by inserting $e_1 \neq e_o$, $e_2 = e_3 = e_o$ and so on as follows:

$$\frac{x}{1 - x} = n - \frac{p(p+n)(c_2 + c_3) + q(q+n+2p)c_3}{C_o(1-x)} \qquad (3)$$

$$\frac{x}{1 - x} = (n + p) + \frac{npc_1 - q(n+p+q)c_3}{C_o(1-x)} \qquad (4)$$

$$\frac{x}{1 - x} = (n + p + q) + \frac{n(p+q)c_1 + q(n+p)c_2}{C_o(1-x)} \qquad (5)$$

(3) and (4) being identical with those derived by Vosburgh and Cooper [1] for the case of two complexes only (insertion of $c_3 = 0$):

$$\frac{x}{1 - x} = n - \frac{p(p+n)c_2}{C_o(1-x)}; \qquad \frac{x}{1 - x} = (n+p) + \frac{npc_1}{C_o(1-x)}$$

These equations make possible an approximate calculation of n and p in cases where the values of the consecutive complexity constants warrant the assumption that c_1 is small when c_2 is maximum and vice versa, provided the corresponding x values can be determined experimentally.

On differentiation of the Y function for the case of two complexes:

$$Y = e_0c_0 + e_1c_1 + e_2c_2 - C_0(1 - x)e_0$$

and of the equation

$$c_0 = C_0(1 - x) - c_1 - c_2$$

with respect to x and combination of the results one obtains

$$\frac{\mathrm{d}Y}{\mathrm{d}x} = (e_1 - e_0)\frac{\mathrm{d}c_1}{\mathrm{d}x} + (e_2 - e_0)\frac{\mathrm{d}c_2}{\mathrm{d}x} \tag{6}$$

Depending on the sign of the two parentheses, Y may have one or two extrema the positions of which generally bear no simple relation to the composition of the complexes.

However, by a suitable choice of the wavelengths at which the measurements are carried out, it becomes possible in some cases to obtain valuable information.

a) If the wavelength can be so chosen that one of the parentheses in (6) vanishes (e. g., $e_2 = e_0$, $e_1 \neq e_0$) Y will assume its extremum value at the x value which renders one of the complex concentrations maximum (in the example mentioned c_1).

b) If $e_1 = e_2$ the extremum condition for Y reduces to

$$\frac{\mathrm{d}c_1}{\mathrm{d}x} + \frac{\mathrm{d}c_2}{\mathrm{d}x} = 0$$

Provided the consecutive complexity constants have sufficiently high values this will take place at an x value close to that at which $\frac{\mathrm{d}c_1}{\mathrm{d}x} = 0$ ($\frac{\mathrm{d}c_2}{\mathrm{d}x}$ still being small in this range).

c) If $e_2 \gg e_1 > e_0$ and the consecutive constants are high, Y will continue to increase after c_1 has reached its maximum. Letting Y_1 denote the difference between the experimental value of P and the value calculated under the assumption that all M is converted into MA_n at $x/(1-x) = n$ and that MA_n does not react further with A, and keeping in mind that the high values of the consecutive constants mean that c_0 will be vanishingly small when c_2 assumes considerable values, we obtain the following maximum condition for Y_1:

$$(e_2 - e_1)\frac{\mathrm{d}c_2}{\mathrm{d}x} = 0$$

Y_1 consequently will have its maximum at the x value that renders c_2 maximum.

In cases where more complexes are formed a discussion similar to the above can be carried out, still under the assumption that the consecutive

constants are high enough so that it is possible to divide the Y curve into intervals in each of which one or more of the concentrations may be neglected.

The choice of wavelengths in accordance with the above requirements is usually made in the way suggested by Vosburgh and Cooper, namely as follows. Solutions containing M and A in ratios such as $C_M/C_A = 1:1, 1:2, ..., 1:6$ are made up and their spectra recorded. It is assumed that these spectra then constitute close enough approximations to the spectra of the complexes of the corresponding composition as to permit the determination of wavelengths fulfilling conditions of the types mentioned in a), b) and c). A somewhat different approach has been employed by Underwood, Toribara and Neuman [20] but the fundamental assumption is the same.

The usefulness of c.v. in this form has been very differently estimated by different authors [7, 8, 21-24]. We shall undertake a closer examination of the general validity of the assumptions involved.

Let us first direct our attention towards the assumption that the consecutive constants are of sufficiently high values to make the above treatment valid. This assumption is also involved in the methods by which suitable wavelengths are chosen. Before attacking this problem it is appropriate to stress a fact that has mainly been emphasized by N. Bjerrum [25] and J. Bjerrum [12], namely that the distribution of the central ion on the different complexes in a given solution is determined solely by the free ligand concentration. In accordance with this conception the conditions in the solutions under consideration can be very conveniently represented by graphs similar to those in Fig. 1.

Considering such graphs we observe two important facts. In the first place, the initial concentrations of the solutions employed should be high enough to keep the complex under consideration at a high degree of formation. For example, in a solution in which $C_{Ni^{++}} = 0.5$ and $C_{NH_3} = 3.0$ the Ni^{++} will not for the most part be present as the 1:6 complex but will be distributed approximately as follows: 50 % $Ni(NH_3)_5^{++}$, 25 % $Ni(NH_3)_6^{++}$ and 25 % $Ni(NH_3)_4^{++}$. At least four times as concentrated solutions must be used in order to make the 1:6 complex prevail. In picking wavelengths it would therefore be wise to examine whether the spectra recorded for the 1:1, 1:2 ... solutions vary considerably with the total concentration. Such examinations have in general not been published in c.v. investigations.

We observe further that in order to justify the above treatment the ranges of existence must be wide enough (the consecutive constants high enough) so that the most part of the central ion can be present in the form of the particular complex under consideration at some appropriate value of the free ligand concentration. As is seen from the graphs this is not always the case. In fact, very often not more than 50 % of the content of central ion can be present in the form of one particular complex at any value of the free ligand concentration. In the case of bi- and poly-dentate ligands the assumption is frequently valid, but in the investigation of unknown systems it is obviously not safe to make predictions regarding these conditions.

In view of these observations it is readily explained why c.v. in many cases has rendered incomplete results. For if the assumptions are not correct, c.v. plots will in general still show maxima, but the interpretation of such data

is apt to lead to unreliable results. An example is the investigation of the cupric-ammonia system by Vosburgh and Cooper [1], to which both of the above objections are valid.

In some cases difficulties of a different nature may arise. The mathematical treatment remains valid if M or A partake in protolytic equilibria provided pH is held constant (see p. 301). It breaks down, however, if polymerizations are involved. Not only will the x values rendering the Y functions maximum be displaced, but if the polymerization products are coloured this may further influence the results. Caution is therefore necessary in cases such as for instance the one referred to by Martell and Calvin [3] as simple and clear-cut, namely the investigation of the uranyl-sulfosalicylate system by Foley and Anderson [26], in which polymerization and hydrolysis of the uranyl ion are likely to take place at the higher pH values.

In recent work [19,27,35] Katzin and co-workers have utilized the light absorption in the ultraviolet of some ligands (NO_3^-, SCN^-) in c.v. experiments. While Beer's law usually holds within the experimental error for transition metal ions in aqueous solution, the optical density of for instance nitrate solutions is not proportional to the formal nitrate concentration. It appears reasonable to expect that the formation of ion pairs or similar aggregates of ions in which the distance between the ions is small will influence the spectra of the ions involved, and more so the less solvated and the more polarizable the ions. In organic solvents of low dielectric constant such interaction is likely to take place to a higher degree than in water. The spectral behaviour of the colourless anions in aqueous and organic solutions is not very thoroughly investigated but at least the spectrum of the nitrate ion appears to be dependent to a considerable degree on the surroundings. Such phenomena may seriously affect the validity of the assumptions involved in c.v., and it is suggested that the validity of Beer's law for the species in question be tested whenever c.v. is extended to fields where this is not already well established.

COMPARISON BETWEEN C. V. AND J. BJERRUM'S METHOD OF CORRESPONDING SOLUTIONS

Finally attention should be called to the fact that another purely optical method of similar experimental simplicity is available for the solution of problems of the type to which c.v. is generally applied, namely J. Bjerrum's method of corresponding solutions [28]. This method may be applied to systems in which complexes of the type MA_n are formed by reversible step reactions, the only condition for the application being that the spectra of the species M, MA ... MA_n are different.

Two solutions (referred to by subscripts 1 and 2) of different total concentrations of M and A are said to be corresponding if:

$$\bar{n}_1 = \bar{n}_2, \text{ and therefore } [A_1] = [A_2],$$

where $\bar{n} = \dfrac{C_A - [A]}{C_M}$ is the formation function. Procedures for finding corresponding solutions have been devised [28]. Since C_{A1}, C_{A2}, C_{M1} and C_{M2} are known it is possible to calculate [A] and n so that each pair of corresponding

solutions yields one point of the formation curve. When the formation curve has been determined the complexity constants may be calculated by standard procedures [30] assuming that all the steps MA ... MA$_{n-1}$ are represented in the equilibrium. This assumption seems to be of a very general if not universal validity. The fact that the formation curves for some systems may be adequately described in terms of fewer parameters than all of the consecutive complexity constants as pointed out by Wormser [29] does not make the logically more satisfactory and in some cases clearly proven conception of a stepwise formation less probable. If in a particular system some of the steps are not employed this will find its expression in the values of the corresponding constants.

The method of corresponding solutions has been applied to the cupric-ammonia system [28] in which case the results were in agreement with those obtained by other methods, to the cupric-chloride system [31] and to the stepwise formation of aquo metallic ions in alcoholic solution [32]. Olerup has independently applied a similar principle to the ferric-chloride system [33].

The method of the corresponding solutions has two advantages over the method of continuous variations:

(I) When applicable, it furnishes quantitative results in terms of complexity constants.

(II) When not applicable, i. e., when the complexity constants or the extinction coefficients have values which make the experimental accuracy low, this is clearly indicated by the experimental results.

The failure of c.v. in this respect makes it an indicative rather than a conclusive method.

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