Iteration Procedures in Solution Chemistry, with Special Reference to Solubility Measurements

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Iteration procedures are often used in solution chemistry. Under unfavourable conditions, an iteration may diverge, converge only slowly, or converge to give an erroneous result. Such cases are illustrated here by the iterations used in solubility measurements to calculate the free ligand concentration. Divergence implies polynuclear complex formation or serious medium effects.

Improvements of the procedures are suggested as well as methods to check the reliability of the procedure used.

The method of solving simultaneous equations by iteration is applied to many problems in solution chemistry, especially when a small correction is applied to some quantity. If this correction successively grows large, one must consider the possibility that the iteration procedure may eventually fail in giving the correct result. One common example of such an iteration is encountered when complex formation is studied by solubility measurements: The free ligand concentration is often obtained by iteration. In the present paper, this iteration will be discussed in some detail. Limitations and pitfalls will be demonstrated, and possible improvements suggested. The conclusion drawn will in principle be valid whenever an iteration is employed.

SOLUBILITY MEASUREMENTS: VARIOUS ITERATION PROCEDURES

For simplicity only solubility measurements employing a simple salt will be considered, *i.e.*, a salt $ML_y(s)$ formed by the central ion M and the ligand ion L.[1]

The problems arise mainly at the right wing of the solubility curve,[1] where the solubility is high, and where there is an increasing uncertainty about the complexes formed. The discussion will therefore be limited to this part of the curve (slope >0; *cf.* p. 1577).

The following equations apply (Notation, see Ref. 1):

$$[L] = C_L - DS \tag{1}$$

where
$$D = \bar{n} - y = \mathrm{d} \log S / \mathrm{d} \log [L] \tag{2}$$

For many systems, DS is negligible compared with C_L over a wide range of concentration, and thus simply $C_L \approx [L]$. However, with increasing S and D, the difference between $[L]$ and C_L may grow to be considerable. Since $[L]$ occurs in eqn. (2) as well as in eqn. (1), some kind of iteration normally has to be employed in order to find consistent values of D and $[L]$.

If the calculation is performed with the aid of a high speed digital computer the following *numerical iteration* is often employed: Starting with $[L] = C_L$ a first set of stability constants is calculated, and from these, $\bar{n}$ and D (eqn. (2)). These values of D are used to give better valus of $[L]$, and so forth.

In manual calculations the numerical iteration is far too tedious. Instead a *graphical iteration* is usually employed: $\log S$ is plotted *versus* $\log C_L$, C_L being used as a first approximation to $[L]$. The slope of the curve, D_0, is determined and hence $[L]_1 = C_L - D_0 S$. Log S is then plotted *vs.* log $[L]_1$ and the procedure is repeated until $[L]$ and D stay constant. If more than one or two steps are required, the procedure is rather time-consuming. It is also difficult to estimate the slope of a curve with sufficient accuracy.

A *point-by-point iteration*, *i.e.* one in which $[L]$ could be obtained for each point without the repeated plotting of curves, would be an attractive possibility. Such an iteration is possible under certain conditions, as the following deduction will show.

Differentiating eqn. (1) with respect to S one obtains

$$\frac{\mathrm{d}[L]}{\mathrm{d}S} = \frac{\mathrm{d}C_L}{\mathrm{d}S} - D - \frac{\mathrm{d}D}{\mathrm{d}S} S$$

Hence
$$\frac{\mathrm{d} \log [L]}{\mathrm{d} \log S} = \frac{1}{[L]} \left(C_L \frac{\mathrm{d} \log C_L}{\mathrm{d} \log S} - S \left(D + \frac{\mathrm{d}D}{\mathrm{d} \ln S} \right) \right)$$

Inverting gives ($\mathrm{d} \log S / \mathrm{d} \log C_L = D_0$)

$$D = \frac{[L]}{C_L D_0^{-1} - S(D + \mathrm{d}D / \mathrm{d} \ln S)}$$

or, since $[L] = C_L - D S$

$$D = \frac{C_L / S - D}{(C_L / S) D_0^{-1} - (D + \mathrm{d}D / \mathrm{d} \ln S)} \tag{3}$$

For iteration purposes:

$$D_{n+1} = \frac{C_L / S - D_n}{(C_L / S) D_0^{-1} - (D_n + \mathrm{d}D_n / \mathrm{d} \ln S)} \tag{4}$$

Thus, D_0 is first determined from a plot of $\log S$ *vs.* $\log C_L$. D is then obtained by eqn. (4). Finally, $[L]$ is calculated by eqn. (1).

The usefulness of this procedure is somewhat limited by the term $dD/d \ln S$ in eqn. (4) representing the change of the slope of the solubility curve. However, in the part of the curve considered here (see above) this change is small compared with D and is of course negligible if D is constant, e.g., when the complex formation is complete.

Neglecting $dD/d \ln S$, the point-by-point iteration has been applied to $Bi^{3+} - Cl^{-}$ data,[2] yielding values of D and [L] not significantly different from those obtained by graphical iteration. (Table 1. The highest values of S were not included in Ref. 2.) The convergence was in most cases very rapid.

Table 1. Solubility data on the bismuth chloride system at $C_H = 1$ M (see Ref. 2). S is corrected for the change in $[H^+]$. The slope D, as obtained by graphical and point-by-point iteration, respectively.

$\dfrac{C_L}{M}$	$\dfrac{S \times 10^4}{M}$	C_L/S	D	
			graph.	point.
0.020	1.86	107.5	1.4	1.4
0.050	8.98	55.7	2.22	2.17
0.100	41.9	23.9	2.65	2.61
0.150	100	15.0	2.80	2.85
0.200	181	11.0	divergence	

Two interesting questions regarding these iterations now emerge:
a) Does the iteration always converge?
b) If it converges, does it then necessarily give the right values of D and [L]?

The discussion of these problems is best founded on eqn. (4). We shall start by showing, however, that the graphical and point-by-point iterations are equivalent, and thus the conclusions drawn from eqn. (4) are valid also for the graphical method.

Consider two adjacent points, with solubilities S and $S + dS$, respectively. In the n:th cycle of the graphical iteration, the slopes D_n and $D_n + \dfrac{dD_n}{dS} \, dS$, respectively, were found for these points. In cycle number $(n+1)$ we find

$$[L]_{n+1} = C_L - D_n S$$

for the solubility S, and

$$[L]_{n+1} + d[L]_{n+1} = C_L + dC_L - \left(D_n + \frac{dD_n}{dS} \, dS \right)(S + dS)$$

for the solubility $S + dS$.

Hence $d\,[L]_{n+1} = dC_L - \left(D_n + \dfrac{dD_n}{dS} \, S \right)dS$. Then, $\log S$ is plotted vs. $\log [L]_{n+1}$, the slope of the resulting curve being

$$D_{n+1} = \frac{d \log S}{d \log [L]_{n+1}} = \frac{dS}{S} \frac{[L]_{n+1}}{d[L]_{n+1}}$$

or
$$D_{n+1} = \frac{dS(C_L - D_n S)}{S(dC_L - (D_n + dD_n/d \ln S) \, dS)}$$

or
$$D_{n+1} = \frac{C_L/S - D_n}{dC_L/dS - (D_n + dD_n/d \ln S)}$$

Finally we recall that

$$D_0 = \frac{d \log S}{d \log C_L} = \frac{dS}{dC_L} \frac{C_L}{S}$$

Hence

$$\frac{dC_L}{dS} = (C_L/S)D_0^{-1}$$

and thus

$$D_{n+1} = \frac{C_L/S - D_n}{(C_L/S)D_0^{-1} - (dD_n/d \ln S + D_n)}$$

which is identical to eqn. (4).

CONVERGENCE OR DIVERGENCE

The iteration (eqn. (4)) converges if eqn. (3) has a real solution, when solved for D.

Eqns. (1) and (2) are based on two assumptions: absence of polynuclear complexes and absence of medium effects. If these assumptions are valid, then eqn. (3) evidently has a real solution. Put in another way, if we find divergence for some part of the solubility curve we may conclude that polynuclear complexes are formed and/or medium changes seriously affect the activity coefficients. (Naturally, convergence does not prove that the complexes are mononuclear.)

If $dD/d \ln S$ is neglected, eqn. (3) has the solution

$$D = \tfrac{1}{2}(1 + (C_L/S)D_0^{-1} \pm \tfrac{1}{2}\sqrt{(1 + (C_L/S)D_0^{-1})^2 - 4 \, C_L/S} \tag{5}$$

which is real if

$$(1 + (C_L/S)D_0^{-1})^2 - 4 \, C_L/S \geq 0 \tag{6}$$

The unequality (6) is thus the condition for convergence. (See also Fig. 1a−b.) Its use may be illustrated with the solubility data on CuCl(s) given by Ahrland and Rawsthorne.[3] Application of the unequality (6) shows that the iteration should diverge for the points where $C_L > 1$ M ($D_0 = 1.85$; $C_L/S \geq 9.6$ required; $C_L/S = 9.8$ when $C_L = 1.000$; $C_L/S = 8.4$ when $C_L = 1.300$). Divergence is in fact found for values of $C_L > 1$ M. The reason is clear: Other evidence [3] strongly indicates a formation of polynuclear complexes (being significant even at lower C_L). Moreover, as S is growing high, medium effects are to be expected.

On the Bi(III) − Cl⁻ system, divergence was similarly found when $C_H = 1$ M and $C_L \geq 0.200$ M (Table 1). Here, the reason for divergence is not immediately clear. The solubilities, though, had to be corrected considerably for the change in [H⁺] caused by the dissolution of BiOCl, and the uncertainty in this correction may be part of the explanation.

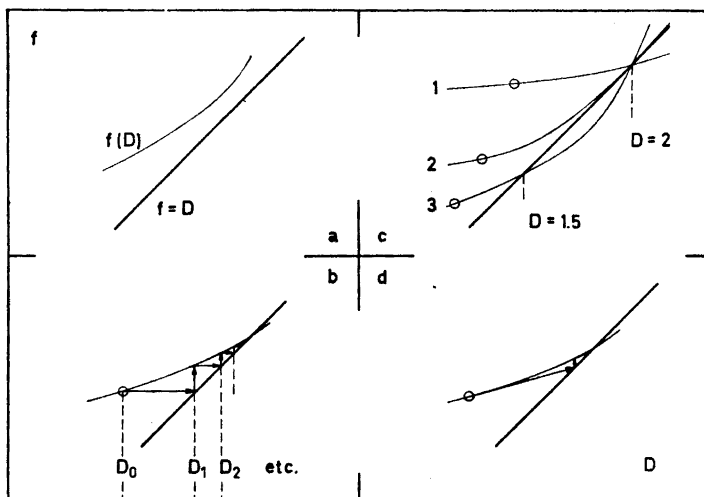In neither of these examples was the neglect of $dD/d \ln S$ of any great importance.

Fig. 1. Curves: the function f (≡right member of eqn. (3)) *versus* D, showing divergence (a) and convergence by eqn. (4) iteration (b) (arrows show the path of iteration); convergence to right or wrong value (below) (c); Newton-Raphson iteration (p. 1578) (d). The circles indicate the start points *i.e.* $D = D_0$.

CONVERGENCE TO WRONG VALUE

Eqn. (3) has two roots. An iteration (eqn. (4)) will converge to one of these roots, and not necessarily to the right one. In an actual case we do not normally know *a priori* which value of D is the right one. The situation is therefore best illustrated by constructed examples.

Consider first a system where one complex dominates in a range of [L], *i.e.* $dD/d \ln S = 0$ in this range. Let, for instance, $D = 2$, implying that $S = K[L]^2$. If a suitable value of the constant K is chosen, one can readily calculate S, C_L, and D_0 for any value of [L]. Fig. 2 shows D_0 and the two roots of eqn. (3) as functions of C_L/S. It can be shown that, under the conditions considered here, an iteration according to eqn. (4) always converges to the lower value of D. Thus (Fig. 2), when $C_L/S \geq 4$, $D = 2$ is obtained, as required, but when $C_L/S < 4$ the iteration gives a value of $D < 2$. Around $C_L/S = 4$ the convergence is very slow. Fig. 1c illustrates the iteration further: when $C_L/S = 7$ (curve 1), $D = 2$ is rapidly obtained; when $C_L/S = 4$ (curve 2) $D = 2$ is obtained but very slowly; when $C_L/S = 3$ (curve 3) $D = 1.5$ is obtained.

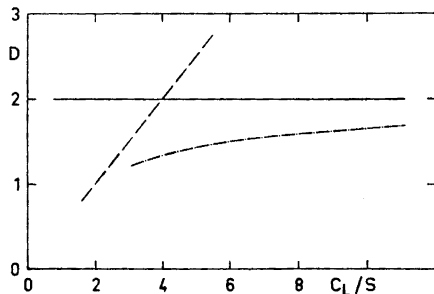*Fig. 2.* $S = 10[L]^2$: D (solid), other root of eqn. (3) (dashes), and D_0 (dots and dashes) *versus* C_L/S.
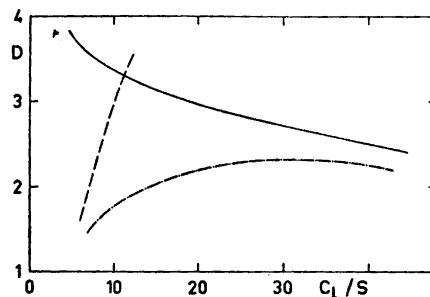

Fig. 3. $S = 1[L]^2 + 1000[L]^4$: D (solid), other root of eqn. (3) (dashes), and D_0 (dots and dashes) *versus* C_L/S.

As another example, we consider a system where D varies. Let, for instance

$$S = 1[L]^2 + 1000[L]^4$$

Fig. 3 shows how D and D_0 vary with C_L/S. The course of the other root of eqn. (3) is also indicated. Again, an erroneous value of D is obtained by the iteration if C_L/S is lower than a certain value (≈ 11 in this example).

As the examples show, the values of C_L/S should not be below the point where the two roots of eqn. (3) coincide. According to eqn. (5), two coinciding roots are obtained when $C_L/S = D^2$, if $dD/d \ln S = 0$ (not far from this value if $dD/d \ln S \neq 0$). Since invariably $C_L/S > D$ (eqn. (1)), the risk of convergence to the wrong root is evidently present only when $D > 1$.

Figs. 2 and 3 show one important feature of the wrong root: its value *decreases* with increasing C_L (decreasing C_L/S) while the right root increases. Since $D = \bar{n} - y$ (eqn. (2)) also $\bar{n}$ would decrease with increasing C_L. This is certainly contrary to expectation, and therefore convergence to the wrong root normally should not pass unnoticed.

Although the limit, $C_L/S = D^2$, has been exceeded in some solubility studies reported in the literature [4-6] the author has not been able to find one where convergence to the wrong root is encountered. When an iteration is attempted, divergence is normally found instead, due to polynuclear complex formation or other reasons (*cf.* above).

CONCLUSIONS

Summarizing, the often used graphical iteration, and the point-by-point iteration described herein, occasionally may diverge, or converge to give erroneous values of D and [L].

The numerical iteration (see above) will probably be more or less sensitive to these risks, depending on the details of the computer program used. For instance, the condition is often imposed that the stability constants be positive. A decreasing value of D is not compatible with this condition, and may thus be rejected.

The point-by-point iteration may be useful for manual calculations, if $dD/d \ln S$ is small compared to D. If a computer is used, an iteration according to eqn. (4) could be a good alternative to the procedures normally used. Since eqn. (4) sometimes results in a slow convergence, a Newton-Raphson type iteration might instead be employed (see Fig. 1d): The steps are taken along the tangent of the curve rather than parallel to the D axis.

As a further alternative, eqn. (3) may be solved *without iteration*. This may, for instance, be done graphically from plots such as those in Fig. 1. (Again, a small $dD/d \ln S$ is required.) Such plots will also show if more than one feasible root exists, if the solution is very sensitive to experimental scatter, etc.

As mentioned, the conclusions drawn herein have in principle general validity. Thus, any iteration may diverge — if the underlying assumptions are invalid — converge only very slowly, or converge to an erroneous value. The risks are greater when the changes in the variables involved are great. A good view of the situation and a check on the reliability of the procedure used can often be obtained from plots similar to those in Fig. 1.

However, it must be emphasized that the best solution of the various problems is to avoid them. Referring again to solubility measurements: when [L] differs appreciably from C_L, [L] should, if possible, be measured directly. If [L] cannot be measured, it is a sound rule to carefully avoid high solubilities.

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Received October 28, 1969.