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# SOLUBILITY MEASUREMENTS AND COMPLEX FORMATION IN SOLUTION

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CONTENTS

## A. INTRODUCTION

### *(i) General*

The measurement of solubility was one of the earliest methods employed to show the existence of complexes in solution, and is still one of the most extensively used methods[1,2]. It seems, however, that the versatility and accuracy of the method has not always been fully appreciated. Also, a lack of familiarity with the equations governing the relationship between solubility and complex formation has sometimes led to bad design of the experiments, to a situation where not all possible information has been extracted from the available data, or even to a misinterpretation of the data. The aim of the present paper is to discuss the various types of salts suitable for solubility study. Equations will be outlined in the more important cases. Some frequently used experimental techniques will be described and commented upon briefly.

Most of the earlier work was obscured by the fact that the variation of the activity coefficients in aqueous electrolyte solutions with the ionic strength was not known. In later studies it was common practice to keep the electrolyte concentrations low, and correct for the activity coefficient variations according to the Debye-Hückel theory. In most of the modern investigations these variations are diminished, usually by maintaining a high and constant ionic strength by the addition of an inert salt, *e.g.* sodium perchlorate or perchloric acid. For a detailed discussion of this subject, see Rossotti[2]. In the discussion that follows, it will be assumed that activity coefficients are kept constant, so that the law of mass action is valid in terms of concentration.

### *(ii) Notation*

Complex formation takes place between a central ion M, and a ligand L. The central ion is usually, but not necessarily, a positively charged metal ion. A complex has the general composition $M_mL_n$, where $m = 1, 2, \ldots$ and $n = 0, 1, 2 \ldots, N$. Often, only mononuclear complexes are formed, *i.e.* $m = 1$ for all complexes. For each complex a stability constant applies (notation follows Ref. 1)

$$\beta_{nm} = [M_mL_n] / [M]^m[L]^n \tag{1}$$

Note that the free central ion ($m = 1$, $n = 0$) is included here, although it is not a complex. Eqn. (1) defines $\beta_{01}$ as 1.

Indexes $m, n, \ldots$ are used to describe the compositions of complexes in solution. Ionic charges are denoted by $i, j, \ldots$ For solid salts, $x, y \ldots$ are used, with the index on M always $= 1$ (*e.g.*, $Sb_2S_3(s)$ is written $ML_y(s)$ where $y = 1.5$).

Unless otherwise stated, the solubility $S$ of a certain salt is defined as the number of moles (formula units) of the salt that dissolve, under the given conditions, in one liter of solution. With the salt written as mentioned, $S$ is normally equal to the total concentration of M in the solution.

### B. SIMPLE SALT

The simpliest application of solubility measurements to the study of complex formation involves the use of a sparingly soluble salt, $ML_y(s)$, formed between the central ion and the ligand. The solubility can be studied as a function of central ion concentration, or more commonly, of ligand ion concentration. Denney and Monk[3] studied the variation of the solubility of barium thiosulphate $BaS_2O_3(s)$ with the barium ion concentration. Leden[4,5] measured the solubility of AgI(s) as a function of $[Ag^+]$ as well as of $[I^-]$. Leden has also performed careful studies of the solubility of AgCl(s) and AgBr(s) in halide solutions[6,7]. Other interesting examples involving ligand ion variation in aqueous solution, are the studies on $SnI_2(s)$[8], on $UF_4(s)$[9], and on HgO(s)[10]. The solubility of AgCl(s) in molten (Na, K)$NO_3$ has been studied by Cigén and Mannerstrand[11].

#### *(i) Equations*

In principle, there is no difference in the mathematical treatment of the two possibilities, variation of [M] or of [L]. Therefore we will only discuss the latter case in detail.

If no complexes were formed, the solubility $S$ would be governed by the solubility product alone

$$K_s = [\mathrm{M}]\,[\mathrm{L}]^y \tag{2}$$
$$S = [\mathrm{M}] = K_s[\mathrm{L}]^{-y}$$

With increasing [L], $S$ would thus be expected to decrease rapidly. The effect of complex formation is to cause $S$ to pass through a minimum, and finally increase at a high [L], where the predominating complexes have a negative charge. If a number of complexes $M_mL_n$ are formed, the solubility is

$$S = \sum_{m,n} m[\mathrm{M}_m\mathrm{L}_n] \tag{3}$$

The ionic charge $i$ of $M_mL_n$ is

$$i = k(n-my) \tag{4}$$

where $k$ is the charge on the ligand ion. Introducing eqns. (1), (2), and (4) into eqn. (3) produces

$$S = \sum_i \left(\sum_m m(K_s)^m \beta_{nm}\right) [\mathrm{L}]^{i/k} \tag{5}$$

This is, or can easily be rearranged to, a polynomial function. From a proper experimental determination of $S$ as a function of [L] it is obviously possible to compute the various prevailing ionic charges $i$, and for each $i$ the numerical value of the coefficient $\sum_m m(K_s)^m\beta_{nm}$. Each value of $i$, however, allows several combinations of $m$ and $n$ (*cf.* eqn. (4)). In other words, solubility measurements of this type do not reveal whether polynuclear complexes are formed or not. (This fact applies also when [M] is varied instead of [L]). Some possible exceptions from this general statement may be mentioned. If the solubility is high, the equilibrium concentration of the ligand differs appreciably from the initially added concentration (*cf.* eqn. (11)). Then, in order to calculate [L] from $C_L$, some assumption has to be made about the $m$ values of the prevailing complexes. The resulting $S$–[L] curve then has to be compatible with the same $m$ values. If such is not the case, these assumed complex compositions have to be ruled out, and some other assumptions tried.

Another possibility is illustrated in the study by Dubey and Ghosh[12] on $Sb_2S_3$(s) in sulfide solutions. They found that the solubility was proportional to $[S^{2-}]$. With our notation, $i/k = 1$, and thus $i = -2$ for the dominating complex. The possible complexes with this charge are $Sb_2S_4^{2-}$, $Sb_4S_7^{2-}$ etc., and it is certainly a good guess to assume that $Sb_2S_4^{2-}$ is the prevailing complex. It is not uncommon also in less obvious cases to assume that the simplest complex is the true one, that is, usually, to assume without rigid proof, that the complexes are mononuclear.

Naturally if the nature of the complexes is known from other studies, the solubility measurements can be used to get values of the constants $\beta_{nm}$. Thus, Leden concluded from potentiometric measurements[13] that $Ag_2I_6^{4-}$ and $Ag_3I_8^{5-}$ were formed at high $[I^-]$. From the solubility of AgI(s), the constants $\beta_{62}$ and $\beta_{83}$ could be determined[5]. Another good idea is to measure the free ligand concentration in the saturated solutions. If [L] differs appreciably from the initial ligand concentration, the nature of the complexes can be judged from this difference (*cf.* eqn. (11)).

If it is assumed or known, that only mononuclear complexes are formed, $m = 1$, equation (5) takes the form

$$S = \sum_{i,n} K_s\beta_n\,[L]^{i/k}$$

or, since $i/k = n-y$

$$S = \sum_n K_s\beta_n[L]^{n-y} = K_s[L]^{-y}X \qquad (6)$$

where

$$X = \sum_n \beta_n[L]^n$$

Thus, $K_sX$ can be experimentally determined as a function of [L]. Hence, the constants $K_s\beta_n$ can be computed with one of the standard methods[2]. If low enough [L] have been used, the free central ion is present to an appreciable extent and $K_s$ ($= K_s\beta_0$) can also be determined[8,11]. If such is not the case, $K_s$ may be determined by other methods[5,14,15]. Finally, knowledge of $K_s$ enables the calculation of the stability constants $\beta_n$.

The formation of mononuclear complexes is usually described by the complex formation function (average ligand number[16]) $\bar{n}$, defined by

$$\bar{n} = (\sum_n n[\mathrm{ML}_n]) \,/\, (\sum_n [\mathrm{ML}_n]) \qquad (7)$$

$\bar{n}$ and $X$ (eqn. (6)) are related by the Bodländer equation[17–19]

$$\frac{\mathrm{d}\log X}{\mathrm{d}\log [\mathrm{L}]} = \bar{n} \qquad (8)$$

Eqns. (6) and (8) give, for mononuclear complexes

$$\frac{\mathrm{d}\log S}{\mathrm{d}\log [\mathrm{L}]} = \bar{n} - y \qquad (9)$$

A corresponding equation in the general case can be derived from eqn. (5)

$$\frac{\mathrm{d}\log S}{\mathrm{d}\log [\mathrm{L}]} = \bar{i}/k \qquad (10)$$

where $\bar{i}$, the average charge, is defined by

$$\bar{i} = (\sum_{m,i} mi[\mathrm{M}_m\mathrm{L}_n{}^i]) \,/\, (\sum_{m,i} m[\mathrm{M}_m\mathrm{L}_n{}^i])$$

Eqn. (10) is also evidently valid when only mononuclear complexes are formed.

### *(ii) Solubility curve*

A plot of log $S$ versus log [L] is called the *solubility curve*, and equation (10) emphasizes the features mentioned above: At low [L], where positively charged complexes dominate $\bar{i}/k < 0$ and the solubility decreases. The minimum is reached when $\bar{i} = 0$, that is when neutral complexes dominate. Finally, at high [L], negatively charged complexes dominate and the solubility increases.

Numerous experimentally obtained solubility curves verify this outline. Fig. 1 shows how the solubility of $\mathrm{SnI_2(s)}$ varies with $[\mathrm{I}^-]$. On the left side the slope is $\approx -2$, showing that $\mathrm{Sn}^{2+}$ predominates at low $[\mathrm{I}^-]$. Complex formation is not completed at $[\mathrm{I}^-] = 1\,\mathrm{M}$; the slope is $\approx +3$, while the limiting complex formed at higher $[\mathrm{I}^-]$ is probably $\mathrm{SnI_8}^{6-}$ or at least $\mathrm{SnI_6}^{4-}$. The concentrations of individual species are indicated. Curves of similar shapes are obtained for the silver

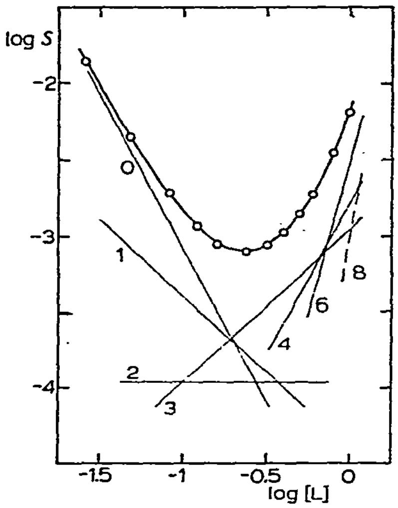

Fig. 1. Curve and circles: Experimentally determined solubilities of $SnI_2$(s) at 25° and 4M ionic strength[8]. Concentrations of individual species, $SnI_n$, are indicated by the straight lines (marked with $n$).

halides[4–7,11,20,21]. Savage and Browne[9] found a more unusual form for the uranium(IV) fluoride solubility curve. The neutral complex $UF_4$ is dominating over a range of $[F^-]$, giving the curve a flat "bottom".

A linear relationship between log $S$ and log [L] indicates that only one species (or species of only one charge) is present in an appreciable concentration.

Occasionally, no negatively charged complexes are formed, and the solubility has no minimum, but approaches a constant value at high ligand concentrations[10].

### *(iii) Computation of* [L]

The equations above require knowledge of the equilibrium free ligand concentration [L], while the solubility is generally measured as a function of the initial concentration $C_L$. If only mononuclear complexes are formed, [L] is then given by

$$[L] = C_L-(\bar{n}-y)S \tag{11a}$$

or, if central ion is added initially

$$[L] = C_L-yC_M-(\bar{n}-y)S \tag{11b}$$

Often, $S$ is so low that $[L] \approx C_L$ (or $C_L-yC_M$). If the difference is appreciable, eqns. (9) and (11) can be used to correct the ligand concentration by iteration[8].

If polynuclear complexes are formed, an equation corresponding to eqn. (11)

can be applied only if $m$ is known. Direct measurement of [L] is preferable in this case[5].

### *(iv) The solid phase*

It is evident that the composition of the solid has to be known exactly, and that it must not change with changing solution composition. The stable bismuth halides at equilibrium with halide solutions of $[H^+] = 1\text{M}$ are BiOCl(s), BiOBr(s) and $BiI_3$(s), respectively[15]. A lack of knowledge of this would obviously lead to an incorrect interpretation of the solubility data.

Changes in the solid phase from one well defined composition to another are usually easily detected, since the change is always accompanied by a break in the solubility curve. Mathematically, the derivative of the solubility curve *decreases* discontinuously. Other types of breaks require some other explanation. There are numerous examples where a sodium salt of the type $Na_xML_y$ (s) is formed at high [L]. The interpretation of the solubility of this type of salt is discussed in section D. Ivanov-Emin *et al.*[22] found a conversion of $Sc(OH)_3$(s) to $Na_3Sc(OH)_6$ at high sodium hydroxide concentrations. Johnston and Leland[23] found a similar change of $Au(OH)_3$(s) to $Na_2HAuO_3$(s). At constant $[Na^+]$ the changes $Tl_2S_2O_3$(s)–$NaTlS_2O_3$(s)[24] and AgSCN(s)—$NaAg(SCN)_2 \cdot 2H_2O$(s)[25], and others have been reported. A sharp break in the solubility curve has also been experienced when $(CH_3)_4NI$(s) was studied[8] in a medium with $[I^-]+[ClO_4^-] = 4\text{M}$. The iodide salt was converted to some salt containing perchlorate, when $[I^-] < 3.3\text{M}$.

The formation of solid solutions is a more serious complication. For instance, if $Ag_2SO_4$(s) is in contact with sodium ion solutions, partial replacement of $Ag^+$ by $Na^+$ in the lattice occurs, resulting in quite anomolous solubilities[26].

## C. SALT CONTAINING ONE AUXILIARY ION

If $ML_y$(s) is too soluble, or for other reasons is unsuitable for solubility measurements, the complex formation between M and L can nevertheless be studied by solubility measurements, if $M'L_y$(s) or $ML'_y$(s) where M′ and L′ are auxiliary ions, are employed. In either case, the solubility can be measured as a function of [M] or of [L]. For symmetry reasons, $M'L_y$(s) *vs.* [L] and $ML'_y$(s) *vs.* [M] are theoretically equivalent, as are $ML'_y$(s) *vs.* [L] and $M'L_y$(s) *vs.* [M]. In practice, however, there are rather wide differences in applicability of the different alternatives.

### *(i) Auxiliary anion*

Solubility studies with an auxiliary anion, and variation of the ligand concentration, are quite common. Sparingly soluble iodates have been used frequently to yield information about the complex formation of metal ions with ligands such as amino acids[27] lactate and hydroxide[3], nitrate and bromide[28]. Bell and George[29] performed a very careful study of $Tl^+$ and $Ca^{2+}$ complex formation with many ligands using the iodate method. Other auxiliary anions employed include[30–33] $Fe(CN)_6{}^{3-}$, $CrO_4{}^{2-}$ and $ClO_4{}^-$.

Complexes with a neutral ligand, notably $NH_3$, can evidently be studied by solubility methods, only if salts with auxiliary anions are employed. Bodländer[19] measured the solubility of AgCl(s) in ammonia solutions at the beginning of this century and found $Ag(NH_3)_2{}^+$ to be the dominating complex. Later, Vosburgh *et al.*[34] used $AgIO_3$(s) and other silver salts, to confirm Bjerrums claim[17] of the existence of $Ag(NH_3)^+$ as an intermediate complex at low $[NH_3]$.

When the solubility of $ML'_y$(s) is studied as a function of [L], the total concentration of either M or L′ can be measured. The following equations apply, if M and L form only mononuclear complexes, and M–L′ or mixed complex formation is negligible

$$K'_s = [M][L']^y \tag{12}$$

$$S = \sum_n [ML_n] = K'_s[L']^{-y} X \tag{13}$$

But

$$[L'] = yS \tag{13a}$$

hence

$$y^y S^{1+y} = K'_s X \tag{14}$$

($X$, see eqn. (6) p. 296).

$K'_s$ can be measured independently, or obtained from the solubility, $S_0$, in L-free solutions, provided M–L′ complexes are completely absent:

$$y^y S_0{}^{1+y} = K'_s \cdot 1 \quad \text{and thus} \quad (S/S_0)^{1+y} = X \tag{15}$$

The slope of the solubility curve (eqns. (8) and (14)) is

$$\mathrm{d}\log S/\mathrm{d}\log[L] = \bar{n}/(1+y) \tag{16}$$

The solubility is monotonically increasing with increasing [L] (*cf.* p. 297). From experimentally determined solubilities, $X$ and hence the stability constants can be determined.

*Polynuclear complexes; M–L′ or mixed complexes.*—The system can be checked for polynuclear as well as for M–L′ complexes or mixed complexes of the type $M_mL_nL'_p$, by varying $C_M$ or $C_L$, keeping [L] constant. If polynuclear complexes $M_mL_n$ are formed, but no M–L′ or mixed complexes, the total concentration of M is

$$[M]_{total} = \sum_{m,n} m[M_mL_n] = \sum_{m,n} m\beta_{nm}(K'_s{}^m)[L]^n[L']^{-my}$$

At a constant [L], we can write

$$[\mathrm{M}]_{\mathrm{total}} = \sum_{m} K_m[\mathrm{L}']^{-my}$$

where $K_m$ are constants, or

$$[\mathrm{M}]_{\mathrm{total}}[\mathrm{L}']^{y}_{\mathrm{total}} = K_1 + \sum_{m>1} K_m[\mathrm{L}']^{-(m-1)y} \tag{17}$$

The formation of M–L′ or mixed complexes will add further, [L′]-dependent terms to the right hand side of eqn. (17). If extra central ion is added

$$[\mathrm{M}]_{\mathrm{total}} = C_{\mathrm{M}}+S \quad \text{and} \quad [\mathrm{L}']_{\mathrm{total}} = yS$$

If, on the other hand, extra L′ is added

$$[\mathrm{M}]_{\mathrm{total}} = S \quad \text{and} \quad [\mathrm{L}']_{\mathrm{total}} = C_{\mathrm{L}'}+yS$$

In either case, a constant product $(C_{\mathrm{M}}+S)S^y$ or $S(C_{\mathrm{L}'}+yS)^y$ respectively proves the absence of polynuclear as well as of M–L′ or mixed complexes, according to eqn. (17). Ideally, the check should be made over the whole range of [L] employed.

King[30] studied $Cd^{2+}-Cl^-$ complexes by measuring the cyanoferrate ion concentration in $Cl^-$ solutions saturated with $Cd_3[Fe(CN)_6]_2(s)$. In order to check for $Cd^{2+}$–$Fe(CN)_6^{3-}$ complexes, $Cd^{2+}$ was added at a constant $[Cl^-]$. It was concluded that the formation of such complexes was negligible. Haight and Nilsson[35] measured the solubility of $PbSO_4(s)$ in bromide solutions. $[SO_4^{2-}]$ was varied at constant $[Br^-]$, and the results ruled out polynuclear and $Pb^{2+}$–$SO_4^{2-}$ complexes.

It may be noted, that if M and L′ do form complexes, these may be studied separately, and a correction can be introduced in eqn. (14). Thus Wise and Davies[36], when studying the solubility of $Ca(IO_3)_2(s)$ in solutions of various ligands, introduced a small correction for the formation of $CaIO_3^+$. The solubility of CuCl(s) in maleic acid solutions was explained by the formation of $Cu^+$ – maleic acid complexes as well as of $Cu^+$–$Cl^-$ complexes and complexes containing both ligands (Andrews and Keefer[37]).

### *(ii) Auxiliary cation*

Equations corresponding to (12)–(17) can be derived for the case when $M'L_y(s)$ is studied with variation of [M]. Thus, the exact composition of the complexes can in principle be elucidated in this case as well, *e.g.* by variation of $C_{M'}$ or of $C_L$ at constant [M].

Examples of this type of measurement are rather scarce. Li and Lo[38] determined the acidity constant for $HIO_3$ from measurements of the solubility of $AgIO_3(s)$ in $HNO_3$ solutions. Denney and Monk[3] studied the complex formation of many divalent ions with $S_2O_3^{2-}$, by the aid of $BaS_2O_3(s)$. The solubility of AgCl(s) in $Pd^{2+}$ solutions was studied by Burger and Dyrssen[39] and by Grinberg *et al.*[40] Tananaev[41] varied $[Al^{3+}]$ over $CaF_2(s)$ in order to study $Al^{3+}$–$F^-$ complexes. He also went further, and introduced $SCN^-$ ions in the solutions, thus studying $Al^{3+}$–$SCN^-$ complexes using a salt which contained neither ion in the complexes of interest. In a similar way Derr and Vosburgh[42] used $AgIO_3(s)$ to study $Ni^{2+}$–$NH_3$ complexes.

Solubility measurements with an auxiliary cation, $M'L_y(s)$, and variation of [L], are in principle *ligand concentration measurements*. For example, $Tl^{III}$ halide complexes were studied[43] by the aid of AgL(s) solubility measurements (L = Cl, Br). The solubility was assumed to be a function of [L] only, (*cf.* eqn. (6) p. 296), *i.e.* independent of the presence of $Tl^{III}$. Thus, the relationship between $S$ and [L] was determined as outlined in section B in solutions containing no thallium(III). When the solutions then contained $C_M$ M $Tl^{III}$ as well, [L] was found from the solubility of AgL(s), by the aid of the determined relationship. Hence, $\bar{n}_M$, the average number of ligand ions per $Tl^{III}$ ion was easily calculated from

$$\bar{n}_M = (C_L - [L])/C_M \tag{18}$$

A small correction was necessary to account for the silver complexes present in solution. Thus, the M′–L complexity has to be known, for the correction in eqn. (18) as well as for the calculation of [L] in M free solutions according to eqn. (11) (p. 298; $\bar{n} = \bar{n}_{M'}$). Detailed knowledge of these complexes is not necessary, however, if the following treatment of the data is employed. The solubility of $M'L_y(s)$ is plotted *versus* $C_L$ (instead of *versus* [L]) for various (constant) $C_M$ values, including $C_M = 0$ (Fig. 2). For any constant $S$, [L] is constant (but not exactly known) according to eqn. (6) p. 296, provided no polynuclear or mixed complexes are formed. Thus, $\bar{n}_M$ and $\bar{n}_{M'}$ are also constant, and

$$C_L(C_M) = [L] + \bar{n}_M C_M + (\bar{n}_{M'} - y)S$$

describes $C_L$ as a function of $C_M$ at constant $S$. When $C_M = 0$:

$$C_L(0) = [L] + (\bar{n}_{M'} - y)S$$

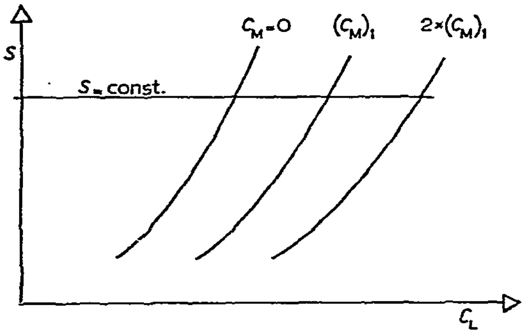

Fig. 2. Solubility of $M'L_y(s)$ for the determination of M–L complexes (see text).

whence

$$C_L(C_M) = C_L(0)+\bar{n}_M C_M \tag{19}$$

and $\bar{n}_M$ is readily calculated without exact knowledge of $\bar{n}_{M'}$ or [L]. This treatment is especially convenient if the solubility is rather high.

The successful use of $M'L_y$(s) requires that its solubility varies rather rapidly with [L]. Strong complex formation M′–L is thus often an advantage in this case.

*Polynuclear complexes.*—Solubility measurements of the type just described, and ligand concentration measurements in general, do not always reveal whether the complexes are mononuclear or not, despite the fact that $C_L$ and $C_M$ can be varied independently. The measured quantity can be written

$$f = \frac{C_L-[L]}{C_M} = \frac{\sum_{m,n} n[M_mL_n]}{\sum_{m,n} m[M_mL_n]}$$

and shows the average of the ratio $n/m$. If for some [L] the value of, say, $f = 2$ is obtained, the complex(es) may be $ML_2$, $M_2L_4$, etc. or a mixture of these. The relative proportions in a mixture of such complexes will change with $C_M$, but $f$ will still be quite independent of $C_M$.

On the other hand, if complexes with different $n/m$ and different $m$ are present, $f$ may vary with $C_M$ at constant [L]. This shows then, that polynuclear complexes are involved. Thus, the absence of polynuclear complexes can hardly be proved, but their presence can occasionally be revealed.

However, if one species of exactly known composition is present to an appreciable extent, the composition and stabilities of the other species can also be elucidated. A systematic variation of $C_M$ and $C_L$ is then required. Notably, if the measurements can be extended to a region where the free central ion is present, methods are available for the characterization of the formed polynuclear complexes from ligand concentration measurements (see Rossotti[2]).

### *(iii) Mixed complexes*

An event bound to interfere with any of the methods in this section is the formation of mixed complexes, M′–M–L or M–L–L′. Mixed complexes with two ligands are quite common. Leden[44] has performed a systematic study of the solubility of AgL(s), L = Cl, Br, in solutions of $NH_3$ and L. The results prove the existence of various complexes containing both ammonia and halide as ligands. Fridman and Sarbaev[45] made a similar study of CuSCN(s) in thiocyanate and iodide solutions, and found mixed $Cu^I$–$SCN^-$–$I^-$ complexes.

When it was attempted to use the AgCl(s) solubility to determine $[Cl^-]$ in $Bi^{III}$ chloride solutions, quite anomalous results were obtained[46]. The best possible explanation seemed to be that chloride complexes containing both $Ag^{I}$ and $Bi^{III}$ were formed.

### D. SALTS CONTAINING THREE DIFFERENT IONS

To enable the investigation of more systems, the solubility of salts containing three different ions can also be studied. In one category are the "double salts" containing two metals, *e.g.* $Na_2Hf(OH)_6(s)$[47], $NaAg(SCN)_2 \cdot 2H_2O(s)$[25], etc. The name double salt alludes to the way of writing them: $2NaOH \cdot Hf(OH)_4$; $NaSCN \cdot AgSCN \cdot 2H_2O$. Often, though, the salts actually contain complex ions. We will refer to this category as $M'_xML_y(s)$. Many such salts have been studied when they have been formed more or less accidentally during the study of simple salts (*cf.* p. 299). Haight *et al.*[8,48–54] have purposely used substituted ammonium salts in an extensive series of solubility studies on post transition metal halide systems. Actinide salts with substituted ammonium ions have been used by Nikolskiĭ *et al.*[55,56].

Numerous "double salts" with a common metal ion exist, but few have been used to study complex formation. Näsänen and Lumme[57] studied $Cu^{II}$ hydroxo-salts: $(Cu^{2+})(OH^-)_{1.5}L_{0.5}(s)$, $L = Cl^-$, $Br^-$ or $\frac{1}{2}SO_4^{2-}$. The results of combined solubility and pH measurements were explained in terms of $Cu^{2+}$–L complexes. The $Bi^{III}$ salts BiOCl(s) and BiOBr(s) have been studied by Ahrland and Grenthe[15], who kept $[H^+]$ high and constant (1 M) in order to avoid hydrolysis and to facilitate the calculations. Yatsimirskiĭ[58], however, measured the solubility of the same salts and varied both $[H^+]$ and [L].

### *(i) Two cations. Equations*

Assume $M'_xML_y(s)$ is studied, *i.e.* the total concentration of M in solution is measured as a function of [L]. A number of complexes $M_mL_n$ are formed, but no M′–L or mixed complexes. Then

$$K_s = [M']^x[M][L]^y$$

and

$$S = \sum_{m,n} m[M_mL_n] = \sum_{m,n} m(K_s)^m\beta_{nm}[L]^{n-my}[M']^{-mx} \tag{20}$$

*Varying M′.*—If no extra M′ is added to the solution, $[M'] = xS$, and there is no way to simplify the general summation. In order to show that this experiment does not reveal polynuclear complexes, we make, for a moment, the approximation that only one complex is present. Then

$$S^{1+xm} = m(K_s)^m x^{-xm}\beta_{nm}[L]^{n-my} = \text{const.}\ [L]^{n-my}$$

Thus, $(n-my)/(1+xm)$ can be determined. However, for each value of this expression, a number of combinations $(m, n)$ are usually possible. This conclusion is also certainly valid in the more complicated situation when many complexes are present at the same time.

However, the values of $m$ can be determined in a separate experiment, by varying [M′] at constant [L]. Then eqn. (20) reads

$$S = \sum_{m,n} K_{nm} \cdot [\mathrm{M}']^{-mx} \qquad [\mathrm{L}] = \text{const.} \tag{21}$$

where $K_{nm}$ are constants. If [M′] and [L] are varied systematically, eqn. (21) can, in principle, be used to determine prevailing values of $m$ as well as of the constants $\beta_{nm}$. However, in the cases where [M′] has been varied at constant [L] only mononuclear complexes have appeared, as proved by the relationship

$$S[\mathrm{M}']^x = \text{const.} \tag{22}$$

Some examples are listed in Table 1. Once it has been established that the complexes are mononuclear, the measurements of $S$ *versus* [L] without additional M′ can be used to determine $n$ and $\beta_n$ for the series of complexes formed. Eqn. (20) is then reduced to

$$S^{1+x} = \sum K_s x^{-x} \beta_n [\mathrm{L}]^{n-y} = K_s x^{-x} X [\mathrm{L}]^{-y} \tag{23}$$

($X$, see eqn. (6) p. 296).

The following equation corresponds to eqn. (9) p. 297

$$\frac{\mathrm{d}\log S}{\mathrm{d}\log [\mathrm{L}]} = \frac{\bar{n}-y}{1+x} \tag{24}$$

When the solubility is not very low, the ligand concentration can be corrected with an equation corresponding to eqn. (11).

*M′–L complexes.*—The presence of M′–L complexes invalidates the data interpretation outlined here. The system M′–L should preferably be studied separ-

TABLE 1

CHECK FOR POLYNUCLEAR COMPLEXES WITH SUBSTITUTED AMMONIUM SALTS, ACCORDING TO EQN. (22). LIGAND CONCENTRATION HELD CONSTANT

| *Salt* | *Product found constant* | *Ref.* |
|---|---|---|
| $[(CH_3)_4N]_3Bi_2Br_9(s)$ | $[(CH_3)_4N^+]^3[Bi]_{tot}^2$ | 52 |
| $[(CH_3)_4N]_3Sb_2Cl_9(s)$ | $[(CH_3)_4N^+]^3[Sb]_{tot}^2$ | 53 |
| $[(CH_3)_4N]SnBr_3(s)$ | $[(CH_3)_4N^+]\,[Sn]_{tot}$ | 51 |
| $[(CH_3)_4N]_2SnI_4(s)$ | $[(CH_3)_4N^+]^2[Sn]_{tot}$ | 8 |
| $M'_2M(NO_3)_6$* | $[M']^2[M]_{tot}$ | 55 |

* M′: various substituted ammonium ions. M: $Th^{IV}$, $U^{IV}$, $Np^{IV}$ or $Pu^{IV}$.

ately. If complexes are formed, a correction can be introduced in eqn. (20). Substituted ammonium ions however have little tendency to form complexes[8].

*Constant M′*.—The equations above become simpler, if [M′] is held constant, as is the case when a sodium salt is formed in a solution of high constant sodium ion concentration[23,24]. Then (from eqn. (20))

$$S = \sum_{m,n} K'_{nm}[\mathrm{L}]^{n-my} \qquad [\mathrm{M}'] = \text{const.} \tag{25}$$

where $K'_{nm}$ are constants. The slope of the solubility curve is thus the average of $(n-my)$, which again (see section B, p. 296) leaves a number of possible combinations $(m, n)$.

However, if a change of the solid phase has been observed, from $\mathrm{ML}_{y'}(\mathrm{s})$ to $\mathrm{M'}_x\mathrm{ML}_y(\mathrm{s})$ for instance, the limiting slopes on both sides of the break can be measured. They are (averages of)

$$a = n-my'$$
$$b = n-my \qquad [\mathrm{M}'] = \text{const.}$$

Hence

$$m = (a-b)/(y-y') \tag{26}$$

and (the average of) $m$ can thus be determined directly, provided the two solid phases have been analyzed. A particularly interesting example is given by Rundcrantz[59] in his study of lanthanide oxalate complexes. The solid $\mathrm{M_2L_3(s)}$ ($y' = 1.5$) changes to $\mathrm{NaML_2(s)}$ ($y = 2$) but the phase change is slow compared to the saturation rate, and it is possible to obtain solubility curves for both solids over practically the whole range of [L] studied. (Fig. 3). If $m$ is constant, eqn. (26) is valid for any [L] and takes, in this case, the form

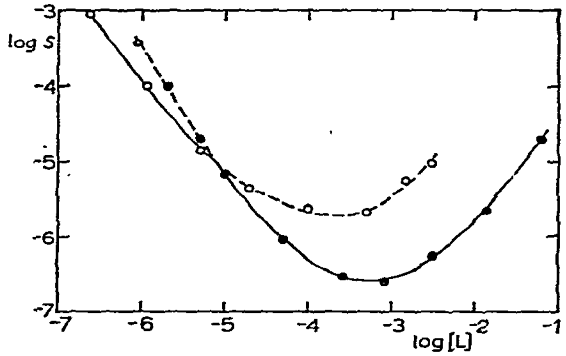

Fig. 3. Europium(III) oxalate system at 20° and ionic strength ≈1 M ([Na$^+$] = 1M). Open circles: $\mathrm{Eu_2(C_2O_4)_3(s)}$. Filled circles: $\mathrm{NaEu(C_2O_4)_2(s)}$. Solid curve: stable phase. Dashed curve: metastable phase. For clarity, several experimental points are omitted. (Solubilities from Ref. 59).

$$m = (a-b)\cdot 2$$

Throughout the range of [L], the difference in the slopes was found to be $\approx \frac{1}{2}$, thus proving that the complexes formed were mononuclear.

### *(ii) Two anions. Equations*

The equations (20)–(26) are directly applicable to measurements of $ML_yL'_z(s)$ as well, if L′ is substituted for M′ and $z$ for $x$. For clarity, we repeat the most important facts.

If no L′-containing complexes are formed, the general expression for the solubility of $ML_yL'_z(s)$ is

$$S = \sum m(K_s)^m \beta_{nm}[L]^{n-my}[L']^{-mz} \tag{27}$$

The ideal approach is to vary both [L] at various constant values of [L′] and [L′] at various constant values of [L]. Then, eqn. (27) gives

$$S = \sum_{m,n} K'_{nm}[L]^{n-my}, \qquad [L'] = \text{const.} \tag{28}$$

$$S = \sum_{m,n} K_{nm}[L']^{-mz}, \qquad [L] = \text{const.} \tag{29}$$

respectively. $K_{nm}$ and $K'_{nm}$ are constants. The variations in $S$ reveal the (average) values of $n-my$ and $mz$, and a complete description of the system is in principle obtainable. If eqn. (29) or other evidence shows that only mononuclear complexes are formed, eqns. (27) and (28) of course take simpler forms

$$S^{1+z} = \sum_n K_s z^{-z}\beta_n[L]^{n-y} = K_s z^{-z}X[L]^{-y}, \qquad [L'] = zS \tag{30}$$

$$S = \sum_n K_n[L]^{n-y} = K'X[L]^{-y}, \qquad [L'] = \text{const.} \tag{31}$$

For BiOCl(s) and BiOBr(s) ($y = 1$) Ahrland and Grenthe[15] knew from emf measurements that no polynuclear complexes were formed. They wrote eqn. (31) in the form

$$S - K'[L]^{-1} = K'X_1$$

where

$$X_1 = (X-1)\,[L]^{-1} = \beta_1 + \beta_2[L] + \ldots + \beta_N[L]^{N-1}.$$

$K'$ was determined separately, and the various $\beta_n$ were computed from the function $X_1$ *versus* [L].

### *(iii) Comparison with previously discussed methods*

The greatest advantages with three ion salts, compared to simple salts, are the increased number of accessible systems, and the possibility of detecting the presence or absence of polynuclear complexes. A disadvantage is the risk that the third ion forms complexes or in other ways interferes with the ions under study. The chance of mixed complex formation is great especially when two anions are present. It is also even more important with three ion salts to know their exact composition over the whole range of solution compositions studied. Thus, for a simple salt, $ML_y(s)$, $y$ is known *a priori*, once it is found that the salt contains only these two ions. For salts $M'_xML_y(s)$ or $ML_yL'_z(s)$, the values of $x$ or $z$, which play a crucial role for data interpretation, have to be determined by direct analysis. This is illustrated by the tetramethylammonium tin(II) halides. The stable salts at equilibrium with chloride[50] and bromide[51] solutions both have the formula $[(CH_3)_4N]SnL_3(s)$ and it would be natural to assume that the iodide salt might have the same formula. However, analysis showed the iodide salt[8] to have the composition $[(CH_3)_4N]_2SnI_4(s)$.

Eqn. (24) indicates one advantage of three ion salts containing two cations. At high [L], the solubility of the simple salt increases very steeply. For instance, the solubility[8] of $SnI_2(s)$ increases with the fourth power of $[I^-]$ or more when $[I^-] > 1$M, with the result that the salt soon can be regarded as "very soluble". The tetramethylammonium ion salt used[8], $[(CH_3)_4N]_2SnI_4(s)$ has a slope $(\bar{n}-4)/3$, or only $\approx 0.5$ at $[I^-] = 1$M, and not more than 1.3 at $[I^-] = 4$M. The solubility of this salt is thus a more convenient, but nevertheless sensitive enough, measure of the complex formation at high $[I^-]$.

## E. SIMULTANEOUS SATURATION WITH TWO SALTS

It is quite a common occurrence that the solubilities of simple salts increase beyond the limits of convenient study at high ligand concentration. $SnI_2(s)$ is, as mentioned, too soluble[8] when $[I^-] > 1$M. The same[5] is true for $AgI(s)$. The solubility of $BiI_3(s)$ is inconveniently high even[15] at $[I^-] = 0.25$M. In most instances, moreover, the situation at high [L] is particularly interesting[8,5,60]. One way to reach higher [L] is to utilize a suitable three ion salt, as described in the previous section. In the bismuth iodide system, solutions were saturated[61] simultaneously with a three ion salt, $[Co(NH_3)_6]BiI_6(s)$, and the ligand salt of the third ion, $[Co(NH_3)_6]I_3(s)$. The total bismuth concentration in solution was measured as a function of $[I^-]$. It turns out, that the solubility curve (see p. 297) has the same shape as that of the simple salt, $BiI_3(s)$, the curve however being displaced to lower solubilities.

Let us denote the simple salt $ML_y(s)$, and the double salt $xM'L_{y'} \cdot ML_y(s)$, the M' salt being $M'L_{y'}(s)$. If a solution is saturated with the two latter salts the two solubility products apply

$$K'_s = [M']^x[M]\,[L]^{xy'+y}$$
$$K''_s = [M']\,[L]^{y'}$$

combined

$$K = [\mathrm{M}]\,[\mathrm{L}]^{y} \tag{32}$$

where $K$ is a new constant. Eqns. (2)–(6) (p. 295) now apply, if $K$ is substituted for $K_s$. Eqn. (9) is exactly the same *i.e.*

$$\frac{\mathrm{d}\log S}{\mathrm{d}\log[\mathrm{L}]} = \bar{n} - y$$

Thus, the solubility curves of $\mathrm{ML}_y(\mathrm{s})$ and that of the described mixture have the same derivatives if the complexes formed are mononuclear.

That the solubility over the mixture is lower than that of $\mathrm{ML}_y(\mathrm{s})$ is obvious from the following consideration. A solution is saturated, at some constant [L], with $\mathrm{M'L}_{y'}(\mathrm{s})$, and [M] is increased until precipitation of either $\mathrm{ML}_y(\mathrm{s})$ or of the double salt occurs. (Only the solubility of the double salt is dependent on the presence of $\mathrm{M'L}_{y'}(\mathrm{s})$.) Obviously, if the solubility of $\mathrm{ML}_y(\mathrm{s})$ were the lower one, the double salt would not be formed at all at this [L]. Thus the condition for the existence of the double salt is that the solubility (= total concentration of M) over the salt mixture is lower than the solubility of $\mathrm{ML}_y(\mathrm{s})$. Because the solubility is lower, the region of convenient measurement is displaced to higher [L]. The solubility over $[\mathrm{Co(NH_3)_6}]\mathrm{BiI_6(s)}$ and $[\mathrm{Co(NH_3)_6}]\mathrm{I_3(s)}$ is lower than that of $\mathrm{BiI_3(s)}$ by a factor $\approx 10^5$, and complex formation can be studied up to $[\mathrm{I}^-] = 4\mathrm{M}$, the limit set by the medium used.

The solubility of $[\mathrm{Co(NH_3)_6}]\mathrm{I_3(s)}$ is very low at high $[\mathrm{I}^-]$, therefore, $[\mathrm{Co(NH_3)_6}]\mathrm{BiI_6(s)}$ reacts as follows

$$[\mathrm{Co(NH_3)_6}]\mathrm{BiI_6(s)} + (n-3)\,[\mathrm{I}^-] \rightarrow [\mathrm{Co(NH_3)_6}]\mathrm{I_3(s)} + \mathrm{BiI}_n{}^{(n-3)-}$$

The solution will thus be automatically saturated with both salts. However, the method works even if the solubility of $\mathrm{M'L}_{y'}(\mathrm{s})$ is higher than that of the double salt, provided a sufficient amount of both salts is added initially to ensure that the solution remains saturated with both.

Compared to three ion salt studies (section D), this two salt method has certain advantages that are important in practice. Weak complex formation between M′ and L does not interfere with the data interpretation outlined here. Only if this complex formation is so strong that the free ligand concentration is affected, is a slight correction necessary. The hexammine cobalt ion does indeed form (outer sphere) iodide compexes[62], but as the solubility of $[\mathrm{Co(NH_3)_6}]\mathrm{I_3(s)}$ is so low, this has no effect whatsoever on the analysis of the $\mathrm{BiI}_n$ system.

Moreover, it is not absolutely essential in this case to know the exact composition of the three ion salt. That is, $x$ does not enter into any of the equations in this section. In fact even if the composition ($x$) changes at some value of [L], the solubility curve will not be affected, since eqn. (32) is valid for both compositions. A phase change will probably, however, result in a slow apparent saturation, especially if the saturator technique is employed (see p. 313).

It may finally be noted that this two salt method could as well be applied with *two* three ion salts, containing the same ions, but in different proportions, that is, with different values of $x$.

## F. EXPERIMENTAL TECHNIQUES

The experimental determination of solubilities usually consists of the following four steps

a) Preparation of the salt.
b) Equilibration salt-solution.
c) Separation salt-saturated solution.
d) Analysis of the saturated solution.

A successful solubility determination requires that all four steps are properly mastered.

### *(i) Preparation of the salt*

In short, the salt should have a known and well defined composition. Different preparations should give the same solubilities, and the solubility should not vary with time. The particles should be of suitable size; small enough to give a rapid equilibration, but not so small that the subsequent separation becomes too difficult.

Some salts are rather sensitive to experimental conditions during their preparation. Iodates are reported[63], for example, to give different solubilities for different precipitation temperatures. Such sensitive salts can of course, with proper care, be used to determine reliable complex constants, while it should be remembered that solubility products and the actual solubilities refer only to specific conditions.

Problems with aging and with too small particles can often be overcome by allowing the precipitate to remain in contact with the supernatant solution for some time[43]. The aging of the solid should of course be checked by periodically repeating the equilibration of some solution and comparing the solubilities obtained.

Although it is more common to prepare the salt in advance, in bulk amounts, many workers form the salt directly during each equilibration, usually by supersaturating the solution. With a preparation in advance, one has more freedom to choose the experimental conditions so that a salt with good properties is obtained. On the other hand, there is always the risk that the prepared salt changes its composition during the subsequent equilibration, making the most careful preparation and analysis meaningless. It is therefore always essential to know the composition of the salt *at equilibrium* with the various solutions studied.

Since an analysis normally requires that the salt has been washed and dried, it may be difficult to analyze the salt without disturbing the equilibrium. Often, though, phase changes are slow, and the salt can be washed with small portions of water without risk. Occasionally the salt can be washed with other solvents than water, *e.g.* ether or ethanol. The salt can be analyzed for two or more of its components without washing, to give the ratio, if excess of these were not added to the solution before equilibration. An example is given in Ref. 8, where $SnI_2(s)$ was analyzed for Sn and I after equilibration with the pure perchlorate medium.

The salt can be analyzed indirectly if the change in the saturated solution of two or more of the components can be measured. Further evidence can be obtained from solubility product relationships[15].

The analysis of the solid phase after every equilibration is thus a difficult as well as timeconsuming task. If it is shown that the composition is the same at both ends of the solubility curve, this is good evidence that the solid has remained unchanged over the whole range studied. A known composition at one point, in connection with a smooth solubility curve (*cf.* p. 299) is also evidence for an unchanged composition. It should be noted, however, that the angle of a break in the solubility curve can be quite small (*cf.* Fig. 3) and may be masked by the experimental scatter. Besides the break in the solubility curve, a phase change may be accompanied by other changes like unusually slow equilibration, or simply a change in colour of the solid. When such indications occur, the possibility of a phase change should be considered.

### *(ii) Equilibration and separation*

Equilibrium between the salt and the solution can be approached from either of two directions, namely, unsaturation or supersaturation. The attainment of equilibrium is usually established when the composition of the solution does not change any more. Ideally, equilibrium should be approached from both directions, and give concurrent results.

The unsaturation approach is more commonly employed and is to be preferred if aging phenomena and other irregularities are to be expected. As mentioned, however, it is useful to use the supersaturation approach occasionally, to check the equilibria. Supersaturation may be attained in a simple way (also with the saturator technique; see below) if the equilibration is started at a temperature where the solubility is higher, and finished at the desired temperature.

The rate of equilibration varies considerably among different salts. Thus, King[30] experienced an almost instant equilibration with $Cd_3[Fe(CN)_6]_2$ in $Cl^-$ solutions. Using a similar technique, Garrett *et al.*[64,65], on the other hand, had to shake the metal oxides studied for several weeks, before the solutions were saturated.

For a certain salt, the rate of equilibration often varies with the composition of the solution. Therefore it is advisable to check the equilibration for all solutions used.

The separation of the solid from the saturated solution should, preferably, be performed at the same temperature as the equilibration. This is especially important when the rate of equilibration is high. On the other hand if the equilibration is very slow, a few minutes' filtration at "room temperature" is certainly without risk.

The complete separation—often a difficult problem, see below—is of special importance when the solubility is at its lowest. If the solubility is *e.g.* $10^{-7}$M, a contamination of $10^{-8}$ g solid in a 10 ml aliquot is sufficient to considerably affect the results.

### (iii) *Equilibration by stirring or shaking*

The most extensively used, and perhaps most natural equilibration technique consists of the agitation of a mixture of solution and solid until equilibrium is attained. The reaction vessel is usually kept in a thermostat and the agitation may be effected by a mechanical stirrer or by shaking or slowly rotating the vessel. Stirring has been used by *e.g.* King[30] and Fridman *et al.*[45]. In molten salt media, equilibration is normally effected by stirring[11,66]. Shaking has been employed by *e.g.* Garrett *et al.*[64,65], Kolthoff and Lingane[67] and workers in this laboratory[15,59,68].

The crucial part of the agitation techniques is not the equilibration itself but the subsequent phase separation. Prolonged agitation, sometimes several weeks, tends to tear the solid into very fine parts. Colloid formation is not uncommon. The behaviour in this respect, however, varies considerably between different solids, and the experimental difficulties vary accordingly.

For the separation, ordinary filtration has naturally been employed frequently[6,64,69]. The use of a filter stick[15] is perhaps the simplest way of performing the filtration at a controlled temperature. Filtration may be facilitated if the solid is allowed to settle (in the thermostat) before filtration[64]. If the sedimentation is rapid and complete, filtration is unnecessary. This simple technique is often used in molten salt media[11,66].

If filtration proves difficult, centrifugation[30,70,71] or ultracentrifugation[72] may be successfully used. However problems with temperature control have been reported[30].

When solutions of low concentrations are shaken in glass vessels, there is a risk that the adsorption on the walls of one or more species affects the stoichiometry appreciably. Kolthoff and Lingane[67], when studying the solubility of $AgIO_3$(s) in neutral salt solutions, found that $Ag^+$ was adsorbed on the glass walls so that $[Ag^+]_{tot} < [_3^-]IO_{tot}$ in the solution. The adsorption was avoided by paraffination.

### *(iv) Saturator techniques*

A rather different approach to the equilibration–separation problem is provided by the saturator technique. A larger amount of solid is then held in a vertical glass tube, usually with a filter at the lower end. The whole saturator is kept in a thermostat. The solution to be equilibrated is run through this bed of solid, and, if the design is good, can be collected at the lower end saturated and filtered at a controlled temperature. Before equilibrating a new solution, the saturator is rinsed with portions of the new solution, which then discarded.

The saturator was first used by Brønsted[73], and later adopted by Davies[74], and is therefore often called a Brønsted–Davies saturator. The name solubility column has also been used[10], because of the principal similarities to *e.g.* chromatography or distillation columns.

The optional size of a column varies widely with the salt used, and has to be determined experimentally in individual cases. Some general features may be mentioned. When solution flows through the bed of solid at a given rate (length units per time unit) the degree of saturation is proportional to the length of the bed. When the bed is long enough to give complete saturation, the flow rate (*volume* units per time unit) may be increased by increasing the cross-sectional area of the bed. Thus from these aspects a long and wide bed of solid is preferable. But besides the fact that a large amount of solid is required, this has the disadvantage that it becomes tedious to rinse the solid when a new solution is introduced. A rather small amount of solid might also be preferred when a radioactive tracer is used in the solid. Moreover, a long bed of fine grained solid may require too high a pressure to force the solution through at a reasonable rate.

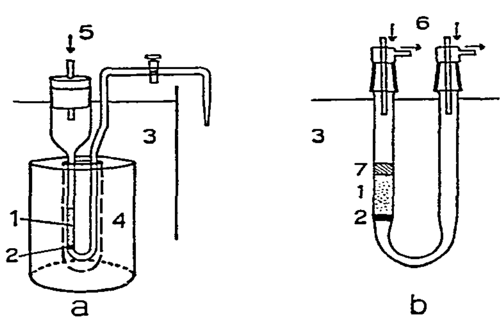

Fig. 4. Saturators used by the author[8,13] for radioactive AgCl (a) and (inactiv $SnI_2$ (b). The tin salt and solution had to be protected against air oxidation.
1. The solid. 2. Fritted glass. 3. Thermostat water. 4. Lead shield. 5. Air pressure. 6. Carbon dioxide. 7. Glass wool.

For one reason or another, therefore, saturators are often designed so that two or more passages of the solution through the solid are required before equilibrium is attained. This may be done with an arrangement similar to that described in Ref. 8 (see also Fig. 4b) the solution being simply pushed back and forth through the solid.

The separation problems are greatly diminished when a saturator is used. While shaking procedures tend to produce fine particles, the opposite tends to be true in a saturator. The finest particles dissolve or are washed away at the beginning with a newly prepared solid. Results which are too high are therefore obtained often with a newly prepared solid[10,43] and the first portions of solution should be discarded.

With a saturator, the result of a single experiment is obtained much faster, compared to shaking—within hours instead of days or weeks. On the other hand, shaking has that advantage that it is easier to equilibrate several samples simultaneously. In the long run, therefore, one technique is not much faster than the other.

With large amounts of fine grained solid in a saturator, the solid may occasionally pack together and develop "channels" for the solution[8]. The natural result is a very slow saturation.

If the composition of the solid phase is changed during the equilibration, the saturator technique is of course less suitable[59].

Both agitation and saturator techniques are well suited for protection against light[43,75], for radiation shielding[43,59], and, as described, for controlled temperature work. Since the solid is kept in one place, the saturator technique is perhaps less hazardous for radioactive work.

### *(v) Analysis of the saturated solution*

The saturated solution can be analyzed using any appropriate method of analysis, and a detailed discussion of this subject is therefore outside the scope of this article.

Methods of analysis frequently employed include gravimetry[5,8,11], volumetry[8] and, for lower solubilities, colorimetry[15,34], polarography[71] and radiometry[5,11,20,21]. By far the widest range of solubilities can be measured with radiometric analysis. Thus Lieser[20] studied the solubility of AgI(s) down to $1.7 \times 10^{-10}$ M with a reported uncertainty of ±6%. The solid was labelled with the $\beta$-emitter $^{111}$Ag.

The possibility that the solubility is affected by the presence of a radioactive tracer has been discussed by some authors[76,77]. Bovington[77] has reported a 10% higher solubility for $BaSO_4$(s) when it was labelled with $^{35}$S, as compared to inactive solid, while $PbSO_4$(s) was unaffected under the same conditions.

### (vi) *Miscellaneous techniques*

Although the vast majority of solubility studies have been performed in the way outlined here, different approaches have occasionally been used which are worth mentioning.

Some workers have equilibrated solutions with a solid in colloidal form and obtained the solubility from the difference in light dispersion before and after equilibration[78,79]. Similarly, the central ion may be added to a ligand ion solution, with powerful stirring, until a Tyndall effect appears[80].

Lietzke and Stoughton[81] mixed known amounts of solid and solution and increased the temperature slowly and with stirring until the crystals disappeared. From many such experiments, solubility isotherms were obtained.

Kinetic techniques have also been employed[77,82]. The rate of dissolution is then studied before the solution is saturated and from a knowledge of the kinetics of the dissolution reaction, the position of the equilibrium is computed. Obviously, special measures have to be taken to make the dissolution rate reproducible. The technique may have certain advantages when the solids studied are not stable[82].

## G. COMPARISON WITH OTHER METHODS*

### (i) *Applicability*

Any method for the study of complex formation in solution is subject to natural limitations of applicability. Thus, potentiometric measurements may be applied to a central ion–ligand system only when a suitable electrode is available, solubility measurements only when a suitable sparingly soluble salt is available, and so forth. Inspection of available data[1] shows that potentiometric measurements of various kinds is, by far, the most extensively used method. However, as is evident from the discussion in previous sections, the solubility method can be applied in many different ways, a fact which renders the method quite a wide applicability.

The applicability of various methods is also dependent on the type and degree of the complex formation to be studied. Solubility measurements can be applied to the study of both weak and strong mononuclear complexes, while the applicability of the method is more limited if polynuclear complexes are also formed.

While the formation of sparingly soluble salts is required for the solubility method, such a formation often limits the applicability of other methods. Potentiometric methods, for instance, often require that the (total) concentration of the

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* A thorough survey of the methods available is given in Ref. 2.

measured species is above a certain minimum, before reliable potentials can be obtained. Solvent extraction or ion exchange methods on the other hand, normally also work well at very low concentrations.

### *(ii) Accuracy*

By *accuracy* we mean the closeness of the finally computed quantities—complex compositions and constants—to the true values. Accuracy in this sence requires good *reproducibility* of the experimentally measured quantities. On the other hand, good reproducibility does not always imply accuracy. Thus, systematic errors may occur in the finally computed quantities, as a result of, *e.g.*, systematic errors in the measurements, or overlooked chemical complications. The uncertainty (random error) of the finally computed quantities is increased if the sensitivity of the experimental method is low, or if the computations are intricate.

The possibilities of chemical complications, *i.e.* reactions besides the complex formation under study, must always be investigated carefully. It is always an advantage if the method used introduces few extra chemicals to the solution. From this aspect, the simple salt solubility method (section B) is more attractive than the solubility methods described in sections C–E. Glass electrode measurements and various non-thermodynamic, *e.g.* spectrophotometric, methods can similarly be regarded as "clean".

A method can be said to have a high *sensitivity* if the change in the experimentally measured quantity is big, when the complex formation proceeds. One factor important for the sensitivity is the degree of directness of the method. For instance, any method involving ligand concentration measurement may be regarded as indirect, and may have a very low sensitivity (if $C_M$ is low compared $C_L$; *cf.* eqn. (18) p. 302). The method discussed on p. 302 and *e.g.* glass electrode studies of systems with weak bases as ligands are also ligand concentration measurements.

The sensitivity of more direct methods of thermodynamic character (potentiometric, solubility methods, etc.), is usually satisfactory. It may be noted, though, that an electrode involving, say, three electrons, like $Bi(Hg)/Bi^{3+}$, is less sensitive than an electrode involving one electron, *e.g.* a glass electrode, other factors being equal. Similarly, a three ion salt may be less sensitive than a simple salt. For instance[8], the sensitivity of $[(CH_3)_4N]_2SnI_4(s)$ is less than that of $SnI_2(s)$ by a factor 3 ($= (1+x)$ in eqn. (24) p. 304), for measurements in the same region of [L].

Methods involving measurement of non-thermodynamic quantities may vary considerably in sensitivity. Thus, if the different complexes formed have very similar spectra, the spectrophotometric method is not very sensitive.

If the various systematic errors are properly mastered, different methods can at least to some degree be compared in terms of reproducibility.

The reproducibility of solubility measurements is often of the magnitude of 1 %, occasionally better (see, *e.g.*, Refs. 29 and 61). The reproducibility is dependent on the analytical procedure used, and may often be improved, if this procedure is refined.

Other methods, also involving the determination of total concentrations, *e.g.* solvent extraction and ion exchange methods, have a comparable reproducibility.

With a potentiometric method, 1% corresponds to *ca* 0.3 mV (for an electrode involving one electron). Glass electrode measurements, for instance, may give better reproducibility, while many metal electrodes, on the other hand, can be reproduced only within 1 mV.

To conclude, solubility measurements may be considered as comparable to any other method for the study of complex formation, with regard to accuracy, and is second only to potentiometric measurements, with regard to applicability.

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