PREFACE

SCOPE OF THE VOLUME

This volume deals with the solubilities of the sulfites, selenites and tellurites of the alkali metals and ammonium, the alkaline-earth metals, and manganese, iron, cobalt, nickel, copper, silver, zinc, cadmium, mercury and lead. Solubility data for binary systems and for all types of multicomponent systems are included. In all systems, one of the solvent components is water; therefore in the few cases where solubilities in other solvents are given, the systems are treated as aqueous multicomponent systems.

NOMENCLATURE

According to the fully systematic IUPAC nomenclature (1), sulfite is sulfate(IV) [or strictly trioxosulfate(IV)], pyrosulfite is disulfate(IV)(2-) or disulfite, selenite is selenate(IV), tellurite is tellurate(IV), etc. The systematic names have not been used in the text, because the trivial names are well-established ones, and are less likely to be misunderstood. Some of these trivial names are IUPAC "accepted names" (1), but others, such as tellurite, are not.

GENERAL COMMENTS

The literature has been covered up to 1984, and as far as we are aware the entire literature has been covered. However, the editors will be grateful if any omissions are brought to their attention, so that they may be included in any updates to the volume.

The solubilities of hydrated compounds are always given in terms of the unhydrated components. When solubility data in the literature were expressed in units of mass % (% w/w in the older literature) or related quantities, or when amount-of-substance concentrations were reported together with the densities of the solutions, conversions to molality (units - mol kg^{-1}) were made by the compilers/evaluators, with use of IUPAC-recommended atomic masses. In many of the compilation sheets, the molalities have been calculated by computer, and expressed in a uniform format with three figures after the decimal point. This sometimes has resulted in the appearance of too many significant figures. We ask the reader to forgive this time-saving device. In the evaluations, the correct number of significant figures is always given.

Phase diagrams are presented for as many as possible of the ternary systems, and also for some quaternary ones. Many of these were plotted by computer from the original data, irrespective of whether or not figures were provided in the original papers. All the computer plots were produced to a uniform format; this means that the diagrams may be superimposed for comparison purposes. For the sake of clarity, the axes are not labelled with numbers; in all cases the scales indicated by the tick marks run from 0 to 100 on each axis, and the units are mass %. For some systems, the phase diagrams given in the original papers are reproduced with the permission of the relevant copyright holders.

For "soluble systems", most of the solubility data are expressed in units of mass %, and conversions were made as stated above. For "sparingly soluble systems", analyses are usually reported as amount-of-substance concentrations, and the actual solubilities are expressed as solubility products, or in terms of other forms of equilibrium constants.

The solubility products quoted are usually analytical "concentration solubility products". Otherwise, definitions like "activity solubility product" or "solubility product based on the activities" or "concentration solubility product, corrected for hydrolysis effects" are given. Only rarely have "thermodynamic" constants been obtained, and usually conditions were insufficiently well defined to allow calculation of thermodynamic constants from the corresponding concentration constants by making activity corrections. The nomenclature used for solubility product constants and other equilibrium constants is that of the IUPAC "Orange Book" (2); otherwise, a definition is provided.

ERRORS

Errors have been expressed in various ways, depending on the information provided in the original paper. Whenever possible, an estimated value of the standard deviation, *s*, of the analyses is given, as recommended in the "Orange Book" (3).

EXPERIMENTAL METHODS

In the most common method for determination of solubility, aqueous solutions or pure water are saturated with one or more solid component(s) under isothermal conditions, and after equilibrium is reached, the compositions of the solutions and of the solid phases are determined analytically. This "isothermal method" is also referred to as the "saturation method" in this volume.

A procedure referred to very frequently is the "remainders" or "wet residues" method of Schreinemakers, which was originally described in 1893 (4). This indirect method for determination of compositions of solid phases involves the analysis of solid plus adhering mother liquor, followed by plotting on the phase diagram, and extrapolation of the line joining the solution-composition point to the wet-solid-composition point. When several such lines are drawn, they should intersect at the point corresponding to the composition of the salt. A fuller description is given by Findlay (5).

All the anions discussed in this volume are anions of weak acids. Thus, for H_2SO_3, $pK_{a1} = 1.8$, $pK_{a2} = 6.8$; for H_2SeO_3, $pK_{a1} = 2.6$, $pK_{a2} = 8.3$; for H_2TeO_3, $pK_{a1} = 6.1$, $pK_{a2} = 9.6$; etc. Therefore, any solution of a salt will undergo hydrolysis to some extent. Generally, this is neglected with the "soluble systems", but with the "sparingly soluble systems", hydrolysis can have a considerable influence on the equilibria, and ought to be taken into account. Where authors have not considered the effect of hydrolysis, or where the calculations have been made in a manner that appears to be incorrect, the compiler has attempted to remedy matters.

The methods used to deal with the quite complicated equilibria are those of Ringbom (6), involving the concepts of "conditional constants" and "side-reaction coefficients".

The conditional stability constant β_n' for a mononuclear metal-ligand complex is, in general form:

$$\beta_n' = \frac{[ML_n]}{[M'][L']^n} \tag{1}$$

where [M'] and [L'] are the "conditional concentrations" of metal and ligand. That is, [M'] is the total concentration of metal ion that has not reacted with the main ligand L, including any bound as hydroxo-complexes; and [L'] is the concentration of ligand L not bound to M, whether L is protonated or non-protonated, or in the form of complexes with other metals. The ratios $[M']/[L] = \alpha_M$ and $[L']/[L] = \alpha_L$ can be calculated from the stability constants of all the complexes formed in side-reactions; α_M and α_L are called "side-reaction coefficients", or just α-coefficients.

In this volume, in nearly all cases, the side-reactions of interest are the reactions of the anions (ligands) with protons. For these reactions

$$\alpha_{L(H)} = 1 + [H^+]K_1 + [H^+]^2K_1K_2 + \ldots \tag{2}$$

where the K's are the protonation (i.e. association) constants. When written in terms of the dissociation constants for a weak dibasic acid, equation (2) becomes

$$\alpha_{L(H)} = 1 + \frac{[H^+]}{K_{a1}} + \frac{[H^+]^2}{K_{a1}K_{a2}} \tag{3}$$

If we now return to the general case, substituting for [M'] and [L'] in equation (1) leads to

$$\beta_n' = \frac{[ML_n]}{[M]\,\alpha_M \cdot [L]^n\alpha_L{}^n} = \frac{\beta_n}{\alpha_M\,\alpha_L{}^n} \tag{4}$$

or

$$\log \beta_n' = \log \beta_n - \log \alpha_M - n \log \alpha_L \tag{5}$$

Although this brief introduction has been given for a generalized stability constant, the Ringbom treatment is equally applicable to solubility equilibria, with the definition of "conditional solubility products". A more detailed discussion of this topic has been given by Inczédy (7).

The hydrolysis phenomenon has frequently been utilized as a method for increasing the solubility of a sparingly soluble salt (by dissolution in acid) to a value at which the concentrations become more readily determinable. That is, experimental determinations are made of the conditional solubility product at various pH values, then the solubility product in pure water is calculated from equation (4) or (5). However, good estimates are required for the acid-dissociation constants if a good value for the pure-aqueous solubility product is to be obtained.

No corrections to allow for hydrolysis were done for the systems involving sulfite and a bivalent metal. Here, usually the total amount of dissolved sulfite is given.

PROCEDURE FOR EVALUATIONS

In the alkali-metal and ammonium systems, the procedure was as follows. The data for a system were collected, and analysed by use of the statistical package MINITAB (8). Regression analysis was done for various polynomial functions, and the best was selected by consideration of the values of s, the standard deviation of the dependent variable about the regression line, and the t-ratios for each coefficient (which show whether the value of the coefficient is statistically significant, or whether it should be better set to zero). Also, histograms and plots of the standardized residuals were examined, because for a correctly selected function these should have an approximately Gaussian distribution. When the best function had been selected, any points which had standard residuals greater than +2 or less than -2 were rejected, then the regression analysis was repeated. Usually, more points then had to be rejected; the procedure was repeated until all the remaining points had standard residuals in the range -2 to +2. Sometimes, several points from a single paper had to be rejected, and it was then decided that the whole set must be unreliable, so it was removed. After rejection of points was completed, a further check was made that the best function had been selected. The final smoothing equation then derived was used to calculate recommended or tentative solubility values for an appropriate series of temperatures, and computer-drawn diagrams showing the data and the calculated regression line(s) were then prepared.

For systems involving sulfite and bivalent metals, a somewhat different procedure was used. After collecting all data for a system, the "best" papers according to consistency of data, determination method, etc. were selected. From the results of these papers, tentative or recommended solubility data were derived. If possible, then a linear multiple regression analysis was done for the function

$$\log X = A + B/T + C \log T \tag{6}$$

with $1/T$ and $\log T$ as independent variables. For these functions, values for the coefficients A, B, and C, and the correlation coefficients are given, and graphs were drawn.

REFERENCES

1. *Nomenclature of Inorganic Chemistry*, IUPAC Definitive Rules 1970, Butterworths, London, 1971.
2. Irving, H.M.N.H.; Freiser, H.; West. T.S. *Compendium of Analytical Nomenclature* IUPAC Publication, Pergamon, Oxford, 1978. p. 54.
3. *Idem. ibid.* p. 9.
4. Schreinemakers, F.A.H. *Z. Phys. Chem.* 1893, 11, 75.
5. Findlay, A. *The Phase Rule and its Applications* 5th *Ed.* Longmans, Green and Co., London, 1923. p. 246. (Also Findlay A.; Campbell, A.N.; Smith, N.O. *9th Ed.* Dover, New York, 1951.)
6. Ringbom, A. *Complexation in Analytical Chemistry* Interscience, New York, 1963.
7. Inczédy, J. *Analytical Applications of Complex Equilibria* Horwood, Chichester, 1976.
8. *MINITAB RELEASE 82/1*, copyright Penn State University.
   Ryan, T.A. Jr.; Joiner, B.L.; Ryan, B.F. *Minitab Student Handbook* Duxbury Press, N. Scituate, Mass., 1976.

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