PREFACE

This volume presents and evaluates solubility data for the oxides and hydroxides of two groups of transition series metals, i.e., copper, silver, gold, and zinc, cadmium, mercury, from Groups I and II of the Periodic Table.

The history of the interest in the solubilities of most of these oxides and hydroxides may be divided into approximately three periods. In the earliest period the interest was mainly in the extent to which these substances were amphoteric. They were all known to show basic characteristics, but there was a question of the extent to which they exhibited acidic behavior. The study of the solubility of these substances in strong bases or alkalies was selected as one method for detecting any such acidic behavior.

The second period occurred during and following World War II. At that time several of these metals were being used as components in an alkaline battery, e.g., mercury-zinc, nickel-cadmium, silver-zinc and silver-cadmium batteries. The study of the solubility of the oxides and hydroxides of these metals was undertaken, again in alkaline solutions but now in solutions of larger concentrations, in an effort to understand and control the electrode reactions occurring in these battery systems.

The third stage is related to interest in the environment. These metals are known to have some toxic characteristics, and it has been of interest to determine to what extent they and their compounds can enter into the environment through dissolution processes. Such studies have been accompanied by the development of analytical procedures and techniques capable of detecting very small quantities of these metals.

The main source used in the search for relevant articles was *Chemical Abstracts* from 1907 to 1984. The search for work published prior to 1907 was limited to: (a) the eighth edition of Gmelin, *Handbuch der Anorganischen Chemie;* (b) the work of Mellor (1); and (c) the references cited in each of the articles used in the preparation of this volume. However, with few exceptions, no works published before 1900 were used for preparing data sheets. The reasons for this are primarily: (a) the matter of the stability or instability of the hydroxides, particularly, was not clearly understood at that time and, as a result, the nature of the solid phases that were used was not well defined; (b) the nature of solutions of electrolytes was not well understood by comparison with today's work and "degree of ionization" was often used to evaluate ionic concentrations; (c) the solubility of the substances studied in this volume is often very small in aqueous solvents and the analytical techniques then available were generally not sensitive enough.

So far as I am aware, all the pertinent articles up to 1984 have been reviewed. A few articles were unavailable during the course of this work, but it appears that the inclusion of these articles (usually in lesser known journals of the eastern European countries) would not have changed to any significant extent the conclusions presented in this volume. However, as these articles become available they will be included in a later update volume.

On the compilation sheets the data are given with the same number of significant figures as are reported by the authors of the original article. However, when calculations are made to present the data in different units, the number of significant figures was sometimes reduced. This was done in accordance with the compiler's estimate of the reproducibility of the data. Further discussion of the validity of the data are presented in the respective Critical Evaluations.

With one exception, all the data included in this volume are for solubilities in aqueous solutions. Very little information has been published about the solubility in non-aqueous solvents of the oxides and hydroxides covered in this volume. One such article is that of Becker (2) which reports the solubility of a variety of compounds in formamide at 298 K. The experimental details are very meager. The solubility of CuO is stated to be less than 0.01 mass % while that of ZnO is merely given as 0.8 g/100 g formamide.

In another article (3) the solubility of CuO in liquid ammonia at 298 K is given as 0.00 g/100 g.

The one exception referred to above is an article dealing with the solubility of Cu_2O and CuO in acetonitrile and in methyl acetate (4). Compilation sheets have been included for this article although only a few pertinent data are given in it. However, these data are not discussed in the Critical Evaluations. The data are included because they appear to be reasonable within the limits of the experimental conditions. There is no other work with which they can be compared.

In many articles the solubility data are presented only in the form of one or more graphs. No data sheets have been prepared for these articles unless it was possible to obtain from the author(s), in a personal communication, the numerical data upon which such graphs were constructed. Thus, e.g., data for the solubility of CuO in non-aqueous media (5, 6) have been omitted from this volume. For the same reason an article dealing with the solubility of Cu_2O in solutions containing diethylenetriamine and sulfuric acid (7) has been excluded from consideration. Furthermore, this article gives no information about experimental details, analytical procedures, or quality of the materials that were used.

Where both the oxide and hydroxide of a metal exist in the solid state the solubility data for both are considered together in the Critical Evaluation. This is a matter of convenience because the dissolution of the oxide in aqueous solutions often produces the hydroxide of the metal. Furthermore, the oxide may be the more stable of the two solids. Often, the hydroxide is metastable with respect to the oxide. The difficulties associated with the preparation of stable oxides or hydroxides and with the attainment of equilibrium between solid and solution have been discussed elsewhere (8).

The transition series metals often have more than one oxidation state. However, there may be no stable oxides or hydroxides corresponding to each of the oxidation states. For the metals discussed in this volume, only copper and silver have solid oxides corresponding to more than one oxidation state. In the Critical Evaluations the solubility data for each oxidation state are discussed separately.

In the Critical Evaluations that follow, stability and formation constant values for some complexes are sometimes presented and evaluated. These values were derived from solubility data and the evaluation of them usually considers similarly derived data. The values are not necessarily compared with similar values obtained by the use of other kinds of experimental data.

The work presented in this volume was not done by one person alone. Besides those who contributed compilation sheets there were many others who helped in other ways, and whose contribution can be recognized here. Conrad Bult and Lynne Hopkins of the Calvin College Library, Drs. A. S. Kertes, J. W. Lorimer, and M. Salomon of the Solubility Data Project all provided considerable help in locating and obtaining copies of the articles that have been reviewed. Special thanks are due to the personnel of the Chemistry Department Library at Michigan State University for the freedom given me to use all their facilities in preparing the materials for this volume. Carol Dirkse and Dr. R. Van Dragt of Calvin College gave indispensable assistance by providing translations of several articles. Dr. I. Khodakovskii of the USSR Academy of Sciences graciously reviewed and commented on the solubility work done under hydrothermal conditions. And then there are the three efficient, helpful, and patient typists: Louise Null, Sue Sweetman and Jan Woudenberg. They did the tedious work of typing, retyping, and more retyping and, out of this ordeal, they have still come up smiling.

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