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SOLUBILITY DATA SERIES
Volume 25
METALS IN MERCURY

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SOLUBILITY DATA SERIES

Volume 25

METALS IN MERCURY

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SOLUBILITY DATA SERIES

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Volume 25

METALS IN MERCURY

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FOREWORD

If the knowledge is
undigested or simply wrong,
more is not better

How to communicate and disseminate numerical data effectively in chemical science and technology has been a problem of serious and growing concern to IUPAC, the International Union of Pure and Applied Chemistry, for the last two decades. The steadily expanding volume of numerical information, the formulation of new interdisciplinary areas in which chemistry is a partner, and the links between these and existing traditional subdisciplines in chemistry, along with an increasing number of users, have been considered as urgent aspects of the information problem in general, and of the numerical data problem in particular.

Among the several numerical data projects initiated and operated by various IUPAC commissions, the *Solubility Data Project* is probably one of the most ambitious ones. It is concerned with preparing a comprehensive critical compilation of data on solubilities in all physical systems, of gases, liquids and solids. Both the basic and applied branches of almost all scientific disciplines require a knowledge of solubilities as a function of solvent, temperature and pressure. Solubility data are basic to the fundamental understanding of processes relevant to agronomy, biology, chemistry, geology and oceanography, medicine and pharmacology, and metallurgy and materials science. Knowledge of solubility is very frequently of great importance to such diverse practical applications as drug dosage and drug solubility in biological fluids, anesthesiology, corrosion by dissolution of metals, properties of glasses, ceramics, concretes and coatings, phase relations in the formation of minerals and alloys, the deposits of minerals and radioactive fission products from ocean waters, the composition of ground waters, and the requirements of oxygen and other gases in life support systems.

The widespread relevance of solubility data to many branches and disciplines of science, medicine, technology and engineering, and the difficulty of recovering solubility data from the literature, lead to the proliferation of published data in an ever increasing number of scientific and technical primary sources. The sheer volume of data has overcome the capacity of the classical secondary and tertiary services to respond effectively.

While the proportion of secondary services of the review article type is generally increasing due to the rapid growth of all forms of primary literature, the review articles become more limited in scope, more specialized. The disturbing phenomenon is that in some disciplines, certainly in chemistry, authors are reluctant to treat even those limited-in-scope reviews exhaustively. There is a trend to preselect the literature, sometimes under the pretext of reducing it to manageable size. The crucial problem with such preselection - as far as numerical data are concerned - is that there is no indication as to whether the material was excluded by design or by a less than thorough literature search. We are equally concerned that most current secondary sources, critical in character as they may be, give scant attention to numerical data.

On the other hand, tertiary sources - handbooks, reference books and other tabulated and graphical compilations - as they exist today are comprehensive but, as a rule, uncritical. They usually attempt to cover whole disciplines, and thus obviously are superficial in treatment. Since they command a wide market, we believe that their service to the advancement of science is at least questionable. Additionally, the change which is taking place in the generation of new and diversified numerical data, and the rate at which this is done, is not reflected in an increased third-level service. The emergence of new tertiary literature sources does not parallel the shift that has occurred in the primary literature.

With the status of current secondary and tertiary services being as briefly stated above, the innovative approach of the *Solubility Data Project* is that its compilation and critical evaluation work involve consolidation and reprocessing services when both activities are based on intellectual and scholarly reworking of information from primary sources. It comprises compact compilation, rationalization and simplification, and the fitting of isolated numerical data into a critically evaluated general framework.

The *Solubility Data Project* has developed a mechanism which involves a number of innovations in exploiting the literature fully, and which contains new elements of a more imaginative approach for transfer of reliable information from primary to secondary/tertiary sources. *The fundamental trend of the Solubility Data Project is toward integration of secondary and tertiary services with the objective of producing in-depth critical analysis and evaluation which are characteristic to secondary services, in a scope as broad as conventional tertiary services.*

Fundamental to the philosophy of the project is the recognition that the basic element of strength is the active participation of career scientists in it. Consolidating primary data, producing a truly critically-evaluated set of numerical data, and synthesizing data in a meaningful relationship are demands considered worthy of the efforts of top scientists. Career scientists, who themselves contribute to science by their involvement in active scientific research, are the backbone of the project. The scholarly work is commissioned to recognized authorities, involving a process of careful selection in the best tradition of IUPAC. This selection in turn is the key to the quality of the output. These top experts are expected to view their specific topics dispassionately, paying equal attention to their own contributions and to those of their peers. They digest literature data into a coherent story by weeding out what is wrong from what is believed to be right. To fulfill this task, the evaluator must cover *all* relevant open literature. No reference is excluded by design and every effort is made to detect every bit of relevant primary source. Poor quality or wrong data are mentioned and explicitly disqualified as such. In fact, it is only when the reliable data are presented alongside the unreliable data that proper justice can be done. The user is bound to have incomparably more confidence in a succinct evaluative commentary and a comprehensive review with a complete bibliography to both good and poor data.

It is the standard practice that the treatment of any given solute-solvent system consists of two essential parts: I. Critical Evaluation and Recommended Values, and II. Compiled Data Sheets.

The Critical Evaluation part gives the following information:

(i) a verbal text of evaluation which discusses the numerical solubility information appearing in the primary sources located in the literature. The evaluation text concerns primarily the quality of data after consideration of the purity of the materials and their characterization, the experimental method employed and the uncertainties in control of physical parameters, the reproducibility of the data, the agreement of the worker's results on accepted test systems with standard values, and finally, the fitting of data, with suitable statistical tests, to mathematical functions;

(ii) a set of recommended numerical data. Whenever possible, the set of recommended data includes weighted average and standard deviations, and a set of smoothing equations derived from the experimental data endorsed by the evaluator;

(iii) a graphical plot of recommended data.

The Compilation part consists of data sheets of the best experimental data in the primary literature. Generally speaking, such independent data sheets are given only to the best and endorsed data covering the known range of experimental parameters. Data sheets based on primary sources where the data are of a lower precision are given only when no better data are available. Experimental data with a precision poorer than considered acceptable are reproduced in the form of data sheets when they are the only known data for a particular system. Such data are considered to be still suitable for some applications, and their presence in the compilation should alert researchers to areas that need more work.

The typical data sheet carries the following information:

(i) components - definition of the system - their names, formulas and Chemical Abstracts registry numbers;
(ii) reference to the primary source where the numerical information is reported. In cases when the primary source is a less common periodical or a report document, published though of limited availability, abstract references are also given;
(iii) experimental variables;
(iv) identification of the compiler;
(v) experimental values as they appear in the primary source. Whenever available, the data may be given both in tabular and graphical form. If auxiliary information is available, the experimental data are converted also to SI units by the compiler.

Under the general heading of Auxiliary Information, the essential experimental details are summarized:

(vi) experimental method used for the generation of data;
(vii) type of apparatus and procedure employed;
(viii) source and purity of materials;
(ix) estimated error;
(x) references relevant to the generation of experimental data as cited in the primary source.

This new approach to numerical data presentation, formulated at the initiation of the project and perfected as experience has accumulated, has been strongly influenced by the diversity of background of those whom we are supposed to serve. We thus deemed it right to preface the evaluation/compilation sheets in each volume with a detailed discussion of the principles of the accurate determination of relevant solubility data and related thermodynamic information.

Finally, the role of education is more than corollary to the efforts we are seeking. The scientific standards advocated here are necessary to strengthen science and technology, and should be regarded as a major effort in the training and formation of the next generation of scientists and engineers. Specifically, we believe that there is going to be an impact of our project on scientific-communication practices. The quality of consolidation adopted by this program offers down-to-earth guidelines, concrete examples which are bound to make primary publication services more responsive than ever before to the needs of users. The self-regulatory message to scientists of the early 1970s to refrain from unnecessary publication has not achieved much. A good fraction of the literature is still cluttered with poor-quality articles. The Weinberg report (in 'Reader in Science Information', ed. J. Sherrod and A. Hodina, Microcard Editions Books, Indian Head, Inc., 1973, p. 292) states that 'admonition to authors to restrain themselves from premature, unnecessary publication can have little effect unless the climate of the entire technical and scholarly community encourages restraint...' We think that projects of this kind translate the climate into operational terms by exerting pressure on authors to avoid submitting low-grade material. The type of our output, we hope, will encourage attention to quality as authors will increasingly realize that their work will not be suited for permanent retrievability unless it meets the standards adopted in this project. It should help to dispel confusion in the minds of many authors of what represents a permanently useful bit of information of an archival value, and what does not.

If we succeed in that aim, even partially, we have then done our share in protecting the scientific community from unwanted and irrelevant, wrong numerical information.

A. S. Kertes

PREFACE

This volume is concerned with the solubility of metals in mercury, and includes all of the metals and the metalloids carbon, silicon and boron. The solubility only in the seventy-six binary amalgams is considered here. The compilation of the solubility data for these binary systems includes numerous reports, such as those published by the U.S. Atomic Energy Commission from its various laboratories. The literature coverage for this volume extends through 1983.

The solubility of a metal in mercury at a given temperature is represented by the concentration of the saturated solution which is in equilibrium with the solid phase. The solid phase may be the pure metal, the metal saturated with mercury, or an intermetallic compound with mercury. This concentration also is represented by the liquidus point at the given temperature on the binary phase diagram. Clearly, the solubility also is represented by the crystallization temperature of the liquid amalgam.

Only those parts of the complete metal-mercury systems are included in which the solid metal, or a metal amalgam, appear as solid phases. In those systems where a phase diagram has been accurately determined, the equilibrium solid phase is clearly defined; the published phase diagrams for these systems are included in the Critical Evaluation, and should correctly aid the reader in assigning the solid-liquid equilibrium. However, there are some systems where there is disagreement on the equilibrium solid phase so that the solid-liquid equilibrium for these systems cannot be accurately defined. There are certain phase diagrams which have been constructed from precise data, but the liquidus data may be somewhat questionable because equilibrium may not have been attained during the short equilibration times employed. Instances of possible supersaturation in the determination of the liquidus from cooling curves are noted by the evaluators. In this volume, the emphasis is on accurate, evaluated solubility data rather than phase relations in the various systems.

Concentrations in the metal-mercury systems are mostly reported in atomic percent, at %, rather than in mole percent. The rationale for the non-SI unit is that each system is represented by the equilibrium of two atomic species, and much of the literature data on binary metallic systems are reported so.

The solubility of a number of metals in mercury, especially the refractory metals, is very low, and often below the experimental detection limit. For such systems only a selected number of data sheets were compiled for those reports which gave the highest solubility limit as determined by a well defined method. However, the solubility in these systems may be estimated by the semiempirical equations of Kozin. The first equation (1) is given by

$$\ln (100x_1) = -0.4 \left[1 + \frac{\Delta H_m (T_m - T)}{R T_m T}\right]^2 \left[\frac{\Delta H_m (T_m - T)}{R T_m T}\right]^{0.001} \qquad [1]$$

where the atomic percent solubility of the metal, $100x_1$, is a function of its enthalpy of fusion, ΔH_m, and its melting point, T_m. Kozin subsequently reported (2) a second solubility equation,

$$\ln (100x_1) = -\left[\frac{\Delta H_m (T_m - T)}{R T_m T}\right]^{1.39} \qquad [2]$$

Equation [2] was derived from the Schroeder relation in which the exponent is unity for ideal solutions. The exponent, 1.39, in eq. [2] results from fitting known values of solubilities in the binary amalgams to ΔH_m and T_m. It was reported by Kozin (2) that the mean standard scatter of points for systems of known solubilities is ±0.028 at a 95% confidence level in eq. [2]. Estimates from this equation for the solubility at 298 K for some of the binary systems are near the experimental values, but there also are systems where the estimates are at great variance from experimental values. For systems of very low solubility, where experimental data are not available, eq. [2] may be applied only as a first approximation.

For some of the metal-Hg systems the data were reported only graphically; some of the liquidus covered an extensive composition range, others only a narrow composition range. Because the numerical data are of interest to many workers, the data points from these graphical presentations were visually read from the curves and are compiled on the data sheets. Admittedly, the error in abstracting such data from the curves may be large, depending on the size of the original figure.

For every system where experimental solubility data were reported, all of the data were plotted on a semilogarithmic paper (of 60 x 20 cm dimensions) as log $(100x_1)$ vs. $(T/K)^{-1}$. The data were then evaluated by visually fitting the best curve. Evaluated solubility data are tabulated at the end of the Critical Evaluation. When at least two independent works agreed within experimental error, the solubility values were assigned to the recommended category. Values were assigned as tentative when only one reliable work was reported, or when the mean value from two or more reliable works was outside of the error limits. In this tabulation, three, two, or one significant figures is assigned for respective precisions that are better than ±1 and ±10% and worse than ±10%. There were no data that agreed to within ±0.1%.

In a number of papers the temperature of the measurement was reported as "room temperature"; in plotting these data on the solubility curve, the temperature was arbitrarily assigned as 293 K.

Data for concentrated solutions which were reported in mol atom dm^{-3} without specifying the density were not useful for this compilation; solubilities in atom percent could not be assigned to these data.

Because of the large number of binary systems in this volume, the presentation is grouped according to the Periodic Table. The non-transition metals are given first in sequence starting from the alkali metals, followed by the transition metals in similar order. The actinides and the unstable radioactive elements are presented at the end of the volume.

Some previous compilations dealing with solubilities in selected amalgam systems (3-10) are considered incomplete, and the data in some of these references erroneous.

The editors acknowledge the encouragement of IUPAC Commission V.5 under whose authorization this work was initiated. The Editor also acknowledges the helpful advice and suggestions made by Dr. Mark Salomon during the course of editing this volume. Acknowledgment also is made to the Westinghouse Electric Corporation for providing the Editor with library and stenographic services during this project. It is also a pleasure to acknowledge the aid of Mrs. Joyce Walsh for the complete typing of this volume.

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INTRODUCTION: THE SOLUBILITY OF SOLIDS IN LIQUIDS

Nature of the Project

The Solubility Data Project (SDP) has as its aim a comprehensive search of the literature for solubilities of gases, liquids, and solids in liquids or solids. Data of suitable precision are compiled on data sheets in a uniform format. The data for each system are evaluated, and where data from different sources agree sufficiently, recommended values are proposed. The evaluation sheets, recommended values, and compiled data sheets are published on consecutive pages.

This series of volumes includes solubilities of solids of all types in liquids of all types.

Definitions

A *mixture* (1,2) describes a gaseous, liquid, or solid phase containing more than one substance, when the substances are all treated in the same way.

A *solution* (1,2) describes a liquid or solid phase containing more than one substance, when for convenience one of the substances, which is called the *solvent* and may itself be a mixture, is treated differently than the other substances, which are called *solutes*. If the sum of the mole fractions of the solutes is small compared to unity, the solution is called a *dilute solution*.

The *solubility* of a substance B is the relative proportion of B (or a substance related chemically to B) in a mixture which is saturated with respect to solid B at a specified temperature and pressure. *Saturated* implies the existence of equilibrium with respect to the processes of dissolution and precipitation; the equilibrium may be stable or metastable. The solubility of a metastable substance is usually greater than that of the corresponding stable substance. (Strictly speaking, it is the activity of the metastable substance that is greater.) Care must be taken to distinguish true metastability from supersaturation, where equilibrium does not exist.

Either point of view, mixture or solution, may be taken in describing solubility. The two points of view find their expression in the quantities used as measures of solubility and in the reference states used for definition of activities and activity coefficients.

The qualifying phrase "substance related chemically to B" requires comment. The composition of the saturated mixture (or solution) can be described in terms of any suitable set of thermodynamic components. Thus, the solubility of a salt hydrate in water is usually given as the relative proportion of anhydrous salt in solution, rather than the relative proportions of hydrated salt and water.

Quantities Used as Measures of Solubility

1. *Mole fraction* of substance B, x_B:

$$x_B = n_B / \sum_{i=1}^{c} n_i \qquad (1)$$

where n_i is the amount of substance of substance i, and c is the number of distinct substances present (often the number of thermodynamic components in the system). *Mole per cent* of B is 100 x_B.

2. *Mass fraction* of substance B, w_B:

$$w_B = m'_B / \sum_{i=1}^{c} m'_i \qquad (2)$$

where m'_i is the mass of substance i. *Mass per cent* of B is 100 w_B. The equivalent terms weight fraction and weight per cent are not used.

3. *Solute mole (mass) fraction* of solute B (3,4):

$$x_{S,B} = n_B / \sum_{i=1}^{c'} n_i = x_B / \sum_{i=1}^{c'} x_i \qquad (3)$$

where the summation is over the solutes only. For the solvent A, $x_{S,A} = x_A$. These quantities are called *Jänecke mole (mass) fractions* in many papers.

4. *Molality* of solute B (1,2) in a solvent A:

$$m_B = n_B/n_A\, M_A \qquad \text{SI base units: mol kg}^{-1} \qquad (4)$$

where M_A is the molar mass of the solvent.

5. *Concentration* of solute B (1,2) in a solution of volume V:

$$c_B = [B] = n_B/V \qquad \text{SI base units: mol m}^{-3} \qquad (5)$$

The terms molarity and molar are not used.

Mole and mass fractions are appropriate to either the mixture or the solution points of view. The other quantities are appropriate to the solution point of view only. In addition of these quantities, the following are useful in conversions between concentrations and other quantities.

6. *Density*: $\rho = m/V$ SI base units: kg m^{-3} (6)

7. *Relative density*: d; the ratio of the density of a mixture to the density of a reference substance under conditions which must be specified for both (1). The symbol d_t^t, will be used for the density of a mixture at t°C, 1 atm divided by the density of water at t'°C, 1 atm.

Other quantities will be defined in the prefaces to individual volumes or on specific data sheets.

Thermodynamics of Solubility

The principal aims of the Solubility Data Project are the tabulation and evaluation of: (a) solubilities as defined above; (b) the nature of the saturating solid phase. Thermodynamic analysis of solubility phenomena has two aims: (a) to provide a rational basis for the construction of functions to represent solubility data; (b) to enable thermodynamic quantities to be extracted from solubility data. Both these aims are difficult to achieve in many cases because of a lack of experimental or theoretical information concerning activity coefficients. Where thermodynamic quantities can be found, they are not evaluated critically, since this task would involve critical evaluation of a large body of data that is not directly relevant to solubility. The following discussion is an outline of the principal thermodynamic relations encountered in discussions of solubility. For more extensive discussions and references, see books on thermodynamics, e.g., (5-10).

Activity Coefficients (1)

(a) *Mixtures.* The activity coefficient f_B of a substance B is given by

$$RT\ \ln(f_B x_B) = \mu_B - \mu_B^* \qquad (7)$$

where μ_B is the chemical potential, and μ_B^* is the chemical potential of pure B at the same temperature and pressure. For any substance B in the mixture,

$$\lim_{x_B \to 1} f_B = 1 \qquad (8)$$

(b) *Solutions.*

(i) *Solute substance, B.* The molal activity coefficient γ_B is given by

$$RT\ \ln(\gamma_B m_B) = \mu_B - (\mu_B - RT\ \ln m_B)^{\infty} \qquad (9)$$

where the superscript $^{\infty}$ indicates an infinitely dilute solution. For any solute B,

$$\gamma_B^{\infty} = 1 \qquad (10)$$

Activity coefficients y_B connected with concentration c_B, and $f_{x,B}$ (called the *rational activity coefficient*) connected with mole fraction x_B are defined in analogous ways. The relations among them are (1,9):

$$\gamma_B = x_A f_{x,B} = V_A^*(1 - \Sigma_s c_s) y_B \qquad (11)$$

or

$$f_{x,B} = (1 + M_A \sum_s m_s)\gamma_B = V_A^* y_B / V_m \quad (12)$$

or

$$y_B = (V_A + M_A \sum_s m_s V_s)\gamma_B / V_A^* = V_m f_{x,B} / V_A^* \quad (13)$$

where the summations are over all solutes, V_A^* is the molar volume of the pure solvent, V_i is the partial molar volume of substance i, and V_m is the molar volume of the solution.

For an electrolyte solute $B \equiv C_{\nu+}A_{\nu-}$, the molal activity is replaced by (9)

$$\gamma_B m_B = \gamma_\pm^{\nu} m_B^{\nu} Q^{\nu} \quad (14)$$

where $\nu = \nu_+ + \nu_-$, $Q = (\nu_+^{\nu_+}\nu_-^{\nu_-})^{1/\nu}$, and $\gamma_\pm$ is the mean ionic molal activity coefficient. A similar relation holds for the concentration activity $y_B c_B$. For the mol fractional activity,

$$f_{x,B}\, x_B = \nu_+^{\nu_+}\nu_-^{\nu_-} f_\pm^{\nu} x_\pm^{\nu} \quad (15)$$

The quantities x_+ and x_- are the ionic mole fractions (9), which for a single solute are

$$x_+ = \nu_+ x_B/[1+(\nu-1)x_B]; \qquad x_- = \nu_- x_B/[1+(\nu-1)x_B] \quad (16)$$

(ii) *Solvent, A:*

The *osmotic coefficient*, ϕ, of a solvent substance A is defined as (1):

$$\phi = (\mu_A^* - \mu_A)/RT\, M_A \sum_s m_s \quad (17)$$

where μ_A^* is the chemical potential of the pure solvent.

The *rational osmotic coefficient*, ϕ_x, is defined as (1):

$$\phi_x = (\mu_A - \mu_A^*)/RT\ell n x_A = \phi M_A \sum_s m_s / \ell n(1 + M_A \sum_s m_s) \quad (18)$$

The activity, a_A, or the activity coefficient f_A is often used for the solvent rather than the osmotic coefficient. The activity coefficient is defined relative to pure A, just as for a mixture.

The Liquid Phase

A general thermodynamic differential equation which gives solubility as a function of temperature, pressure and composition can be derived. The approach is that of Kirkwood and Oppenheim (7). Consider a solid mixture containing c' thermodynamic components i. The Gibbs-Duhem equation for this mixture is:

$$\sum_{i=1}^{c'} x_i'(S_i'dT - V_i'dp + d\mu_i) = 0 \quad (19)$$

A liquid mixture in equilibrium with this solid phase contains c thermodynamic components i, where, usually, $c > c'$. The Gibbs-Duhem equation for the liquid mixture is:

$$\sum_{i=1}^{c'} x_i(S_i dT - V_i dp + d\mu_i) + \sum_{i=c'+1}^{c} x_i(S_i dT - V_i dp + d\mu_i) = 0 \quad (20)$$

Eliminate $d\mu_1$ by multiplying (19) by x_1 and (20) x_1'. After some algebra, and use of:

$$d\mu_i = \sum_{j=2}^{c} G_{ij} dx_j - S_i dT + V_i dp \quad (21)$$

where (7)

$$G_{ij} = (\partial\mu_i/\partial x_j)_{T,P,x_i\neq x_j} \quad (22)$$

it is found that

$$\sum_{i=2}^{c'}\sum_{j=2}^{c}(x_i' - x_i x_1'/x_1)G_{ij}dx_j - (x_1'/x_1)\sum_{i=c'+1}^{c}\sum_{j=2}^{c} x_i G_{ij} dx_j = \sum_{i=1}^{c'} x_i'(H_i - H_i')dT/T - \sum_{i=1}^{c'} x_i'(V_i - V_i')dp \quad (23)$$

where

$$H_i - H_i' = T(S_i - S_i') \tag{24}$$

is the enthalpy of transfer of component i from the solid to the liquid phase, at a given temperature, pressure and composition, and H_i, S_i, V_i are the partial molar enthalpy, entropy, and volume of component i. Several special cases (all with pressure held constant) will be considered. Other cases will appear in individual evaluations.

(a) Solubility as a function of temperature.

Consider a binary solid compound A_nB in a single solvent A. There is no fundamental thermodynamic distinction between a binary compound of A and B which dissociates completely or partially on melting and a solid mixture of A and B; the binary compound can be regarded as a solid mixture of constant composition. Thus, with c = 2, c' = 1, $x_A' = n/(n+1)$, $x_B' = 1/(n+1)$, eqn (23) becomes

$$(1/x_B - n/x_A)\{1+(\frac{\partial \ell n f_B}{\partial \ell n x_B})_{T,P}\}dx_B = (nH_A + H_B - H_{AB}^*)\,dT/RT^2 \tag{25}$$

where the mole fractional activity coefficient has been introduced. If the mixture is a non-electrolyte, and the activity coefficients are given by the expression for a simple mixture (6):

$$RT\ \ell n\ f_B = wx_A^2 \tag{26}$$

then it can be shown that, if w is independent of temperature, eqn (25) can be integrated (cf. (5), Chap. XXIII, sect. 5). The enthalpy term becomes

$$nH_A + H_B - H_{AB}^* = \Delta H_{AB} + n(H_A - H_A^*) + (H_B - H_B^*)$$

$$= \Delta H_{AB} + w(nx_B^2 + x_A^2) \tag{27}$$

where ΔH_{AB} is the enthalpy of melting and dissociation of one mole of pure solid A_nB, and H_A^*, H_B^* are the molar enthalpies of pure liquid A and B. The differential equation becomes

$$R\ d\ \ell n\{x_B(1-x_B)^n\} = -\Delta H_{AB}\ d(\frac{1}{T}) - w\ d(\frac{x_A^2 + nx_B^2}{T}) \tag{28}$$

Integration from x_B,T to $x_B = 1/(1+n)$, $T = T^*$, the melting point of the pure binary compound, gives:

$$\ell n\{x_B(1-x_B)^n\} \simeq \ell n\{\frac{n^n}{(1+n)^{n+1}}\} - \{\frac{\Delta H_{AB}^* - T^*\Delta C_p^*}{R}\}\ (\frac{1}{T} - \frac{1}{T^*})$$

$$+ \frac{\Delta C_p^*}{R}\ell n(\frac{T}{T^*}) - \frac{w}{R}\{\frac{x_A + nx_B}{T} - \frac{n}{(n+1)T^*}\} \tag{29}$$

where ΔC_p^* is the change in molar heat capacity accompanying fusion plus decomposition of the compound at temperature T*, (assumed here to be independent of temperature and composition), and ΔH_{AB}^* is the corresponding change in enthalpy at T = T*. Equation (29) has the general form

$$\ell n\{x_B(1-x_B)^n\} = A_1 + A_2/T + A_3\ell nT + A_4(x_A^2 + nx_B^2)/T \tag{30}$$

If the solid contains only component B, n = 0 in eqn (29) and (30).

If the infinite dilution standard state is used in eqn (25), eqn (26) becomes

$$RT\ \ell n\ f_{x,B} = w(x_A^2 - 1) \tag{31}$$

and (27) becomes

$$nH_A + H_B - H_{AB} = (nH_A^* + H_B^\infty - H_{AB}^*) + n(H_A - H_A^*) + (H_B - H_B^\infty) = \Delta H_{AB}^\infty + w(nx_B^2 + x_A^2 - 1) \tag{32}$$

where the first term, ΔH_{AB}^∞, is the enthalpy of melting and dissociation of solid compound A_nB to the infinitely dilute state of solute B in solvent A; H_B^∞ is the partial molar enthalpy of the solute at infinite dilution. Clearly, the integral of eqn (25) will have the same form as eqn (29), with $\Delta H_{AB}^\infty(T^*)$, $\Delta C_p^\infty(T^*)$ replacing ΔH_{AB}^* and ΔC_p^* and $x_A^2 - 1$ replacing x_A^2 in the last term.

If the liquid phase is an aqueous electrolyte solution, and the solid is a salt hydrate, the above treatment needs slight modification. Using rational mean activity coefficients, eqn (25) becomes

$$R\nu(1/x_B - n/x_A)\{1+(\partial \ell n f_\pm/\partial \ell n x_\pm)_{T,P}\}dx_B/\{1+(\nu-1)x_B\}$$

$$= \{\Delta H^\infty_{AB} + n(H_A - H_A^*) + (H_B - H_B^\infty)\}d(1/T) \quad (33)$$

If the terms involving activity coefficients and partial molar enthalpies are negligible, then integration gives (cf. (11)):

$$\ell n\{\frac{x_B^\nu(1-x_B)^n}{1+(\nu-1)x_B^{n+\nu}}\} = \ell n\{\frac{n^n}{(n+\nu)^{n+\nu}}\} - \{\frac{\Delta H^\infty_{AB}(T^*) - T^*\Delta C_p^*}{R}\}(\frac{1}{T} - \frac{1}{T^*}) + \frac{\Delta C_p^*}{R}\ell n(T/T^*) \quad (34)$$

A similar equation (with $\nu=2$ and without the heat capacity terms) has been used to fit solubility data for some $MOH-H_2O$ systems, where M is an alkali metal; the enthalpy values obtained agreed well with known values (11). In many cases, data on activity coefficients (9) and partial molal enthalpies (8,10) in concentrated solution indicate that the terms involving these quantities are not negligible, although they may remain roughly constant along the solubility temperature curve.

The above analysis shows clearly that a rational thermodynamic basis exists for functional representation of solubility-temperature curves in two-component systems, but may be difficult to apply because of lack of experimental or theoretical knowledge of activity coefficients and partial molar enthalpies. Other phenomena which are related ultimately to the stoichiometric activity coefficients and which complicate interpretation include ion pairing, formation of complex ions, and hydrolysis. Similar considerations hold for the variation of solubility with pressure, except that the effects are relatively smaller at the pressures used in many investigations of solubility (5).

(b) Solubility as a function of composition.

At constant temperature and pressure, the chemical potential of a saturating solid phase is constant:

$$\mu^*_{A_nB} = \mu_{A_nB}(sln) = n\mu_A + \mu_B \quad (35)$$

$$= (n\mu_A^* + \nu_+\mu_+^\infty + \nu_-\mu_-^\infty) + nRT\,\ell n f_A x_A + \nu RT\,\ell n \gamma_\pm m_\pm Q_\pm \quad (36)$$

for a salt hydrate A_nB which dissociates to water, (A), and a salt, B, one mole of which ionizes to give ν_+ cations and ν_- anions in a solution in which other substances (ionized or not) may be present. If the saturated solution is sufficiently dilute, $f_A = x_A = 1$, and the quantity K^0_{s0} in

$$\Delta G^\infty \equiv (\nu_+\mu_+^\infty + \nu_-\mu_-^\infty + n\mu_A^* - \mu_{AB}^*)$$

$$= -RT\,\ell n\, K^0_{s0}$$

$$= -RT\,\ell n\, Q^\nu \gamma_\pm^\nu m_+^{\nu_+} m_-^{\nu_-} \quad (37)$$

is called the *solubility product* of the salt. (It should be noted that it is not customary to extend this definition to hydrated salts, but there is no reason why they should be excluded.) Values of the solubility product are often given on mole fraction or concentration scales. In dilute solutions, the theoretical behaviour of the activity coefficients as a function of ionic strength is often sufficiently well known that reliable extrapolations to infinite dilution can be made, and values of K^0_{s0} can be determined. In more concentrated solutions, the same problems with activity coefficients that were outlined in the section on variation of solubility with temperature still occur. If these complications do not arise, the solubility of a hydrate salt $C_{\nu_+}A_{\nu_-}\cdot nH_2O$ in the presence of other solutes is given by eqn (36) as

$$\nu\,\ell n\{m_B/m_B(0)\} = -\nu\ell n\{\gamma_\pm/\gamma_\pm(0)\} - n\,\ell n(a_{H_2O}/a_{H_2O}(0)) \quad (38)$$

where a_{H_2O} is the activity of water in the saturated solution, m_B is the molality of the salt in the saturated solution, and (0) indicates absence of other solutes. Similar considerations hold for non-electrolytes.

The Solid Phase

The definition of solubility permits the occurrence of a single solid phase which may be a pure anhydrous compound, a salt hydrate, a non-stoichiometric compound, or a solid mixture (or solid solution, or "mixed crystals"), and may be stable or metastable. As well, any number of solid phases consistent with the requirements of the phase rule may be present. Metastable solid phases are of widespread occurrence, and may appear as polymorphic (or allotropic) forms or crystal solvates whose rate of transition to more stable forms is very slow. Surface heterogeneity may also give rise to metastability, either when one solid precipitates on the surface of another, or if the size of the solid particles is sufficiently small that surface effects become important. In either case, the solid is not in stable equilibrium with the solution. The stability of a solid may also be affected by the atmosphere in which the system is equilibrated.

Many of these phenomena require very careful, and often prolonged, equilibration for their investigation and elimination. A very general analytical method, the "wet residues" method of Schreinemakers (12) (see a text on physical chemistry) is usually used to investigate the composition of solid phases in equilibrium with salt solutions. In principle, the same method can be used with systems of other types. Many other techniques for examination of solids, in particular X-ray, optical, and thermal analysis methods, are used in conjunction with chemical analyses (including the wet residues method).

COMPILATIONS AND EVALUATIONS

The formats for the compilations and critical evaluations have been standardized for all volumes. A brief description of the data sheets has been given in the FOREWORD; additional explanation is given below.

Guide to the Compilations

The format used for the compilations is, for the most part, self-explanatory. The details presented below are those which are not found in the FOREWORD or which are not self-evident.

Components. Each component is listed according to IUPAC name, formula, and Chemical Abstracts (CA) Registry Number. The formula is given either in terms of the IUPAC or Hill (13) system and the choice of formula is governed by what is usual for most current users: i.e. IUPAC for inorganic compounds, and Hill system for organic compounds. Components are ordered according to:

(a) saturating components;
(b) non-saturating components in alphanumerical order;
(c) solvents in alphanumerical order.

The saturating components are arranged in order according to a 18-column, 2-row periodic table:

Columns 1,2: H, groups IA, IIA;
3,12: transition elements (groups IIIB to VIIB, group VIII, groups IB, IIB);
13-18: groups IIIA-VIIA, noble gases.
Row 1: Ce to Lu;
Row 2: Th to the end of the known elements, in order of atomic number.

Salt hydrates are generally not considered to be saturating components since most solubilities are expressed in terms of the anhydrous salt. The existence of hydrates or solvates is carefully noted in the texts, and CA Registry Numbers are given where available, usually in the critical evaluation. Mineralogical names are also quoted, along with their CA Registry Numbers, again usually in the critical evaluation.

Original Measurements. References are abbreviated in the forms given by *Chemical Abstracts Service Source Index (CASSI)*. Names originally in other than Roman alphabets are given as transliterated by *Chemical Abstracts*.

Experimental Values. Data are reported in the units used in the original publication, with the exception that modern *names* for units and quantities are used; e.g., mass per cent for weight per cent; mol dm^{-3} for molar; etc. Both mass and molar values are given. Usually, only one type of value (e.g., mass per cent) is found in the original paper, and the compiler has added the other type of value (e.g., mole per cent) from computer calculations based on 1976 atomic weights (14). Errors in calculations and fitting equations in original papers have been noted and corrected, by computer calculations where necessary.

Method. Source and Purity of Materials. Abbreviations used in *Chemical Abstracts* are often used here to save space.

Estimated Error. If these data were omitted by the original authors, and if relevant information is available, the compilers have attempted to

estimate errors from the internal consistency of data and type of apparatus used. Methods used by the compilers for estimating and reporting errors are based on the papers by Ku and Eisenhart (15).

Comments and/or Additional Data. Many compilations include this section which provides short comments relevant to the general nature of the work or additional experimental and thermodynamic data which are judged by the compiler to be of value to the reader.

References. See the above description for Original Measurements.

Guide to the Evaluations

The evaluator's task is to check whether the compiled data are correct, to assess the reliability and quality of the data, to estimate errors where necessary, and to recommend "best" values. The evaluation takes the form of a summary in which all the data supplied by the compiler have been critically reviewed. A brief description of the evaluation sheets is given below.

Components. See the description for the Compilations.

Evaluator. Name and date up to which the literature was checked.

Critical Evaluation

(a) Critical text. The evaluator produces text evaluating *all* the published data for each given system. Thus, in this section the evaluator review the merits or shortcomings of the various data. Only published data are considered; even published data can be considered only if the experimental data permit an assessment of reliability.

(b) Fitting equations. If the use of a smoothing equation is justifiable, the evaluator may provide an equation representing the solubility as a function of the variables reported on all the compilation sheets.

(c) Graphical summary. In addition to (b) above, graphical summaries are often given.

(d) Recommended values. Data are *recommended* if the results of at least two independent groups are available and they are in good agreement, and if the evaluator has no doubt as to the adequacy and reliability of the applied experimental and computational procedures. Data are reported as *tentative* if only one set of measurements is available, or if the evaluator considers some aspect of the computational or experimental method as mildly undesirable but estimates that it should cause only minor errors. Data are considered as *doubtful* if the evaluator considers some aspect of the computational or experimental method as undesirable but still considers the data to have some value in those instances where the order of magnitude of the solubility is needed. Data determined by an inadequate method or under ill-defined conditions are *rejected*. However references to these data are included in the evaluation together with a comment by the evaluator as to the reason for their rejection.

(e) References. All pertinent references are given here. References to those data which, by virtue of their poor precision, have been rejected and not compiled are also listed in this section.

(f) Units. While the original data may be reported in the units used by the investigators, the final recommended values are reported in S.I. units (1,16) when the data can be accurately converted.

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COMPONENTS:	EVALUATOR:
(1) Lithium; Li; [7439-93-2] (2) Mercury; Hg; [7439-97-6]	C. Guminski; Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland July, 1985

CRITICAL EVALUATION:

Maey (1) was the first to report the solubility of lithium in mercury at room temperature by determining the specific volume of the amalgam, but the solubility of 0.9 at % is too low and is rejected. Kerp and coworkers (2) determined the solubility by the analyses of the samples after filtration of the equilibrated mixture of Li and Hg. These authors determined the lithium solubilities at four temperatures between 273 and 373 K, with values ranging from 1.1 to 3.6 at %, respectively. Smith and Bennett (3) determined a solubility of 1.34 at % at 295 K by a method similar to that of Kerp et al. Richards and Garrod-Thomas (4) reported a solubility of 1.05 at % at room temperature, but this value is too low and is rejected. Zukovsky (5) reported the first extensive determination of the solubility curve over the complete composition range by thermal analysis; it was found that the concentration of Li in the saturated amalgam was 0.9 at % at the eutectic temperature of 231 K, and that the concentration increased to 49.6 at % at 872 K. Above the latter temperature the liquids were completely miscible. Grube and Wolf (6) also determined the solubility curve over the complete concentration range by thermal analysis, and the results of these authors agreed with those of Zukovsky in the concentration range of 20-85 at % Li. Also, Grube and Wolf confirmed the eutectic temperature of 231 K, but at 0.6 at % Li. However, there was a wide discrepancy between the solubility curve of Zukovsky and of Grube and Wolf at lithium concentrations above 85 at %. Strachan and Harris (7) reported a room temperature solubility of 0.66 at % that is too low and is rejected. Kozin (8) estimated a solubility of 66.49 at % at 298 K, but this solubility is inconsistent with experimental data because the author neglected the strong interactions of lithium and mercury.

Gladyshev and coworkers (9) determined a consistent lithium solubility of 1.37 and 2.1 at % at 293 and 313 K, respectively, by a potentiometric method. Cogley and Butler (10) determined the EMF of concentration cells with a non-aqueous electrolyte, and also obtained a consistent solubility of 1.33 at % at 299 K; however, their earlier result of 2.0 at % at 298 K (11) was overstated and is rejected. Korshunov et al. (12) reported a solubility of 1.1 at % at 293 K, but no experimental details were given by these authors. Dean (16) reported a 298 K solubility of 1.25 at % which is consistent with accepted values; the amalgam was prepared by electrolysis from LiOH, but no experimental details were described by this author. Onstott and coworkers (17,18) performed careful determinations at 295.4 K and obtained a solubility of 1.27 at %. A value of 1.3 at % at 296 may be suggested from potentiometric measurements of Horner and Schmitt (19). Based on calorimetric titration, Filippova and coworkers (13-15) reported that the saturated Li amalgam contains 1.20 at % Li at 298 K.

In summary, there is good agreement among the results of (10, 16-19), whereas the thermoanalytical data of (5,6) are significantly overstated at temperatures below 473 K.

Figure 1 shows the phase diagram reported by Hultgren et al. (20); this phase diagram is based mainly on the data of (2), (5) and (6). The intermetallic compounds which have been verified are Hg_3Li, Hg_2Li, HgLi, $HgLi_2$, $HgLi_3$ and $HgLi_6$.

Recommended (r) and tentative values of Li solubility in Hg:

(Continued next page)

COMPONENTS:	EVALUATOR:
(1) Lithium; Li; [7439-93-2] (2) Mercury; Hg; [7439-97-6]	C. Guminski; Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland July, 1985

CRITICAL EVALUATION: (continued)

Recommended (r) and tentative values of Li solubility in Hg:

T/K	Soly/at %	Reference
231	0.6	[6]
293	1.2[a]	[3,9,12,17,18]
298	1.3 (r)	[10,16-19]
323	2.2[b]	[5,9]
373	5[b]	[5]
473	13	[5]
573	25	[5]
673	33	[5,6]
773	39[b]	[5,6]
873	50.0	[5]

[a] Mean value from data of cited references.

[b] Interpolated value from data of cited references.

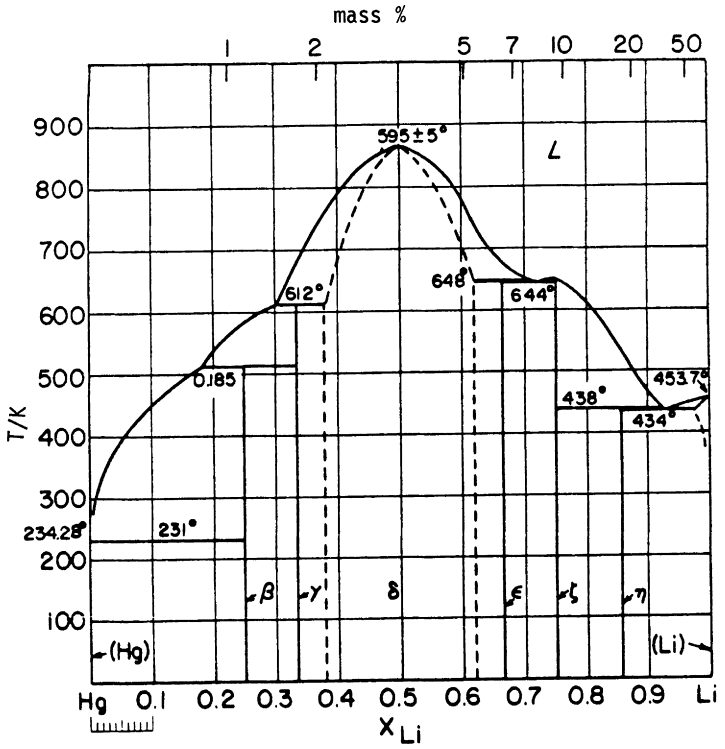

Fig. 1. The Li-Hg phase diagram (20).

(Continued next page)

COMPONENTS:	EVALUATOR:
(1) Lithium; Li; [7439-93-2] (2) Mercury; Hg; [7439-97-6]	C. Guminski; Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland July, 1985

CRITICAL EVALUATION: (Continued)

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