The Experimental Determination of Solubilities
Wiley Series in Solution Chemistry

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Volume 6
The Experimental Determination of Solubilities
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The Experimental Determination of Solubilities

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Wiley Series in Solution Chemistry
Volume 6
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Series Preface

There are many aspects of solution chemistry. This is apparent from the wide range of topics that have been discussed during recent International Conferences on Solution Chemistry and International Symposia on Solubility Phenomena. The Wiley Series in Solution Chemistry was launched to fill the need to present authoritative, comprehensive and up-to-date accounts of these many aspects. Internationally recognized experts from research or teaching institutions in various countries have been invited to contribute to the series.

Volumes in print or in preparation cover experimental investigation, theoretical interpretation and prediction of physical chemical properties and behaviour of solutions. They also contain accounts of industrial applications and environmental consequences of properties of solutions.

Subject areas for the series include: solutions of electrolytes, liquid mixtures, chemical equilibria in solution, acid–base equilibria, vapour–liquid equilibria, liquid–liquid equilibria, solid–liquid equilibria, equilibria in analytical chemistry, dissolution of gases in liquids, dissolution and precipitation, solubility in cryogenic solvents, molten salt systems, solubility measurement techniques, solid solutions, reactions within the solid phase, ion transport reactions away from the interface (i.e. in homogeneous bulk systems), liquid crystalline systems, solutions of macrocyclic compounds (including macrocyclic electrolytes), polymer systems, molecular techniques for properties of solutions, complex and multi-component solutions, applications of solution chemistry to materials and metallurgy (oxide solutions, alloys, mattes, etc.), medical aspects of solubility, and environmental issues involving solution phenomena and homogeneous component phenomena.

Current and future volumes in the series include both single-authored and multi-authored research monographs and reference level works as well as edited collections of themed reviews and articles. They all contain comprehensive bibliographies.

Volumes in the series are important reading for chemists, physicists, chemical engineers and technologists as well as environmental scientists in academic and industrial institutions.

May 1996

Peter Fogg
Solubility is perhaps the most fundamental of all chemical phenomena. The significance of what dissolves what, to what extent, at what temperature and pressure, and the effects of other species, was recognized even by the early alchemists. In more recent times the importance of solubility phenomena has been recognized throughout science. In medicine, the solubility of gases in liquids forms the basis of life itself (oxygen in blood), of anesthesia, and of some types of poisoning. In the environment, solubility influences the weathering of rocks, the creation of soils and the composition of natural water bodies. The behavior and fate of many chemicals, both naturally occurring and synthetic, e.g. the cycling of CO$_2$ by the oceans, the uptake of pesticide residues by shellfish, etc., are also governed by solubility phenomena.

In industry, solubility phenomena are critical for the extraction of petroleum products, metals, essential oils, dyes, pharmaceuticals, pigments, food-stuffs from natural resources and also their transformation into an ever-wider range of useful products. And, of course, much of chemistry itself depends on the manipulation of solubility phenomena to perform syntheses, separations, purifications and analyses.

The importance of the quantitative measurement of solubilities has been recognized for a long time and vast amounts of solubility data have been reported in the scientific literature over many years. Because solubility phenomena are of such widespread occurrence and importance, such data are particularly widely scattered throughout the scientific and medical literature. As anyone who has ever had cause to find or use solubility data will know that, whilst there are some systems that have been investigated almost ad infinitum, there are many more for which even the most basic information is unavailable.

For these reasons the International Union of Pure and Applied Chemistry (IUPAC) set up a working group in 1974, later to become the Commission on Solubility Data under the chairmanship of the late Professor A.S. (Steven) Kertes to collect, collate, and evaluate all the available solubility data. The Commission’s work has been published as the Solubility Data Series which commenced in 1979 and, more than seventy-five volumes later, shows no sign...
of completion. Both the editors of this book and many of its contributors have been members of this on-going Commission at various times.

During this mammoth undertaking it became obvious that, despite the great advances in chemistry and instrumentation that have taken place during the Twentieth century, many of the published solubility data were of poor reliability. One example will suffice. It may surprise many readers that the solubilities of benzene in water from 0–50 °C, which are not particularly hard to measure and which are probably the best characterized of all liquid–liquid systems, are known to an accuracy of no better than ±5% (relative). Outside this temperature range the accuracy is even worse! The reasons for this situation vary from system to system. One of the most important reasons, noted by the compilers and evaluators of the Solubility Data Series, has been the use of inappropriate or inadequate methods for the determination of solubility. Accordingly, the Commission on Solubility Data decided that the future quality of solubility measurements would be well served by the publication of a book that codifies the reliable procedures for the measurement of all types of solubility data, as assessed by experienced researchers in the various areas.

Of course, because of the importance of solubility data in science and industry, there have been numerous reviews of specific types of solubility measurement, e.g. the determination of gases in liquids (R. Battino and H.L. Clever, Chem. Rev., 66, 395 (1966) or in molten slats (D. Bratland, K. Grjotehim, C. Krohn and K. Matzfied, Acta. Chem. Scand., 20, 1811 (1966). However, with the notable exception of the short chapter on solubility determination in the Techniques of Chemistry series, no book has appeared that covers the whole range of solubility measurements.

One of the problems of codifying the procedures for the experimental determination of solubilities is the extent of the field. Thus, although there are some broad commonalties in solubility measurements such as the need to control temperature, the widely varying nature of the problems of measuring, say, the solubility of a gas in a polymer and that of a solid electrolyte in water, have created a very diverse set of experimental traditions. The purpose of this book then, is to bring together for the first time, into one publication, a comprehensive account of the reliable experimental techniques for the measurement of solubilities of virtually all types.

The book is divided into five major sections. The first covers the fundamental thermodynamic and kinetic backgrounds necessary for a full understanding of solubility phenomena. In a book whose focus is decidedly experimental these chapters are necessarily brief. The next three sections cover, at varying lengths, the major types of solubility determinations according to the physical state of the solute: gases, liquids, and solids. The final section covers a number of technologically important areas whose character or traditions are sufficiently different to justify their separation. Although the particular coverage offered in each chapter has been left largely to
the discretion of the individual authors, the overall aim of the editors has been to provide a comprehensive, but not encyclopedic, coverage of the reliable methods in a particular area. Whenever possible, diagrams of apparatus of proven capability have been included so as to enable novice investigators to quickly develop reliable apparatus of their own. This book is not concerned with solubility data *per se*, but rather with its measurement. Nevertheless, where appropriate, authors have also included sets of data whose reliability is well established to enable new workers in an area to assess properly the quality of their apparatus, technique and data. Such information is vital for the assessment of new equipment designs. Some areas are too diverse for such recommendations. In these cases readers are referred to relevant volumes of the *Solubility Data Series* or other publications for critically evaluated data with which they can test their procedure and apparatus.

Although this book aims to provide a broad coverage of the experimental methods for all types of solubility measurements, a few topics which some readers might have expected to be included, have been omitted. For example, a number of volumes on the solubilities of pharmaceuticals have appeared in the *Solubility Data Series*, however, it was felt that the principles or procedures for the determination of such solubilities were adequately covered in Chapter 4. The only significant area which has not been covered is that of solids in solids (metals in metals) and in supercooled liquids. These topics are more appropriately addressed in metallurgical or ceramics contexts.

It should be noted that the authors of Chapter 2.1 (Solubility of Gases in Liquids) have departed from the nomenclature and definition of quantities currently recommended by IUPAC as they prefer to use the nomenclature found in the original literature. They feel that this will be easier for the reader. They also wished to have their contribution stand alone without the need to cross-reference the introductory material.
Acknowledgements

The editors would like to express their sincere gratitude to the following people who played significant roles in the development and production of this textbook.

First, Colin Young (formerly of the University of Melbourne) acted as one of the original editors and was instrumental in soliciting several of the contributors to this book. Secondly, Professor John W. (Jack) Lorimer (University of Western Ontario) made significant contributions to the overall editing of many of the chapters and was always available for consultation.

Thirdly, we wish to acknowledge the assistance provided by Professor James Grow (New Jersey Institute of Technology) for converting much of the original manuscript onto a CD. Finally, Peggy Schel is thanked for her pains-taking efforts in retyping several of the chapters.

Finally, we would like to thank all of our contributors for their patience and dedication in what has been a very long and difficult gestation.

Reg Tomkins
Glenn Hefter
List of Symbols

Only general symbols are given. Specific uses of the symbols are defined in the text.

- \( a \) relative activity
- \( a \) lattice parameter
- \( A \) area
- \( A, B, C \) components of a system
- \( A_i \) coefficient in thermodynamic equation for temperature dependence
- \( A^\gamma = 3A^\theta \) Debye–Hückel parameter for activity coefficient in Pitzer equations
- \( A^\phi \) Debye–Hückel parameter for osmotic coefficient in Pitzer equations
- \( b = 1.2 \) universal parameter in Pitzer equations; Debye–Hückel ion size parameter
- \( B \) second virial coefficient (volume form)
- \( B_i \) coefficient in series for critical curve
- \( B' \) second virial coefficient (pressure form)
- \( B_{ij} \) second virial coefficient in a gas mixture (volume form)
- \( B^\gamma \) second virial coefficient for activity coefficient of a salt in Pitzer equations
- \( B^\phi \) second virial coefficient for osmotic coefficient of a salt in Pitzer equations
- \( c \) amount (of substance) concentration
- \( c \) total number of components in a system
- \( C \) third virial coefficient (volume form)
- \( C' \) third virial coefficient (pressure form)
- \( C_i \) coefficient in Redlich–Kister equation
- \( C_{ijk} \) third virial coefficient in a gas mixture (volume form)
- \( C^\gamma \) third virial coefficient for activity coefficient of a salt in Pitzer equations
- \( C^\phi \) third virial coefficient for osmotic coefficient of a salt in Pitzer equations
- \( C_p \) heat capacity at constant pressure
### List of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>chlorinity</td>
</tr>
<tr>
<td>C_w</td>
<td>'weight solubility'</td>
</tr>
<tr>
<td>d</td>
<td>relative (mass) density</td>
</tr>
<tr>
<td>d'</td>
<td>hydraulic diameter</td>
</tr>
<tr>
<td>D</td>
<td>distribution coefficient</td>
</tr>
<tr>
<td>D'</td>
<td>diffusion coefficient</td>
</tr>
<tr>
<td>E</td>
<td>electromotive force; cell voltage</td>
</tr>
<tr>
<td>f</td>
<td>variance or degrees of freedom in a system</td>
</tr>
<tr>
<td>f'</td>
<td>fugacity</td>
</tr>
<tr>
<td>f''</td>
<td>activity coefficient referenced to Raoult's law</td>
</tr>
<tr>
<td>f''''</td>
<td>electrostatic term for activity coefficient in Pitzer equations</td>
</tr>
<tr>
<td>f'''''</td>
<td>electrostatic term for osmotic coefficient in Pitzer equations</td>
</tr>
<tr>
<td>F</td>
<td>Faraday constant</td>
</tr>
<tr>
<td>F</td>
<td>exit volume flow rate (in chromatographic column)</td>
</tr>
<tr>
<td>F</td>
<td>Fisher F-statistic</td>
</tr>
<tr>
<td>F_{1,n-p,\alpha}</td>
<td>Fisher F-statistic for 1 and n – p degrees of freedom at confidence level ( \alpha )</td>
</tr>
<tr>
<td>F_{c}</td>
<td>magnetic force, x-component</td>
</tr>
<tr>
<td>F(p)</td>
<td>function used in conversion of gas solubility quantities</td>
</tr>
<tr>
<td>F(m/m_0)</td>
<td>function giving mass dependence of precipitation rate</td>
</tr>
<tr>
<td>g, G</td>
<td>gas</td>
</tr>
<tr>
<td>g_p, g(c)</td>
<td>growth functions (see Chapter 2)</td>
</tr>
<tr>
<td>G(T)</td>
<td>function used in temperature dependence of solubility</td>
</tr>
<tr>
<td>G</td>
<td>Gibbs energy</td>
</tr>
<tr>
<td>h(r)</td>
<td>growth function (see Chapter 2)</td>
</tr>
<tr>
<td>H</td>
<td>enthalpy</td>
</tr>
<tr>
<td>H_x dH_x/dx</td>
<td>one-dimensional magnetic field strength</td>
</tr>
<tr>
<td>i</td>
<td>electric current</td>
</tr>
<tr>
<td>I</td>
<td>double saturation point (eutonic point)</td>
</tr>
<tr>
<td>I</td>
<td>X-ray intensity</td>
</tr>
<tr>
<td>I_c</td>
<td>ionic strength (amount concentration basis)</td>
</tr>
<tr>
<td>I_m</td>
<td>ionic strength (molality basis)</td>
</tr>
<tr>
<td>I_P</td>
<td>integral in Poynting correction</td>
</tr>
<tr>
<td>J</td>
<td>growth or precipitation rate</td>
</tr>
<tr>
<td>J</td>
<td>pressure gradient (in chromatographic column)</td>
</tr>
<tr>
<td>k</td>
<td>rate constant (in general)</td>
</tr>
<tr>
<td>k</td>
<td>proportionality constant relating salinity and chlorinity</td>
</tr>
<tr>
<td>k</td>
<td>capacity factor (in gas chromatography)</td>
</tr>
<tr>
<td>k_{H}</td>
<td>Henry's law constant, mole fraction scale</td>
</tr>
<tr>
<td>k^{(m)}_{H}</td>
<td>Henry's law constant, molality scale</td>
</tr>
</tbody>
</table>
List of Symbols

- $k_{H}$: Henry’s law constant, amount concentration scale
- $k_{syz}$: generalized salting-out coefficient
- $k$, $K$: various constants (defined in text)
- $K$: equilibrium constant
- $K_s$: solubility constant (formerly solubility product)
- $l$, $L$: liquid
- $l$: length
- $L$: hydraulic length
- $L^*$: Ostwald coefficient, pure solvent reference
- $m$: mass
- $m$: molality
- $m^{(w)}$: aquamolality, solvomolality
- $M$: molar mass
- $M_r$: relative molar mass (molecular weight)
- $M$: average molar mass
- $\bar{M}_{r,n}$: number-average molecular weight/relative molar mass
- $\bar{M}_{r,w}$: mass-average molecular weight/relative molar mass
- $\bar{M}_{r,z}$: z-average molecular weight/relative molar mass
- $n$: amount of substance
- $n$: number of electrons in electrochemical reaction
- $n$: number of experimental points
- $N$: number of entities
- $N_A$: Avogadro constant
- $p$, $P$: pressure
- $P$: number of species
- $P$: number of parameters
- $P$: number of phases
- $Pe$: Péclet number
- $p$: characteristic property
- $Q$: quantity of heat
- $Q$: ion product
- $r$: mole ratio (amount ratio, number ratio)
- $r$: radius
- $r$: rate of loss of mass in corrosion
- $R$: molar gas constant
- $R$: electric resistance
- $Re$: Reynolds number
- $R_p$: sum of squares of deviations for $p$ parameters
- $s$: solubility (in general)
- $s$, $S$: solid
- $S$: Kuenen coefficient, solution reference
- $S^*$: Kuenen coefficient, pure solvent reference
**List of Symbols**

\( S \)  
entropy

\( S \)  
salinity

\( S \)  
saturation ratio

\( S_{c} \)  
Schmidt number

\( S_{h} \)  
Sherwood number

\( t \)  
time

\( T \)  
thermodynamic temperature

\( T_{c} \)  
critical temperature

\( T_{r} \)  
reference temperature

\( T_{L} \)  
lower critical solution temperature

\( T_{U} \)  
upper critical solution temperature

\( U \)  
relative velocity

\( v \)  
flow velocity

\( V \)  
volume

\( w \)  
mass fraction

\( w \)  
molar energy parameter

\( w \)  
Wegner correction in critical equation

\( w_{s} \)  
solute mass fraction of solute substance

\( w_{h} \)  
solute mass fraction of solvent substance

\( x \)  
amount (mole) fraction

\( x_{s} \)  
solute amount (mole) fraction of solute substance

\( x_{n} \)  
solvent amount (mole) fraction of solvent substance

\( x' \)  
ionic amount (mole) fraction of solvent

\( x_{+}, x_{-} \)  
ionic amount (mole) fractions of cation, anion

\( X \)  
composition (in general)

\( y \)  
amount (mole) fraction in vapor phase; experimental variable

\( z \)  
charge number of ion

\( z \)  
generalized composition in salting-out equation

\( Z \)  
compression factor (compressibility factor)

\( \alpha \)  
Bunsen coefficient, solution reference

\( \alpha^{*} \)  
Bunsen coefficient, pure solvent reference

\( \alpha \)  
second critical index

\( \alpha_{1} \)  
= 1.4 or 2.0; parameter in Pitzer equations

\( \alpha_{2} \)  
= 12.0; parameter in Pitzer equations

\( \beta \)  
absorption coefficient

\( \beta \)  
critical index

\( \beta_{c} \)  
corrosion constant in turbulent flow

\( \varrho_{i}^{(0)}, \varrho_{i}^{(1)}, \varrho_{i}^{(2)} \)  
parameters in Pitzer equations

\( \gamma \)  
mass density (= mass concentration)

\( \gamma_{c} \)  
activity coefficient on amount concentration scale

\( \gamma_{m} \)  
activity coefficient on molality scale
List of Symbols

\( \gamma_x \) activity coefficient on (asymmetric) mole fraction scale; rational activity coefficient

\( \gamma_\pm = (\gamma_+ v_+ \gamma_- v_-)^{1/\nu} \) mean ionic activity coefficient, molality scale

\( \delta \) degree of dissociation or association

\( \delta \) diffusion layer thickness

\( \delta \) attenuation decrement for torsional vibrations

\( \delta_{AB} = 2B_{AB} - B_{AA} - B_{BB} \)

\( \zeta \) mass ratio

\( \varepsilon \) extension constant of a spring

\( \eta \) viscosity, dynamic viscosity

\( \theta = 1 - T/T_c \)

\( \theta \) Bragg angle in X-ray diffraction

\( \lambda \) cryoscopic or freezing point constant

\( \mu \) chemical potential

\( \mu \) magnetic permeability

\( \mu_i \) mass coefficient of X-ray absorption at wavelength \( i \)

\( v_+, v_- \) stoichiometric numbers of cation, anion

\( v = v_+ + v_- \)

\( v_\pm = (v_+ v_-)^{1/\nu} \)

\( v \) kinematic viscosity

\( v \) potential sweep rate

\( \xi \) equilibrium parameter (\( T, p, \) composition)

\( \rho \) mass density (mass concentration)

\( \rho \) electrical resistivity

\( \sigma \) surface tension

\( \tau \) transition time

\( \phi \) fugacity coefficient

\( \phi \) volume fraction

\( \phi_s \) solvent volume fraction

\( \phi_m \) osmotic coefficient of solvent, molality basis (‘practical’ osmotic coefficient)

\( \phi_x \) osmotic coefficient of solvent, mole fraction basis (‘rational’ osmotic coefficient)

\( \chi \) magnetic susceptibility

\( \Omega \) mean atomic volume

Mathematical quantities

\( \tilde{\partial}_T, \tilde{\partial}^2_T \) First and second derivatives with respect to \( T \)

\( \ln \) natural logarithm

\( \log \) common logarithm

\( \Delta_r \) finite difference: final state – initial state for process \( r \); e.g.,

\( \Delta_{fus}H_m, B \) molar enthalpy of fusion of pure substance \( B \)
**List of Symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>ð</td>
<td>partial derivative</td>
</tr>
<tr>
<td>%</td>
<td>per cent, percent</td>
</tr>
<tr>
<td>‰</td>
<td>permille, per mille, per mill, permil, pro mille</td>
</tr>
</tbody>
</table>

**Superscripts**
- E: thermodynamic excess (function)
- g: gas
- id: ideal reference state
- l: liquid
- α, β, ...: phase designations
- o, Θ: standard state; standard; degree
- ∞: infinite dilution
- *: pure substance
- –: average (overbar)

**Subscripts**
- A: substance; solvent substance
- B: substance; solute substance
- C: substance; solvent substance
- M: metal
- p: polymer
- fus: fusion
- t: transfer
- trs: transition
- sln: dissolution
- vap: vaporization