

INTRODUCTION TO THE SOLUBILITY DATA SERIES

SOLUBILITY OF LIQUIDS IN LIQUIDS

NATURE OF THE PROJECT

The Solubility Data project (SDP) has as its aim a comprehensive review of published data for solubilities of gases, liquids and solids in liquids or solids. Data of suitable precision are compiled for each publication 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 is concerned primarily with liquid-liquid systems, but a limited number of related solid-liquid, fluid-fluid and multicomponent (organic-water-salt) systems are included where it is considered logical and appropriate. Solubilities at elevated and low temperatures and at elevated pressures have also been included, as it is considered inappropriate to establish artificial limits on the data presented if they are considered relevant or useful.

For some systems, the two components may be miscible in all proportions at certain temperatures and pressures. Data on reported miscibility gaps and upper and lower critical solution temperatures are included where appropriate and when available.

COMPILATIONS AND EVALUATIONS

The formats for the compilations and critical evaluations have been standardized for all volumes. A description of these formats follows.

Compilations

The format used for the compilations is, for the most part, self-explanatory. A compilation sheet is divided into boxes, with detailed contents described below.

Components: Each component is listed according to IUPAC name, formula, and Chemical Abstracts (CA) Registry Number. The Chemical Abstracts name is also included if this differs from the IUPAC name, as are trivial names if appropriate. IUPAC and common names are cross-referenced to Chemical Abstracts names in the System Index.

The formula is given either in terms of the IUPAC or Hill (1) 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 on a given compilation sheet 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 the IUPAC 18-column periodic table with two additional rows:

Columns 1 and 2:	H, alkali elements, ammonium, alkaline earth elements
Columns 3 to 12:	transition elements
Columns 13 to 17:	boron, carbon, nitrogen groups; chalcogenides, halogens
Column 18:	noble gases
Row 1:	Ce to Lu
Row 2:	Th to the end of the known elements, in order of atomic number.

Organic compounds within each Hill formula are ordered in the following succession:

- (a) by degree of unsaturation
- (b) by order of increasing chain length in the parent hydrocarbon
- (c) by order of increasing chain length of hydrocarbon branches
- (d) numerically by position of unsaturation
- (e) numerically by position by substitution
- (f) alphabetically by IUPAC name.

Example:	
C ₅ H ₈	cyclopentane 2-methyl-1,3-butadiene 1,4-pentadiene 1-pentyne
C ₅ H ₁₀	cyclopentane 3-methyl-1-butene 2-methyl-2-butene 1-pentene 2-pentene
C ₅ H ₁₂	2,2-dimethylpropane 2-methylbutane pentane
C ₅ H ₁₂ O	2,2-dimethyl-1-propanol 2-methyl-1-butanol 2-methyl-2-butanol 3-methyl-1-butanol 3-methyl-2-butanol 1-pentanol 2-pentanol 3-pentanol
C ₆ H ₁₂ O	cyclohexanol 4-methyl-1-penten-3-ol 1-hexen-3-ol 4-hexen-3-ol

Deuterated (²H) compounds follow immediately the corresponding H compounds.

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. In the case of multiple entries (for example, translations) an asterisk indicates the publication used for compilation of the data.

Variables: Ranges of temperature, pressure, etc. are indicated here.

Prepared by: The names of all compilers are given here.

Experimental Values: Components are described as (1), (2), etc., as defined in the "Components" box. 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. In most cases, 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 1989 atomic weights (2). Temperatures are expressed as *t*/°C, *t*/°F or *T*/K as in the original; if necessary, conversions to *T*/K are made, sometimes in the compilations, and always in the critical evaluation. However, the author's units are expressed according to IUPAC recommendations (3) as far as possible.

Errors in calculations, fitting equations, etc. are noted, and where possible corrected. Material inserted by the compiler is identified by the word "compiler" or by the compiler's name in parentheses or in a footnote. In addition, compiler-calculated values of mole or mass fractions are included if the original data do not use these units. If densities are reported in the original paper, conversions from concentrations to mole fractions are included, but otherwise this is done in the evaluation, with the values and sources of the densities being quoted and referenced.

Details of smoothing equations (with limits) are included if they are present in the original publication and if the temperature or pressure ranges are wide enough to justify this procedure and if the compiler finds that the equations are consistent with the data.

The precision of the original data is preserved when derived quantities are calculated, if necessary by the inclusion of one additional significant figure. In some cases graphs have been included, either to illustrate presented data more clearly, or if this is the only information in the original. Full grids are not usually inserted as it is not intended that users should read data from the graphs.

Method: The apparatus and procedure are mentioned briefly. Abbreviations used in Chemical Abstracts are often used here to save space, reference being made to sources of further detail if these are cited in the original paper.

Source and Purity of Materials: For each component, referred to as (1), (2), etc., the following information (in this order and in abbreviated form) is provided if available in the original paper: source and specified method of preparation; properties; degree of purity.

Estimated Error: If estimated errors were omitted by the original authors, and if relevant information is available, the compilers have attempted to estimate errors (identified by "compiler" or the compiler's name in parentheses or in a footnote) from the internal consistency of data and type of apparatus used. Methods used by the compilers for estimating and reporting errors are based on Ku and Eisenhart (4).

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: The format for these follows the format for the Original Measurements box, except that final page numbers are omitted. References (usually cited in the original paper) are given where relevant to interpretation of the compiled data, or where cross-reference can be made to other compilations.

Evaluations

The evaluator's task is 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. There are only three boxes on a typical evaluation sheet, and these are described below.

Components: The format is the same as on the Compilation sheets.

Evaluator: The name and affiliation of the evaluator(s) and date up to which the literature was checked.

Critical Evaluation:

(a) Critical text. The evaluator checks that the compiled data are correct, assesses their reliability and quality, estimates errors where necessary, and recommends numerical values based on all the published data (including theses, reports and patents) for each given system. Thus, the evaluator reviews the merits or shortcomings of the various data. Only published data are considered. Documented rejection of some published data may occur at this stage, and the corresponding compilations may be removed.

The solubility of comparatively few systems is known with sufficient accuracy to enable a set of recommended values to be presented. Although many systems have been studied by at least two workers, the range of temperatures is often sufficiently different to make meaningful comparison impossible.

Occasionally, it is not clear why two groups of workers obtained very different but internally consistent sets of results at the same temperature, although both sets of results were obtained by reliable methods. In such cases, a definitive assessment may not be possible. In some cases, two or more sets of data have been classified as tentative even though the sets are mutually inconsistent.

(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, stating the limits within which it should be used.

(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 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, including all those publications appearing in the accompanying compilation sheets and those which, by virtue of their poor precision, have been rejected and not compiled.

(f) Units. While the original data may be reported in the units used by the investigators, the final recommended values are reported in SI units (3) when the data can be converted accurately.

QUANTITIES AND UNITS USED IN COMPILATION AND EVALUATION OF SOLUBILITY DATA

Mixtures, Solutions and Solubilities

A *mixture* (5, 6) describes a gaseous, liquid or solid phase containing more than one substance, where the substances are all treated in the same way.

A *solution* (5, 6) 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 solute 1 (solid, liquid or gas) is the analytical composition of a saturated solution, expressed in terms of the proportion of the designated solute in a designated solvent (7).

"Saturated" implies equilibrium with respect to the processes of dissolution and demixing; the equilibrium may be stable or metastable. The solubility of a substance in metastable equilibrium is usually greater than that of the same substance in stable equilibrium. (Strictly speaking, it is the activity of the substance in metastable equilibrium 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 reference states used for definition of activities, activity coefficients and osmotic coefficients. Note that the composition of a saturated mixture (or solution) can be described in terms of any suitable set of thermodynamic components.

Physicochemical Quantities and Units

Solubilities of solids have been the subject of research for a long time, and have been expressed in a great many ways, as described below. In each case, specification of the temperature and either partial or total pressure of the saturating gaseous component is necessary. The nomenclature and units follow, where possible, ref. (3). A few quantities follow the ISO standards (8) or the German standard (9); see a review by Cvitaš (10) for details.

A note on nomenclature. The nomenclature of the IUPAC *Green Book* (3) calls the solute component B and the solvent component A. In compilations and evaluations, the first-named component (component 1) is the solute, and the second (component 2 for a two-component system) is the solvent. The reader should bear these distinctions in nomenclature in mind when comparing equations given here with those in the *Green Book*.

1. *Mole fraction* of substance 1, x_1 or $x(1)$ (condensed phases), y_1 (gases):

$$x_1 = n_1 / \sum_{s=1}^c n_s \quad [1]$$

where n_s is the amount of substance of s , and c is the number of distinct substances present (often the number of thermodynamic components in the system). *Mole per cent* of substance 1 is $100 x_1$.

2. *Ionic mole fractions* of salt i , x_{i+} , x_{i-} :

For a mixture of s binary salts i , each of which ionizes completely into ν_{s+} cations and ν_{s-} anions, with $\nu_s = \nu_{s+} + \nu_{s-}$ and a mixture of p non-electrolytes j , of which some may be solvent components, a generalization of the definition in (11) gives:

$$x_{i+} = \frac{\nu_{i+} x_i}{1 + \sum_{i=1}^s (\nu_i - 1) x_s}, \quad x_{i-} = \frac{\nu_{i-} x_i}{\nu_{i+}} \quad i = 1 \dots s \quad [2]$$

$$x_j' = \frac{x_j}{1 + \sum_{i=1}^s (\nu_i - 1) x_i}, \quad j = (s+1), \dots, p \quad [3]$$

The sum of these mole fractions is unity, so that, with $c = s + p$,

$$\sum_{i=1}^s (x_{i+} + x_{i-}) + \sum_{i=s+1}^c x_i' = 1 \quad [4]$$

General conversions to other units in multicomponent systems are complicated. For a three-component system containing non-electrolyte 1, electrolyte 2 and solvent 3,

$$x_1 = \frac{v_{2+} x_1'}{v_{2+} - (v_2 - 1)x_{2+}}, \quad x_2 = \frac{x_{2+}}{v_{2+} - (v_2 - 1)x_{2+}} \quad [5]$$

These relations are used in solubility equations for salts, and for tabulation of salt effects on solubilities of gases (see below).

3. *Mass fraction* of substance 1, w_1 or $w(1)$:

$$w_1 = g_1 / \sum_{s=1}^c g_s \quad [6]$$

where g_s is the mass of substance s . *Mass per cent* of substance 1 is $100 w_1$. The equivalent terms *weight fraction*, *weight per cent* and *g (1)/100 g solution* are no longer used.

4. *Molality* of solute 1 in a solvent 2, m_1 :

$$m_1 = n_1 / n_2 M_2 \quad [7]$$

SI base units: mol kg⁻¹. Here, M_2 is the molar mass of the solvent.

5. *Aquamolality*, *Solvomolality* of substance 1 in a mixed solvent with components 2, 3 (12), $m_1^{(3)}$:

$$m_1^{(3)} = m_1 \bar{M} / M_3 \quad [8]$$

SI base units: mol kg⁻¹. Here, the average molar mass of the solvent is

$$\bar{M} = x_2' M_2 + (1 - x_2') M_3 \quad [9]$$

and x_2' is the solvent mole fraction of component 2. This term is used most frequently in discussing comparative solubilities in water (component 2) and heavy water (component 3) and in their mixtures.

6. *Amount concentration* of solute 1 in a solution of volume V , c_1 :

$$c_1 = [\text{formula of solute}] = n_1 / V \quad [10]$$

SI base units: mol m⁻³. The symbol c_1 is preferred to [formula of solute], but both are used. The old terms *molarity*, *molar* and *moles per unit volume* are no longer used.

7. *Mass concentration* of solute 1 in a solution of volume V , ρ_1 : SI base units: kg m⁻³.

$$\rho_1 = g_1 / V \quad [11]$$

8. *Mole ratio*, $r_{A,B}$ (dimensionless) (10)

$$r_{A,B} = n_1 / n_2 \quad [12]$$

Mass ratio, symbol $\zeta_{A,B}$, may be defined analogously (10).

Mole and mass fractions are appropriate to either the mixture or the solution point of view. The other quantities are appropriate to the solution point of view only. Conversions between pairs of these quantities can be carried out using the equations given in Table 1 at the end of this Introduction. Other useful quantities will be defined in the prefaces to individual volumes or on specific data sheets.

9. *Density*, ρ :

$$\rho = g / V \quad [13]$$

SI base units: kg m^{-3} . Here g is the total mass of the system.

10. *Relative density*, $d = \rho/\rho^0$: the ratio of the density of a mixture at temperature t , pressure p to the density of a reference substance at temperature t' , pressure p' . For liquid solutions, the reference substance is often water at 4°C, 1 bar. (In some cases 1 atm is used instead of 1 bar.) The term *specific gravity* is no longer used.

Thermodynamics of Solubility

Thermodynamic analysis of solubility phenomena provides a rational basis for the construction of functions to represent solubility data, and thus aids in evaluation, and sometimes enables thermodynamic quantities to be extracted. Both these are often difficult to achieve because of a lack of experimental or theoretical activity coefficients. Where thermodynamic quantities can be found, they are not evaluated critically, since this task would involve examination of a large body of data that is not directly relevant to solubility. Where possible, procedures for evaluation are based on established thermodynamic methods. Specific procedures used in a particular volume will be described in the Preface to that volume.

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