

## INTRODUCTION TO 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,  $x_B$ :

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

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,  $w_B$ :

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

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):

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

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:

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

where  $M_A$  is the molar mass of the solvent.

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

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

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<sup>-3</sup> (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  $t^\circ\text{C}$ , 1 atm divided by the density of water at  $t'^\circ\text{C}$ , 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

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

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

$$\lim_{x_B \rightarrow 1} f_B = 1 \quad (8)$$

(b) Solutions.

(i) Solute substance, B. The molal activity coefficient  $\gamma_B$  is given by

$$RT \ln(\gamma_B m_B) = \mu_B - (\mu_B - RT \ln m_B)^\infty \quad (9)$$

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

$$\gamma_B^\infty = 1 \quad (10)$$

Activity coefficients  $\gamma_B$  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):

$$\gamma_B = x_A f_{x,B} = V_A^*(1 - \sum_S c_S) \gamma_B \quad (11)$$

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  $B \equiv C_{v_+} A_{v_-}$ , the molal activity is replaced by (9)

$$\gamma_B^{m_B} = \gamma_{\pm}^{v_+ v_-} Q^v \quad (14)$$

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

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

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

$$x_+ = v_+ x_B / [1 + (v-1) x_B]; \quad x_- = v_- x_B / [1 + (v-1) x_B] \quad (16)$$

(ii) Solvent, A:

The osmotic coefficient,  $\phi$ , of a solvent substance A is defined as (1):

$$\phi = (\mu_A^* - \mu_A) / RT M_A \sum_S m_S \quad (17)$$

where  $\mu_A^*$  is the chemical potential of the pure solvent.

The rational osmotic coefficient,  $\phi_x$ , is defined as (1):

$$\phi_x = (\mu_A - \mu_A^*) / RT \ln x_A = \phi M_A \sum_S m_S / \ln(1 + M_A \sum_S m_S) \quad (18)$$

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  $d\mu_i$  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

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

where

$$H_i - H_i' = T(S_i - S_i') \quad (24)$$

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

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

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):

$$RT \ln f_B = w x_A^2 \quad (26)$$

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

$$\begin{aligned} nH_A + H_B - H_{AB}^* &= \Delta H_{AB} + n(H_A - H_A^*) + (H_B - H_B^*) \\ &= \Delta H_{AB} + w(n x_B^2 + x_A^2) \end{aligned} \quad (27)$$

where  $\Delta H_{AB}$  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

$$R d \ln \{ x_B (1-x_B)^n \} = -\Delta H_{AB} d\left(\frac{1}{T}\right) - w d\left(\frac{x_A^2 + n x_B^2}{T}\right) \quad (28)$$

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

$$\begin{aligned} \ln \{ x_B (1-x_B)^n \} &\approx \ln \left\{ \frac{n^n}{(1+n)^{n+1}} \right\} - \left\{ \frac{\Delta H_{AB}^* - T^* \Delta C_p^*}{R} \right\} \left( \frac{1}{T} - \frac{1}{T^*} \right) \\ &+ \frac{\Delta C_p^*}{R} \ln \left( \frac{T}{T^*} \right) - \frac{w}{R} \left\{ \frac{x_A^2 + n x_B^2}{T} - \frac{n}{(n+1) T^*} \right\} \end{aligned} \quad (29)$$

where  $\Delta C_p^*$  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  $\Delta H_{AB}^*$  is the corresponding change in enthalpy at  $T = T^*$ . Equation (29) has the general form

$$\ln \{ x_B (1-x_B)^n \} = A_1 + A_2/T + A_3 \ln T + A_4 (x_A^2 + n x_B^2)/T \quad (30)$$

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

$$RT \ln f_{x,B} = w(x_A^2 - 1) \quad (31)$$

and (27) becomes

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

where the first term,  $\Delta H_{AB}^\infty$ , is the enthalpy of melting and dissociation of solid compound  $A_nB$  to the infinitely dilute state of solute  $B$  in solvent  $A$ ;  $H_B^\infty$  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  $\Delta H_{AB}^*$  and  $\Delta C_p^*$  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

$$Rv(1/x_B - n/x_A) \{1 + (\partial \ln f_{\pm} / \partial \ln x_{\pm})_{T,P}\} dx_B / \{1 + (v-1)x_B\} \\ = \{\Delta H_{AB}^{\infty} + n(H_A - H_A^*) + (H_B - H_B^*)\} d(1/T) \quad (33)$$

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

$$\ln \left\{ \frac{x_B^v (1-x_B)^n}{1+(v-1)x_B} \right\}^{n+v} = \ln \left\{ \frac{n^n}{(n+v)^{n+v}} \right\} - \left\{ \frac{\Delta H_{AB}^{\infty} (T^*) - T^* \Delta C_P^*}{R} \right\} \left( \frac{1}{T} - \frac{1}{T^*} \right) + \frac{\Delta C_P^*}{R} \ln(T/T^*) \quad (34)$$

A similar equation (with  $v=2$  and without the heat capacity terms) has been used to fit solubility data for some MOH=H<sub>2</sub>O 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:

$$\mu_{A_n B}^* = \mu_{A_n B}(\text{sln}) = n\mu_A + \mu_B \quad (35)$$

$$= (n\mu_A^* + v_+ \mu_+^{\infty} + v_- \mu_-^{\infty}) + nRT \ln f_{\lambda} x_A \\ + vRT \ln \gamma_{\pm} m_{\pm} Q_{\pm} \quad (36)$$

for a salt hydrate A<sub>n</sub>B which dissociates to water, (A), and a salt, B, one mole of which ionizes to give v<sub>+</sub> cations and v<sub>-</sub> anions in a solution in which other substances (ionized or not) may be present. If the saturated solution is sufficiently dilute, f<sub>A</sub> = x<sub>A</sub> = 1, and the quantity K<sub>S0</sub><sup>0</sup> in

$$\Delta G^{\infty} \equiv (v_+ \mu_+^{\infty} + v_- \mu_-^{\infty} + n\mu_A^* - \mu_{AB}^*) \\ = -RT \ln K_{S0}^0 \\ = -RT \ln Q^v \gamma_{\pm}^v m_+^{v_+} m_-^{v_-} \quad (37)$$

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<sub>S0</sub><sup>0</sup> 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<sub>v+</sub>A<sub>v-</sub>·nH<sub>2</sub>O in the presence of other solutes is given by eqn (36) as

$$v \ln \{m_B/m_B(0)\} = -v \ln \{\gamma_{\pm}/\gamma_{\pm}(0)\} - n \ln \{a_{H_2O}/a_{H_2O}(0)\} \quad (38)$$

where a<sub>H<sub>2</sub>O</sub> is the activity of water in the saturated solution, m<sub>B</sub> 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<sup>-3</sup> 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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R. Cohen-Adad, Villeurbanne,  
France

J.W. Lorimer, London, Canada

M. Salomon, Fair Haven, New  
Jersey, U.S.A.