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.

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 meta-stable. The solubility of a substance in metastable equilibrium is usually greater than that of the corresponding substance in stable equliibrium. (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 quantities used as measures of solubility and in the reference states used for definition of activities, activity coefficients and osmotic 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:*

$$x_B = n_B / \sum_{s=1}^{c} n_s \qquad [1]$$

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 B is 100 x_B.*

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

$$w_B = m_B' / \sum_{s=1}^{c} m_s' \qquad [2]$$

where m_s' is the mass of substance s. *Mass per cent* 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):*

$$x_{s,B} = m_B / \sum_{s=1}^{c'} m_s = x_B / \sum_{s=1}^{c'} x_s \qquad [3]$$

$$w_{s,B} = m_B' / \sum_{s=1}^{c} m_s' = w_B / \sum_{s=1}^{c'} w_s \qquad [3a]$$

where the summation is over the solutes only. For the solvent A, $x_{S,A} = x_A/(1 - x_A)$, $w_{S,A} = w_A/(1 - w_A)$. 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 symbol c_B is preferred to $[B]$, but both are used. The terms *molarity* and *molar* are not used.

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 among these quantities can be carried out using the equations given in Table 1-1 following this Introduction. Other useful quantities will be defined in the prefaces to individual volumes or on specific data sheets.

In addition to the quantities defined above, the following are useful in conversions between concentrations and other quantities.

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

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 bar divided by the density of water at t'°C, 1 bar. (In some cases 1 atm = 101.325 kPa is used instead of 1 bar = 100 kPa.)

8. *A note on nomenclature.* The above definitions use the nomenclature of the IUPAC Green Book (1), in which a solute is called B and a solvent 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 nomenclature and theoretical equations given in this Introduction with equations and nomenclature used on the evaluation and compilation 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 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 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 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., (5-12).

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 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 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 ∞ indicates an infinitely dilute solution. For any solute B,

$$\gamma_B^\infty = 1 \qquad [10]$$

Activity coefficients y_B connected with concentrations c_B, and $f_{x,B}$ (called the *rational activity coefficient*) connected with mole fractions x_B are defined in analogous ways. The relations among them are (1, 9), where ρ^* is the density of the pure solvent:

$$f_B = (1 + M_A\sum_s m_s)\gamma_B = [\rho + \sum_s (M_A - M_s)c_s]y_B/\rho^* \qquad [11]$$

$$\gamma_B = (1 - \sum_s x_s)f_{x,B} = (\rho - \sum_s M_s c_s)y_B/\rho^* \qquad [12]$$

$$y_B = \rho^* f_{x,B}[1 + \sum_s (M_s/M_A - 1)x_B]/\rho = \rho^*(1 + \sum_s M_s m_s)\gamma_B/\rho \qquad [13]$$

For an electrolyte solute $B = C_{\nu_+}A_{\nu_-}$, the activity on the molality scale is replaced by (9)

$$\gamma_B m_B = \gamma_\pm^\nu m_B^\nu Q^\nu \qquad [14]$$

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

$$f_{x,B}x_B = Q^\nu f_\pm^\nu x_\pm^\nu \qquad [15]$$

where $x_\pm = (x_+ x_-)^{1/\nu}$. The quantities x_+ and x_- are the ionic mole fractions (9), which are

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

where ν_s is the sum of the stoichiometric coefficients for the ions in a salt with mole fraction x_s. Note that the mole fraction of solvent is now

$$x_A' = (1 - \sum_s \nu_s x_s)/[1 + \sum_s (\nu_s - 1)x_s] \qquad [17]$$

so that

$$x_A' + \sum_s \nu_s x_s = 1 \qquad [18]$$

The relations among the various mean ionic activity coefficients are:

$$f_\pm = (1 + M_A\sum_s \nu_s ms)\gamma_\pm = [\rho + \sum_s (\nu_s M_A - M_s)c_s]y_\pm/\rho^* \qquad [19]$$

$$\gamma_\pm = \frac{(1 - \sum_s x_s)f_\pm}{1 + \sum_s (\nu_s - 1)x_s} = (\rho - \sum_s M_s c_s)y_\pm/\rho^* \qquad [20]$$

$$y_\pm = \frac{\rho^*[1 + \sum_s (M_s/M_A - 1)xs]f_\pm}{\rho[1 + \sum_s (\nu_s - 1)x_s]} = \rho^*(1 + \sum_s M_s m_s)\gamma_\pm/\rho \qquad [21]$$

(ii) *Solvent, A:*

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

$$\phi = (\mu_A^* - \mu_A)/RT\, M_A \sum_s m_s \qquad [22]$$

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

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

$$\phi_x = (\mu_A - \mu_A^*)/RT\ln x_A = \phi M_A \sum_s m_s/\ln(1 + M_A \sum_s m_s) \qquad [23]$$

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

For a mixed solvent, the molar mass in the above equations is replaced by the average molar mass; i.e., for a two-component solvent with components J, K, M_A becomes

$$M_A = M_J + (M_K - M_J)x_{v,K} \qquad [24]$$

where $x_{v,K}$ is the *solvent* mole fraction of component K.

The osmotic coefficient is related directly to the vapor pressure, p, of a solution in equilibrium with vapor containing A only by (12, p.306):

$$\phi M_A\sum_s \nu_s m_s = -\ln(p/p_A^*) + (V_{m,A}^* - B_{AA})(p - p_A^*)/RT \qquad [25]$$

where p_A^*, $V_{m,A}^*$ are the vapor pressure and molar volume of pure solvent A, and B_{AA} is the second virial coefficient of the vapor.

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 similar to that of Kirkwood and Oppenheim (7); see also (11, 12). Consider a solid mixture containing c thermodynamic components i. The Gibbs-Duhem equation for this mixture is:

$$\sum_{i=1}^{c} x_i'(S_i'dT - V_i'dp + d\mu_i') = 0 \qquad [26]$$

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

$$\sum_{i=1}^{c} x_i(S_idT - V_idp + d\mu_i') + \sum_{i=c+1}^{c'} x_i(S_idT - V_idp + d\mu_i) = 0 \qquad [27]$$

Subtract [26] from [27] and use the equation

$$d\mu_i = (d\mu_i)_{T,p} - S_idT + V_idp \qquad [28]$$

and the Gibbs-Duhem equation at constant temperature and pressure:

$$\sum_{i=1}^{c} x_i(d\mu_i')_{T,p} + \sum_{i=c+1}^{c'} x_i(d\mu_i)_{T,p} = 0 \qquad [29]$$

The resulting equation is:

$$RT\sum_{i=1}^{c} x_i'(dlna_i)_{T,p} = \sum_{i=1}^{c} x_i'(H_i - H_i')dT/T - \sum_{i=1}^{c} x_i'(V_i - V_i')dp \qquad [30]$$

where

$$H_i - H_i' = T(S_i - S_i') \qquad [31]$$

is the enthalpy of transfer of component i from the solid to the liquid phase at a given temperature, pressure and composition, with H_i and S_i the partial molar enthalpy and entropy of component i.

Use of the equations

$$H_i - H_i^0 = -RT^2(\partial lna_i/\partial T)_{x,p} \qquad [32]$$

and

$$V_i - V_i^0 = RT(\partial lna_i/\partial p)_{x,T} \qquad [33]$$

where superscript o indicates an arbitrary reference state gives:

$$RT\sum_{i=1}^{c} x_i'dlna_i = \sum_{i=1}^{c} x_i'(H_i^0 - H_i')dT/T - \sum_{i=1}^{c} x_i'(V_i^0 - V_i')dp \qquad [34]$$

where

$$dlna_i = (dlna_i)_{T,p} + (\partial lna_i/\partial T)_{x,p} + (\partial lna_i/\partial p)_{x,T} \qquad [35]$$

The terms involving enthalpies and volumes in the solid phase can be written as:

$$\sum_{i=1}^{c} x_i'H_i' = H_S^* \qquad \sum_{i=1}^{c} x_i'V_i' = V_S^* \qquad [36]$$

With eqn [36], the final general solubility equation may then be written:

$$R\sum_{i=1}^{c} x_i'dlna_i = (H_S^* - \sum_{i=1}^{c} x_i'H_i^0)d(1/T) - (V_S^* - \sum_{i=1}^{c} x_i'V_i^0)dp/T \qquad [37]$$

Note that those components which are not present in both phases do not appear in the solubility equation. However, they do affect the solubility through their effect on the activities of the solutes.

Several applications of eqn [37] (all with pressure held constant) will be discussed below. Other cases will be discussed 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 $c = 2$, $x_A' = n/(n + 1)$, $x_B' = 1/(n + 1)$, eqn [37] becomes:

$$d\ln(a_A^n a_B) = -\Delta H_{AB}^0 d(1/RT) \qquad [38]$$

where

$$\Delta H_{AB}^0 = nH_A + H_B - (n + 1)H_s^* \qquad [39]$$

is the molar enthalpy of melting and dissociation of pure solid A_nB to form A and B in their reference states. Integration between T and T_0, the melting point of the pure binary compound A_nB, gives:

$$\ln(a_A^n a_B) = \ln(a_A^n a_B)_{T=T_0} - \int_{T_0}^{T} \Delta H_{AB}^0 d(1/RT) \qquad [40]$$

(i) Non-electrolytes

In eqn [32], introduce the pure liquids as reference states. Then, using a simple first-order dependence of ΔH_{AB}^* on temperature, and assuming that the activitity coefficients conform to those for a simple mixture (6):

$$RT \ln f_A = w x_B^2 \qquad RT \ln f_B = w x_A^2 \qquad [41]$$

then, if w is independent of temperature, eqn [32] and [33] give:

$$\ln\{x_B(1-x_B)^n\} + \ln\left\{\frac{n^n}{(1 + n)^{n+1}}\right\} = G(T) \qquad [42]$$

where

$$G(T) = -\left\{\frac{\Delta H_{AB}^* - T^*\Delta C_p^*}{R}\right\}\left\{\frac{1}{T} - \frac{1}{T^*}\right\}$$
$$+ \frac{\Delta C_p^*}{R} \ln(T/T^*) - \frac{w}{R}\left\{\frac{x_A^2 + n x_B^2}{T} - \frac{n}{(n + 1)T^*}\right\} \qquad [43]$$

where ΔC_p^* is the change in molar heat capacity accompanying fusion plus decomposition of the pure compound to pure liquid A and B 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 [42] has the general form:

$$\ln\{x_B(1-x_B)^n\} = A_1 + A_2/(T/K) + A_3\ln(T/K) + A_4(x_A^2 + n x_B^2)/(T/K) \quad [44]$$

If the solid contains only component B, then $n = 0$ in eqn [42] to [44].

If the infinite dilution reference state is used, then:

$$RT \ln f_{x,B} = w(x_A^2 - 1) \qquad [45]$$

and [39] becomes

$$\Delta H_{AB}^\infty = nH_A^* + H_B^\infty - (n + 1)H_s^* \qquad [46]$$

where ΔH_{AB}^∞ is the enthalpy of melting and dissociation of solid compound A_nB to the infinitely dilute reference state of solute B in solvent A; H_A^* and H_B^∞ are the partial molar enthalpies of the solute and solvent at infinite dilution. Clearly, the integral of eqn [32] will have the same form as eqn [35], with ΔH_{AB}^∞ replacing ΔH_{AB}^*, ΔC_p^∞ replacing ΔC_p^*, and $x_A^2 - 1$ replacing x_A^2 in the last term.

See (5) and (11) for applications of these equations to experimental data.

(ii) Electrolytes

(a) Mole fraction scale

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 [34] becomes:

$$\ln\left\{\frac{x_B{}^{\nu}(1 - x_B)^n}{[1 + (\nu - 1)x_B]^{n+\nu}}\right\} - \ln\left\{\frac{n^n}{(n + \nu)^{n+\nu}}\right\} + \ln\left\{\left[\frac{f_B}{f_B{}^*}\right]^{\nu}\left[\frac{f_A}{f_A{}^*}\right]^n\right\}$$

$$ = - \left\{\frac{\Delta H_{AB}{}^* - T^*\Delta C_p{}^*}{R}\right\}\left\{\frac{1}{T} - \frac{1}{T^*}\right\} + \frac{\Delta C p^*}{R}\ln(T/T^*) \qquad [47]$$

where superscript * indicates the pure salt hydrate. If it is assumed
that the activity coefficients follow the same temperature dependence as
the right-hand side of eqn [47] (13-16), the thermochemical quantities on
the right-hand side of eqn [47] are not rigorous thermodynamic enthalpies
and heat capacities, but are apparent quantities only. Data on activity
coefficients (9) in concentrated solutions indicate that the terms
involving these quantities are not negligible, and their dependence on
temperature and composition along the solubility-temperature curve is a
subject of current research.

A similar equation (with $\nu = 2$ and without the heat capacity terms or
activity coefficients) has been used to fit solubility data for some
MOH-H_2O systems, where M is an alkali metal (13); enthalpy values obtained
agreed well with known values. The full equation has been deduced by
another method in (14) and applied to MCl$_2$-H_2O systems in (14) and (15).
For a summary of the use of equation [47] and similar equations, see (14).

(2) Molality scale

Substitution of the mean activities on the molality scale in eqn [40]
gives:

$$\nu\ln\left[\frac{\gamma_{\pm}m_B}{\gamma_{\pm}{}^*m_B{}^*}\right] - \nu(m_B/m_B{}^* - 1) - \nu\{m_B(\phi - 1)/m_B{}^* - \phi^* + 1\}$$

$$= G(T) \qquad [48]$$

where $G(T)$ is the same as in eqn [47], $m_B{}^* = 1/nM_A$ is the molality of the
anhydrous salt in the pure salt hydrate and $\gamma_{\pm}$ and ϕ are the mean activity
coefficient and the osmotic coefficient, respectively. Use of the osmotic
coefficient for the activity of the solvent leads, therefore, to an
equation that has a different appearance to [47]; the content is
identical. However, while eqn [47] can be used over the whole range of'
composition ($0 < x_B < 1$), the molality in eqn [48] becomes infinite at x_B
= 1; use of eqn [48] is therefore confined to solutions sufficiently
dilute that the molality is a useful measure of composition. The
essentials of eqn [48] were deduced by Williamson (17); however, the form
used here appears first in the *Solubility Data Series*. For typical
applications (where activity and osmotic coefficients are not considered
explicitly, so that the enthalpies and heat capacities are apparent
values, as explained above), see (18).

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:

$$\mu_{A_nB}{}^* = \mu_{A_nB}(\text{sln}) = n\mu_A + \mu_B \qquad [49]$$

$$= (n\mu_A{}^* + \nu_+\mu_+{}^{\infty} + \nu_-\mu_-{}^{\infty}) + nRT\,\ln f_A x_A$$

$$+ \nu RT\,\ln(\gamma_{\pm}m_{\pm}Q)$$

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_s in

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

$$= -RT\,\ln K_s$$

$$\doteq -\nu RT \ln(Q \gamma_{\pm} m_B) \qquad\qquad\qquad [50]$$

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_S 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 $C_\nu A_\nu \cdot n H_2 O$ in the presence of other solutes is given by eqn [50] as

$$\nu \ln\{m_B/m_B(0)\} \doteq -\nu \ln\{\gamma_{\pm}/\gamma_{\pm}(0)\} - n \ln\{a_A/a_A(0)\} \qquad\qquad [51]$$

where a_A 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.

Consideration of *complex mixed ligand equilibria* in the solution phase are also frequently of importance in the interpretation of solubility equilibria. For nomenclature connected with these equilibria (and solubility equilibria as well), see (19, 20).

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. See (21) for the modern formulation of the effect of particle size on solubility. 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 (22), is often used to investigate the composition of solid phases in equilibrium with salt solutions. This method has been reviewed in (23), where [see also (24)] least-squares methods for evaluating the composition of the solid phase from wet residue data (or initial composition data) and solubilities are described. 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 (25) 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 periodic table with two additional rows:
    Columns 1 and 2: H, alkali elements, ammonium, alkaline earth elements
            3 to 12: transition elements
           13 to 17: boron, carbon, nitrogen groups; chalcogenides, halogens
                 18: 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 text, 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 1983 atomic weights (26).

    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
and reporting errors are based on the papers by Ku and Eisenhart (27).

    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 reviews 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 considered 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, 28) when the data can be accurately converted.

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September, 1986   R. Cohen-Adad,
                                          Villeurbanne, France

                                       J. W. Lorimer,
                                          London, Ontario, Canada

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

Table I-1

Quantities Used as Measures of Solubility of Solute B
Conversion Table for Multicomponent Systems
Containing Solvent A and Solutes s

	mole fraction $x_B =$	mass fraction $w_B =$	molality $m_B =$	concentration $c_B =$
x_B	x_B	$\dfrac{M_B x_B}{M_A + \sum_s (M_s - M_A) x_s}$	$\dfrac{x_B}{M_A(1 - \sum_s x_s)}$	$\dfrac{\rho x_B}{M_A + \sum_s (M_s - M_A) x_s}$
w_B	$\dfrac{w_B/M_B}{1/M_A + \sum_s (1/M_s - 1/M_A) w_s}$	w_B	$\dfrac{w_B}{M_B(1 - \sum_s w_s)}$	$\rho w_B / M_B$
m_B	$\dfrac{M_A m_B}{1 + M_A \sum_s m_s}$	$\dfrac{M_B m_B}{1 + \sum_s m_s M_s}$	m_B	$\dfrac{\rho m_B}{1 + \sum_s M_s m_s}$
c_B	$\dfrac{M_A c_B}{\rho + \sum_s (M_A - M_s) c_s}$	$M_B c_B / \rho$	$\dfrac{c_B}{\rho - \sum_s M_s c_s}$	c_B

ρ = density of solution
M_A, M_B, M_s = molar masses of solvent, solute B, other solutes s
Formulas are given in forms suitable for rapid computation; all calculations should be made using SI base units.