

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION*

SUBCOMMITTEE ON SOLUBILITY AND EQUILIBRIUM DATA**

GLOSSARY OF TERMS RELATED TO SOLUBILITY

(IUPAC Recommendations 2008)

Prepared for publication by

HEINZ GAMSJÄGER¹, JOHN W. LORIMER², PIRKETTA SCHARLIN³, AND
DAVID G. SHAW^{4,‡}

¹*Lehrstuhl für Physikalische Chemie, Montanuniversität Leoben, Franz-Josef-Straße 18, A-8700 Leoben, Austria;* ²*Department of Chemistry, The University of Western Ontario, London, ON N6A 5B7, Canada;* ³*Department of Chemistry, University of Turku, FIN-20014, Turku, Finland;* ⁴*Institute of Marine Science, University of Alaska at Fairbanks, Fairbanks, AK 99775-7220, USA*

*Membership of the Analytical Chemistry Division during the final preparation of this report was as follows:

President: R. Lobinski (France); **Titular Members:** K. J. Powell (New Zealand); A. Fajgelj (Slovenia); R. M. Smith (UK); M. Bonardi (Italy); P. De Bièvre (Belgium); B. Hibbert (Australia); J.-Å. Jönsson (Sweden); J. Labuda (Slovakia); W. Lund (Norway); **Associate Members:** Z. Chai (China); H. Gamsjäger (Austria); U. Karst (Germany); D. W. Kutner (Poland); P. Minkinen (Finland); K. Murray (USA); **National Representatives:** C. Balarew (Bulgaria); E. Dominguez (Spain); S. Kocaoba (Turkey); Z. Mester (Canada); B. Spivakov (Russia); W. Wang (China); E. Zagatto (Brazil); **Provisional Member:** N. Torto (Botswana).

**Membership of the Subcommittee on Solubility and Equilibrium Data during final preparation of this report was as follows:

Chairman: H. Gamsjäger; **Members:** W. Hummel, D. E. Knox, E. Königsberger, J. W. Lorimer, M. Salomon, D. G. Shaw, W. Voigt, H. Wanner.

‡Corresponding author: E-mail: ffdgs@uaf.edu

Republication or reproduction of this report or its storage and/or dissemination by electronic means is permitted without the need for formal IUPAC permission on condition that an acknowledgment, with full reference to the source, along with use of the copyright symbol ©, the name IUPAC, and the year of publication, are prominently visible. Publication of a translation into another language is subject to the additional condition of prior approval from the relevant IUPAC National Adhering Organization.

Glossary of terms related to solubility

(IUPAC Recommendations 2008)

Abstract: Phenomena related to the solubility of solids, liquids, and gases with one another are of interest to scientists and technologists in an array of disciplines. The diversity of backgrounds of individuals concerned with solubility creates a potential for confusion and miscommunication and heightens the need for an authoritative glossary of terms related to solubility. This glossary defines 166 terms used to describe solubility and related phenomena. The definitions are consistent with one another and with recommendations of the International Union of Pure and Applied Chemistry for terminology and nomenclature.

Keywords: solubility; phase equilibria; solution equilibria; solid-state equilibria; molten salt equilibria; thermodynamics; IUPAC Analytical Chemistry Division.

1. INTRODUCTION

Disciplines concerned with solubility and related phenomena extend well beyond the traditional branches of chemistry to a wide range of biomedical, environmental, and industrial fields including, for example, mineralogy, pharmacology, oceanography, and petroleum engineering. The diversity in the technical backgrounds and training of individuals concerned with solubility heightens the potential for confusion and miscommunication of both concepts and data related to solubility. This glossary seeks to reduce such confusion and miscommunication by presenting a set of solubility-related terms that are consistent with one another and with IUPAC recommendations for chemical terminology (the online “Gold Book”) [1], as well as with specific recommendations for quantities, units, and symbols (the “Green Book”, 3rd ed.) [2].

This glossary defines 166 terms which were selected by the authors as the central set related to solubility. Within each definition, terms defined elsewhere in the glossary are indicated by *italics* upon their first use. Inevitably, some users will seek terms that are not defined here or will wish to consult definitions of terms used in these definitions. In both cases, the authors recommend the IUPAC *Compendium of Chemical Terminology* (the “Gold Book”), particularly the online version [1]. The authors also recommend the IUPAC publication *Quantities, Units and Symbols in Physical Chemistry*, 3rd ed. (the “Green Book”) [2] as an authoritative and consistent guide to the presentation of chemical data.

Definitions of particular terms have, in many cases, been expanded or modified compared to the corresponding definitions given in the Gold Book [1], which means that such definitions have been modified compared to the original IUPAC recommendations used to prepare entries in the Gold Book. The objective has been to make the definitions as clear and as useful as possible within the general format of the glossary, but without changing significantly the meaning of the Gold Book entries. Definitions taken from another source conclude with a notation “from [ref]” to indicate that source; where a definition in any source has been modified to produce the definition given here, the notation is “modified from [ref]”. Where synonymous terms are in common usage, the recommended term (“main term”) is followed on the second line of the glossary entry (and on subsequent lines where necessary) by the synonym or synonyms which are then followed by the definition and notes, if any. The synonyms are also listed separately in their proper alphabetical position, with the annotation “See (main term)”. This approach can, for instance, be observed by consulting the entries for “mole ratio” (a main term) and “amount ratio” (its synonym).

2. GLOSSARY OF TERMS

absorption coefficient, β^* (in gas solubility)

Volume V^g of an amount n_B^1 of a dissolved gas at a given *standard temperature*, usually $T^\ominus = 273.15$ K, and total *standard pressure* p^\ominus divided by the volume of the solvent of volume V^l that contains an amount n_A of *solvent* at the same temperature T and pressure p .

Note 1: There is only one absorption coefficient, as compared to the *Bunsen*, *Ostwald*, and *Kuenen coefficients*, because the solvent in the definition is always the pure solvent, not the gaseous solution. The mathematical definition is

absorption coefficient, pure solvent reference (indicated by superscript *)

$$\beta_B^* = V_B^g(T, p_A + p_B = p^\ominus, n_B^1) / V^l(T, p^\ominus, n_A)$$

where p_A, p_B are the partial pressures of solvent and gas.

Note 2: For an ideal gas, the absorption coefficient and *Bunsen coefficient* α^* are related by

$$\beta^* / \alpha^* = p_B / p^\ominus = (1 - p_A / p^\ominus)$$

since V^g is inversely proportional to pressure.

Note 3: The relations between the *molality* $m_B(p^\ominus)$ or *mole fraction* $x_B(p^\ominus)$ of dissolved gas and the absorption coefficients are

$$\frac{1}{x_B(p^\ominus)} = 1 + \frac{1}{m_B(p^\ominus) M_A} = 1 + \frac{RT^\ominus Z_B^\ominus (1 + p_A / p^\ominus)}{p^\ominus V_{m,A} \beta_B^*}$$

where $V_A, V_{m,A}$ are the respective partial molar volume and molar volume of the solvent and Z_B is the compression factor of the gas.

Note 4: The absorption coefficient and the related quantities for expression of gas solubility, the *Bunsen*, *Kuenen*, and *Ostwald coefficients*, appear frequently in the older literature of gas solubility determination. However, the modern practice, recommended here, is to express gas solubility as *molality*, *mole fraction*, or *mole ratio*.

From [3].

activity, a

relative activity

Factor in relation between chemical potential and composition of a mixture or solution. For a substance B,

$$a_B = \exp\left(\frac{\mu_B - \mu_B^\ominus}{RT}\right)$$

where superscript \ominus denotes a standard chemical potential.

Note 1: The choice of standard state for the chemical potential must be specified.

Note 2: An equivalent definition is

$$a_B = \lambda_B / \lambda_B^\ominus$$

where

$$\lambda_{\text{B}}^{\ominus} = \exp\left(\frac{\mu_{\text{B}}^{\ominus}}{RT}\right)$$

with λ the absolute activity.

Note 3: Appears only as cross-references between activity and relative activity in [1].
From [2].

activity coefficient, f , γ_m , γ_c , γ_x

Dimensionless correction factor that multiplies the quantity used to express the composition of the substance (usually *mole fraction*, *molality*, or *amount concentration*) to produce the (relative) *activity* of the substance.

- (a) Referenced to *Raoult's law*, *mole fraction* basis. For a substance B in a liquid or solid *mixture* containing mole fractions x_{A} , x_{B} , x_{C} , ... of the substances A, B, C, ...: a dimensionless quantity f_{B} defined in terms of the chemical potential μ_{B} of B in the mixture by

$$RT \ln(x_{\text{B}}f_{\text{B}}) = RT \ln a_{\text{B}} = \mu_{\text{B}}(T, p, x) - \mu_{\text{B}}^*(T, p)$$

where x denotes the set of mole fractions x_{A} , x_{B} , x_{C} , ... and μ_{B}^* is the standard chemical potential, defined as the value for pure B. The activity coefficient has the value 1 for pure substance B.

- (b) Referenced to *Henry's law*, *molality* basis. For a *solute* B in a *solution* (especially a dilute liquid solution) containing molalities m_{B} , m_{C} , ... of *solutes* B, C, ... in a *solvent* A: a dimensionless quantity $\gamma_{m,\text{B}}$ defined in terms of the chemical potential μ_{B} of B in the solution by

$$RT \ln(\gamma_{m,\text{B}}m_{\text{B}}/m^{\ominus}) = RT \ln a_{\text{B}} = \mu_{\text{B}} - \mu_{m,\text{B}}^{\ominus}$$

$$\mu_{m,\text{B}}^{\ominus} = \lim_{m_{\text{B}} \rightarrow 0} \left[\mu_{\text{B}} - RT \ln(m_{\text{B}}/m^{\ominus}) \right]$$

where $m^{\ominus} = 1 \text{ mol kg}^{-1}$ is the *standard molality* and $\mu_{m,\text{B}}^{\ominus}$ is the standard chemical potential, defined as the value at infinite dilution of all solutes. The activity coefficient has the value 1 at infinite dilution of all solutes.

- (c) Referenced to Henry's law, *amount concentration* basis. For a *solute* B in a *solution* (especially a dilute liquid solution) containing amount concentrations c_{B} , c_{C} , ... of *solutes* B, C, ... in a *solvent* A: a dimensionless quantity $\gamma_{c,\text{B}}$ defined in terms of the chemical potential μ_{B} of B in the solution by

$$RT \ln(\gamma_{c,\text{B}}c_{\text{B}}/c^{\ominus}) = RT \ln a_{\text{B}} = \mu_{\text{B}} - \mu_{c,\text{B}}^{\ominus}$$

$$\mu_{c,\text{B}}^{\ominus} = \lim_{c_{\text{B}} \rightarrow 0} \left[\mu_{\text{B}} - RT \ln(c_{\text{B}}/c^{\ominus}) \right]$$

where $c^{\ominus} = 1 \text{ mol dm}^{-3}$ is the *standard amount concentration* and $\mu_{c,\text{B}}^{\ominus}$ is the standard chemical potential, defined as the value at infinite dilution of all solutes. The activity coefficient has the value 1 at infinite dilution of all solutes.

- (d) Referenced to Henry's law, mole fraction basis. For a solute B in a solution (especially a dilute liquid solution) containing mole fractions x_B, x_C, \dots of solutes B, C, ... in a solvent A: a dimensionless quantity $\gamma_{x,B}$ defined in terms of the chemical potential μ_B of B in the solution by

$$RT \ln(\gamma_{x,B} x_B) = RT \ln a_B = \mu_B - \mu_{x,B}^\ominus$$

$$\mu_{x,B}^\ominus = \lim_{x_B \rightarrow 0} \left[\mu_B - RT \ln(\gamma_{x,B} x_B) \right]$$

where $\mu_{x,B}^\ominus$ is the standard chemical potential, defined as the value at infinite dilution of all solutes. The activity coefficient has the value 1 at infinite dilution of all solutes.

See also *activity coefficient at infinite dilution*.

Modified from [1,2].

activity coefficient at infinite dilution, f^∞

For a substance B, *activity coefficient* f_B extrapolated to *infinite dilution*:

$$\ln f_B^\infty = \lim_{x_B \rightarrow 0} \left(\frac{\mu_B - \mu_B^*}{RT} - \ln x_B \right)$$

Note 1: Useful for dilute *mixtures* as an alternative to the standard chemical potential on a *molarity* basis.

Note 2: The relation between the activity coefficient at infinite dilution and the standard chemical potentials is, for a solute B in a solvent A,

$$\ln f_B^\infty = \frac{\mu_{m,B}^\ominus - \mu_B^*}{RT} - \ln(M_A m_B^\ominus)$$

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

See also *activity coefficient*.

amount

See *amount of substance*.

amount concentration, c

amount-of-substance concentration

concentration

substance concentration (in clinical chemistry)

molarity (in older literature).

Amount of a *constituent* in a *mixture* divided by the volume of the *mixture*.

Note 1: For constituent B, amount concentration is often denoted [B].

Note 2: Concentration alone may be used where there is no ambiguity about its meaning.

Note 3: The common unit is mole per cubic decimeter (mol dm^{-3}) or mole per liter (mol L^{-1}) sometimes denoted by (small capital) M.

Modified from [1].

amount fraction, x

See *mole fraction*.

amount of substance, n

amount

chemical amount

Base quantity in the SI system of quantities. It is the number of elementary entities divided by the Avogadro constant.

Note 1: Amount of substance is proportional to the number of entities, the proportionality constant being the reciprocal Avogadro constant. Therefore, amount of substance, just as number of entities, must be accompanied by a specification of the type of entities.

Note 2: The words “of substance” may be replaced by the specification of the entity, for example: amount of chlorine atoms, $n(\text{Cl})$, amount of chlorine molecules, $n(\text{Cl}_2)$. No specification of the entity might lead to ambiguities [amount of sulfur could stand for $n(\text{S})$, $n(\text{S}_8)$, etc.], but in many cases the implied entity is assumed to be known: for molecular compounds, it is usually the molecule [e.g., amount of benzene usually means $n(\text{C}_6\text{H}_6)$]; for ionic compounds, it is the simplest formula unit [e.g., amount of sodium chloride usually means $n(\text{NaCl})$]; and for metals, it is the atom [e.g., amount of silver usually stands for $n(\text{Ag})$].

Note 3: In some derived quantities, the words “of substance” are also omitted, e.g., *amount concentration*, *amount fraction*. Thus, in many cases the name of the base quantity is shortened to amount, and to avoid possible confusion with the general meaning of the word, the attribute chemical is added. Chemical amount is hence the alternative name for amount of substance. In the field of clinical chemistry, the words “of substance” should not be omitted and abbreviations such as substance concentration (for amount of substance concentration) and substance fraction are in use. The quantity had no name prior to 1969 and was simply referred to as the number of moles.

From [1,2].

amount-of-substance fraction

See *mole fraction*.

amount ratio, r

See *mole ratio*.

analytical method (in determination of solubility)

Class of experimental procedures for *solubility* determination in which a *saturated solution* is prepared and then analyzed to determine composition.

See also *synthetic method*.

aquamolality, $m^{(C)}$

solvomolality

For a solute B in a system containing solvent A and a reference solvent C,

$$m_B^{(C)} = m_B \bar{M} / M_C$$

where m_B is the molality of B, M_C is the molar mass of a reference component, and \bar{M} is the average molar mass of a mixed solvent, defined for a system containing two solvents as

$$\bar{M} = x_{v,A} M_A + (1 - x_{v,A}) M_C$$

with $x_{v,A}$ the *solvent amount fraction* of solvent A.

Note 1: Used most frequently in discussing comparative solubilities in water (C) and heavy water (A) and their mixtures, but applies to any reference component, where *solvomolality* is a more appropriate term.

Note 2: For history and equivalence with older definitions, see [5].

azeotropic point

azeotrope

For a *mixture*, temperature and pressure (the azeotropic temperature and pressure) at which the compositions of the liquid and vapor phases become equal (the azeotropic composition), but the intensive properties of the two phases (such as molar volume) are different.

See also *critical point*.

From [6].

binary system

System containing two *components*.

See also *unary system*, *ternary system*, *higher-order system*.

binodal curve

See *coexistence curve*.

Bunsen coefficient, α

Volume V^g of an amount n_B^1 of a gas dissolved at a given *standard temperature* T^\ominus (usually 273.15 K) and given *standard (partial) pressure* p_B^\ominus (1 bar = 0.1 MPa or, in older literature, 1 atm) divided by the volume of the *solvent* V^l containing an amount n_A of solvent at temperature T and the given total pressure p^\ominus .

Note 1: There are two Bunsen coefficients, depending on whether the liquid is the *equilibrium* solution or the pure liquid, with mathematical definitions:

$$\begin{aligned} \text{Bunsen coefficient, solution reference} \quad \alpha_B &= V^g(T^\ominus, p^\ominus, n_B^1) / V^l(T, p^\ominus, n_A, n_B^1) \\ \text{Bunsen coefficient, pure solvent reference} \quad \alpha_B^* &= V^g(T^\ominus, p^\ominus, n_B^1) / V^l(T, p^\ominus, n_A) \end{aligned}$$

where n_B^1 is the amount of dissolved gas in the liquid solution.

Note 2: The relations between the *molality* $m_B(p^\ominus)$ or mole fraction $x_B(p^\ominus)$ of dissolved gas and the Bunsen coefficients are

$$\frac{1}{x_B(p^\ominus)} = 1 + \frac{1}{m_B(p^\ominus)M_A} = 1 + \frac{RT^\ominus Z_B^\ominus(T^\ominus)}{p^\ominus V_A \alpha_B}$$

$$\frac{1}{x_B(p^\ominus)} = 1 + \frac{1}{m_B(p^\ominus)M_A} = 1 + \frac{RT^\ominus Z_B^\ominus(T^\ominus)}{p^\ominus V_{m,A} \alpha_B^*}$$

where V_A , $V_{m,A}$ are the respective partial molar volume and molar volume of the solvent and Z_B is the compression factor of the gas.

Note 3: The Bunsen coefficient and the related quantities for expression of gas solubility; *absorption coefficient*, *Kuenen coefficient*, and *Ostwald coefficient* appear frequently in the older literature of gas solubility determination. However, the modern practice, recommended here, is to express gas solubility as *molality*, *mole fraction*, or *mole ratio*.

From [5].

catatectic reaction

See *metatectic reaction*.

chemical amount

See *amount of substance*.

chlorinity, Cl , w_{Cl}

Mass of dissolved halides (reported as chloride) in sea water, brackish water, brine, or other saline *solution* divided by the mass of the solution.

Note 1: For a sample of sea water, 0.328 534 times the mass of pure reference silver, “Atomgewichtssilber”, necessary to precipitate the halides (chloride + bromide + iodide, but expressed as chloride) contained in a sample of sea water divided by the mass of this sample.

Note 2: Used (especially before 1978) in calculating *salinity*, and based on the assumption that the concentration ratios of the principal salts in sea water are constant throughout the oceans. This assumption is only approximate.

Note 3: The symbol Cl is recommended in [8].

Note 4: Before 1978, the usual unit for Cl expressed as a *mass fraction* was *permil* (no longer recommended). Now it is usually expressed as g kg^{-1} with or without the units given explicitly.

Example: the chlorinity of a sample of sea water is $w_{Cl} = 19.375\ 0\ ‰$ or $19.375\ 0\ \text{g kg}^{-1}$ or $19.375\ 0 \times 10^{-3}$ or $19.375\ 0$.

See also *salinity*.

From [7,8].

Clarke–Glew equation

Semi-empirical equation describing the temperature dependence of the standard Gibbs energy of solution,

$$\Delta_{\text{sln}} G^{\circ}(T, p^{\circ})/RT = A_0 + A_1(T_{\text{ref}}/T) + A_2 \ln(T/T_{\text{ref}}) + A_3(T/T_{\text{ref}}) + A_4(T/T_{\text{ref}})^2 + \dots$$

where the A_i are constants that can be related to thermodynamic quantities (but subject to uncertainty because of statistical correlations among the fitting coefficients) and T_{ref} is a reference temperature.

See also *Clarke–Glew–Weiss equation*.

Modified from [5,9].

Clarke–Glew–Weiss equation

Clarke–Glew equation with $T_{\text{ref}} = 100$ K.

Modified from [5,10].

cloud point

Critical solution point, particularly when used as an end-point of a turbidometric titration to determine *solubility*.

See also *synthetic method*.

coexistence curve

binodal curve

conodal curve

Boundary of stable *phase* separation (limits of solubility) in a liquid or solid *system* of two or more *components*.

Note 1: The locus of the compositions of two co-existing phases on a phase diagram.

Note 2: In a *binary system*, a plot of experimental variables such as temperature or pressure, or of theoretical variables such as Gibbs energy, against *mole fraction* displays the coexistence curve. In *ternary* or *higher-order systems*, coexistence curves are displayed on a plot of composition at constant temperature or pressure, usually on a *ternary diagram*.

See also *critical solution point*, *spinodal curve*, *conjugate phases*.

Modified from [11,12].

common ion effect

Decrease in solubility of a salt when a second *non-saturating* salt with one ion in common with the salt is added to its *saturated solution*.

Note: Restricted in practice to composition regions where common ions do not form soluble complexes with the saturating salt and to salts with sufficiently low *solubility* and at sufficiently low *ionic strengths* that the *activity coefficient* of the salt is close to unity. At higher ionic strengths, or for salts with high solubility, the activity coefficient usually decreases with addition of non-saturating salt, resulting in a higher solubility.

component

thermodynamic component

independent component

Constituent whose *amount* or concentration can be varied independently in a *mixture*.

Note: The number of components in a given *system* is the minimum number of independent species necessary to define the composition of all *phases* of that system. Relations among the constituents, such as charge balance or chemical *equilibria*, must be taken

into account in determining the number of components. The term “component” is also often used in the more general sense defined under *constituent*.

Modified from [1].

compression factor, Z

compressibility factor

Product of pressure and molar volume divided by the gas constant and thermodynamic temperature. For an ideal gas it is equal to 1.

From [1].

congruent transition

Transition in which the two-phase equilibrium of *melting*, vaporization, or allotropism of a compound involves phases of the same composition.

From [1,12].

conjugate phases

Two *phases* of variable composition in mutual thermodynamic *equilibrium*.

See also *coexistence curve*.

Modified from [1].

conodal

connodal

See *tie line*.

From [11].

conodal curve

connodal curve

See *coexistence curve*.

constituent

Chemical species present in a *system*.

See also *component*.

Modified from [1].

critical index, β

Index in the basic equation describing a *coexistence curve*

$$\beta = \lim_{T \rightarrow T_c} \left(\frac{\partial \ln(x'' - x')}{\partial \ln|T - T_c|} \right)$$

where x'' , x' are the mole fractions of one *component* in the respective concentrated and dilute phases and T_c is the *critical solution temperature*.

From [11].

critical point

For a pure phase, temperature and pressure (the critical temperature, T_c , and pressure, p_c) at which intensive properties of liquid and vapor (density, heat capacity, etc.) become equal.

For a *mixture*, temperature, pressure, and composition (the critical temperature, pressure, and composition) at which the compositions of the liquid and vapor phases, as well as intensive properties of the liquid and vapor phases, become equal.

Note: For a pure phase, the highest temperature (*critical temperature*) and pressure (*critical pressure*) at which both a gaseous and a liquid phase can exist.

See also *azeotropic point*, *critical solution point*.
Modified from [6].

critical solution point

cloud point

consolute point

plait point (ternary and higher-order systems)

In a *binary system*, point with coordinates critical solution temperature (CST) or critical solution pressure (CSP) and critical composition on a temperature-composition or pressure-composition *phase diagram* at which the distinction between coexistent *phases* disappears.

In *ternary* and *higher-order systems*, composition below or above which, on a ternary or higher composition phase diagram at constant temperature and pressure, the distinction between coexistent phases disappears, and *tie-lines* between coexisting phases become tangential to the *coexistence curve*.

Note 1: Disappearance of the distinction between phases corresponds to disappearance of a *miscibility gap*; see *mutual solubility*.

Note 2: The locus of the plait point composition against temperature is called the plait point curve.

Note 3: In solid–solid, solid–liquid, and liquid–liquid systems, both upper and lower critical solution temperatures (UCST, LCST) or upper and lower critical solution pressures (UCSP, LCSP) can occur. In some systems, both can be observed.

Note 4: In principle, there is no distinction between critical solution points in liquid–liquid or solid–solid systems and critical points in liquid–vapor systems. In binary systems, both types of points are determined by the derivatives of the Gibbs energy with respect to mole fraction

$$\begin{aligned}(\partial^2 G_m / \partial x^2)_{T,p} &= 0, & (\partial^3 G_m / \partial x^3)_{T,p} &= 0, \\ (\partial^4 G_m / \partial x^4)_{T,p} &> 0\end{aligned}$$

See *critical point*.

Modified from [1,12,13].

crystallization

Formation of a crystalline solid *phase* from either (a) a solid, liquid, or gaseous *mixture* or *solution*, or (b) a pure liquid or gas.

Note: Crystallization usually occurs under laboratory conditions by altering the temperature or pressure of a *system*, or by evaporation of a *solvent*.

Modified from [1,12].

data

Experimental results, often numerical.

Note 1: The term is plural; its singular form is datum.

Note 2: Data directly obtained from experimental apparatus may be referred to as raw data. Raw data may be subjected to numerical operations (unit conversions, etc.) to give transformed data, which maintain a point-for-point correspondence with the raw data. However, the use of the term “data” to refer to the results of numerical modeling operations or other elaborate calculations is controversial and discouraged. The latter are better referred to as “results” and, when presented graphically, are usually represented by smooth lines.

density, ρ

mass density

Mass of a pure substance, mixture, or solution divided by its volume.

From [2].

dissolution

Process of mixing of two or more *phases* with the formation of one new homogeneous phase (i.e., the *solution*).

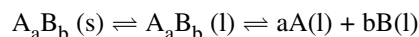
Modified from [1,12].

dystectic reaction

congruent melting

indifferent melting

Isobaric, reversible melting or *dissolution* with either complete or partial dissociation on heating of a solid compound, A_aB_b , formed by *components* A and B



where the forward arrows indicate the direction of heating.

Note 1: The dystectic temperature is a maximum ($dT/dx = 0$) of the melting temperature-composition curve. The dystectic point is the isobarically invariant maximum at the dystectic composition and dystectic temperature, where the compositions of the liquid and solid *phases* are equal. The composition of a non-stoichiometric compound is also equal to that of the *melt* at the dystectic temperature and composition.

Note 2: From Greek δύστηκτος, difficult (or highest) melting.

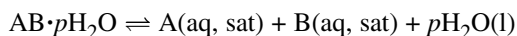
Note 3: Occasionally, a similar reaction takes place in the subsolidus region. Quite appropriately, it is called a dystectoid reaction.

Examples: systems $SO_3 + H_2O$ [14], $Mg + Sn$ [15].

From [14,16].

dystonic reaction

Reversible *dissolution* in an isothermal, isobaric *system* of three or more *components* characterized by dissolution and *saturation* with a stoichiometric compound consisting of two or more of these components. The *equilibrium* process is, for example,



Note 1: The chemical potential of *solvent* and consequently its *partial pressure* reaches a maximum value at the dystonic composition or point, which is isothermally and isobarically invariant.

Note 2: Dystonic points have been detected in aqueous media only.

Note 3: From Greek δύστονος, difficult (highest) tension (vapor pressure).

Examples: systems $\text{Na}_2\text{SO}_4 + \text{ZnSO}_4 + \text{H}_2\text{O}$, $\text{Na}_2\text{SO}_4 + \text{CdSO}_4 + \text{H}_2\text{O}$, $\text{Na}_2\text{SO}_4 + \text{CuSO}_4 + \text{H}_2\text{O}$.
See also *eutonic reaction*, *peritonic reaction*.

equilibrium

State of a *system* in which the macroscopic properties of each *phase* of the system become uniform and independent of time. If the temperature is uniform throughout the system, a state of thermal equilibrium has been reached; if the pressure is uniform, a state of hydrostatic equilibrium has been reached; and if the chemical potential of each component is uniform, a state of chemical equilibrium has been reached. If all these quantities become uniform, the system is said to be in a state of complete thermodynamic equilibrium.

Note 1: Complete thermodynamic equilibrium can be expressed in many ways, depending on which variables are of interest. For solubility purposes, the important variables are T , p and the chemical potentials μ_i of the C components. Equilibrium conditions involving these variables may be obtained by the condition that the variation of the Gibbs energy, expressed in terms of T , p and the amount of substance n_i of the C components, is zero, $\delta G(T, p, n_i) = 0$ (i.e., the Gibbs energy is a minimum). If the variation is negative, an irreversible change of the system can occur.

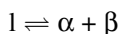
Note 2: Solubility equilibrium is an example of a state of complete thermodynamic equilibrium. For example, a saturated solution of a solid in a liquid at a fixed temperature and pressure is in a state of complete thermodynamic equilibrium. If the system is subjected to a small increase in temperature, a small portion of solid will dissolve to restore the equilibrium (if the solubility increases with temperature), while if there is a small decrease in temperature, a small portion of solid will precipitate. This is the basis for determining accurate values of solubility by approaching the equilibrium solubility from both *supersaturation* and *undersaturation* directions.

Note 3: In [1], chemical equilibrium is defined. The definition here is more inclusive.

Modified and extended from [1].

eutectic reaction

Isothermal reversible reaction of a liquid *phase* l which is transformed into two (or more) different solid phases α and β during the cooling of a *system*. In a *binary system*,



where l is a liquid phase, α , β are solid phases, and the forward arrow indicates the direction of cooling. The *equilibrium* reaction occurs along the eutectic line at the eutectic temperature. At the eutectic composition, the compositions of the liquid and solid phases are equal, and intermediate to the compositions of the solid phases of the system.

Note 1: The solid phases may be pure phases, solid mixtures, or binary compounds.

Note 2: The eutectic line and composition (hence point) are isobaric invariants of the system, and represent the composition and the minimum melting temperature along the two intersecting melting curves.

Note 3: From Greek ευτηκτος, easy (or lowest) melting.

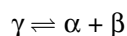
Note 4: The definition in [1] has been extended, but with eutectic temperature and composition included in the definition.

Example: system Ag + Cu [15] and many salt + water systems.

Modified from [1,12,16].

eutectoid reaction

Isothermal reversible reaction of a solid mixture *phase* γ which is transformed into two (or more) different solid (pure, binary compound or mixture) phases α and β during the cooling of a *system*. In a *binary system*,



where the forward arrow indicates the direction of cooling. The *equilibrium* reaction occurs along the eutectoid line at the eutectoid temperature. At the eutectoid composition, the compositions of the high-temperature solid phase and the mechanical mixture of the low-temperature solid phases are equal, and intermediate to the compositions of the pure solid phases α and β . This composition and the eutectoid temperature, which are isobaric invariants of the system, define the eutectoid point.

Note: Derived from Greek and Latin, meaning “resembling a eutectic”.

Example: system Fe + C [15].

See *eutectic reaction*, Note 2.

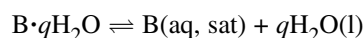
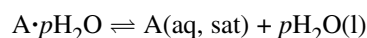
Modified from [1,12,16].

eutonic reaction

isothermally invariant reaction

(isothermally and isobarically invariant) reaction of double saturation

Reversible *dissolution* in a *system* of three or more *components* characterized by the composition of a *solution* that is simultaneously saturated with respect to all (at least two or more) dissolved *solutes*. The two simultaneous equilibrium processes are, for example,



Note 1: The eutonic point is invariant in a *ternary system* at a given temperature and pressure.

Note 2: The chemical potential of solvent decreases along the two solubility curves that intersect at the eutonic point, and thus reaches a minimum value at that point. Thus, colligative properties (that depend on solvent activity) reach a minimum value at the eutonic point. For example, if the solutes are nonvolatile and the solvent is volatile, the vapor pressure reaches a minimum value.

Note 3: Eutonic points have been detected in aqueous media only.

Note 4: From Greek ευτονος, easy (or lowest) tension (or vapor pressure).

Examples: systems $\text{Na}_2\text{SO}_4 + \text{ZnSO}_4 + \text{H}_2\text{O}$, $\text{Na}_2\text{SO}_4 + \text{CdSO}_4 + \text{H}_2\text{O}$, $\text{Na}_2\text{SO}_4 + \text{CuSO}_4 + \text{H}_2\text{O}$.

See also *eutonic reaction*, *peritonic reaction*.
Introduced in [17].

fitting equation

smoothing equation

Theoretically based or empirical equation for interpolation of *data* over a range of temperature, pressure, composition, or other variable.

Note: The use of a fitting equation for extrapolation of data beyond the equation's known range of validity is a potential source of extreme error.

fugacity, f_B , \tilde{p}_B

For a substance B in a gaseous *mixture*,

$$f_B = \lambda_B \lim_{p \rightarrow 0} (p_B / \lambda_B)_T$$

where p_B is the *partial pressure* of B and λ_B its absolute activity.

SI unit: Pa.

From [1,2].

fugacity coefficient, φ

fugacity divided by the *partial pressure* of a gaseous *constituent*.

Modified from [1].

Gibbs–Duhem equation

Equation relating the intensive variables T , p and the C chemical potentials μ_i in a *phase*

$$SdT - Vdp + \sum_{i=1}^C n_i d\mu_i = 0$$

where C is the total number of *components* i in a phase.

Note 1: Note that the variables in this equation are the intensive quantities T , p and μ_i .

Note 2: The Gibbs–Duhem equation may be written in terms of intensive quantities,

$$\sum_{i=1}^C n_i (S_i dT - V_i dp + d\mu_i) = 0$$

where S_i , V_i , x_i are the respective partial molar entropy, partial molar volume, and mole fraction of component i .

Note 3: There is a Gibbs–Duhem equation for each phase in a *system* exhibiting multiphase equilibria. Application of the conditions for an *equilibrium* state leads to the *phase rule* as one example of the application of this equation. When equilibrium conditions are applied, T , p and μ are equal in all phases of an equilibrated system, while S_i , V_i , and x_i are not.

From [14].

Gibbs energy of transfer

Change in Gibbs energy at a given temperature and pressure for transfer of a substance between two different phases.

Gibbs–Kononov equations

van der Waals' equations

Pair of equations for a binary mixture of components A and B that relate the variables T, p , in one phase of variable composition, α , to the variables T, p , in a coexisting equilibrium phase of variable composition, β :

$$\begin{aligned}
 & -\frac{(1-x_B^\beta)\Delta_\alpha^\beta H_A + x_B^\beta\Delta_\alpha^\beta H_B}{T}dT + \left[(1-x_B^\beta)\Delta_\alpha^\beta V_A + x_B^\beta\Delta_\alpha^\beta V_B \right]dp + \\
 & \left(x_B^\alpha - x_B^\beta \right) \left(\frac{\partial^2 G_m^\alpha}{\partial x_B^{\alpha 2}} \right)_{T,p} dx_B^\alpha = 0 \\
 & -\frac{(1-x_B^\alpha)\Delta_\alpha^\beta H_A + x_B^\alpha\Delta_\alpha^\beta H_B}{T}dT + \left[(1-x_B^\alpha)\Delta_\alpha^\beta V_A + x_B^\alpha\Delta_\alpha^\beta V_B \right]dp + \\
 & \left(x_B^\alpha - x_B^\beta \right) \left(\frac{\partial^2 G_m^\beta}{\partial x_B^{\beta 2}} \right)_{T,p} dx_B^\beta = 0
 \end{aligned}$$

where $\Delta_\alpha^\beta H_A = H_A^\beta - H_A^\alpha$, $\Delta_\alpha^\beta V_A = V_A^\beta - V_A^\alpha$ are the enthalpy and volume of transfer of component A from phase α to phase β , and similarly for component B.

Note 1: $\left(\frac{\partial^2 G_m}{\partial x_B^2} \right)_{T,p} > 0$ (condition for diffusional stability). This quantity may also be expressed in terms of the derivatives of the chemical potentials, using

$$\left(\frac{\partial^2 G_m}{\partial x_B^2} \right)_{T,p} = -\frac{1}{x_B} \left(\frac{\partial \mu_A}{\partial x_B} \right)_{T,p} = \frac{1}{x_A} \left(\frac{\partial \mu_B}{\partial x_B} \right)_{T,p}$$

Note 2: These equations show that an extremum occurs for each phase equation when the compositions of the two phases are equal, and that the slope of the T -composition or p -composition curve is zero for each phase equation at the extremum.

Note 3: Sometimes the German transliteration Kononow is found.

From [13,14].

Henry's law

Fugacity (\tilde{p}_B) of a solute (B) in a solution is directly proportional to the activity (a_B) of the solute

$$\tilde{p}_B = a_{x,B} p^\ominus / K_{x,B} = \gamma_{x,B} x_B k_{H,B}$$

where $K_{x,B}$ is the solubility coefficient for infinite dilution, i.e., for pure solvent, $\gamma_{x,B}$ is the activity coefficient (referenced to Henry's law, mole fraction basis), x_B is the equilibrium mole fraction of dissolved gas and $k_{H,B}$ is the Henry's law constant.

Note 1: Obsolete terminology (rational activity, chemical activity) from [1] has been updated.

Note 2: The solubility constant is the standard equilibrium constant for the equilibrium $B(g) \rightleftharpoons B(\text{satd l})$, while the Henry's law constant is the standard equilibrium constant for the equilibrium $B(\text{satd l}) \rightleftharpoons B(g)$. Thus, the two constants are reciprocals of one another, to within a factor of standard pressure. The definition of the solubility constant $K_{x,B}$ as a dimensionless quantity is

$$K_{x,B} = \gamma_{x,B} p^\ominus / \tilde{p}_B = \exp \left[\frac{\mu_B^\ominus(g,T) - \mu_{x,B}^\ominus(l;T,p)}{RT} \right]$$

Note 3: For the solvent (A), the above relation is called *Raoult's law*, and the proportionality factor is the fugacity of the pure solvent, \tilde{p}_A^*

$$\tilde{p}_A = \tilde{p}_A^* a_A = f_A x_A$$

where f_A is the activity coefficient of A referenced to Raoult's law at mole fraction x_A .

Note 4: Henry's law is used often as a limiting law for converting solubility *data* from the experimental pressure to standard partial pressure, provided the mole fraction of the gas in the liquid is small and that the difference in pressures is small.

See *activity coefficient, solubility coefficient, Henry's law constant, Raoult's law, Poynting correction*. Modified from [1].

Henry's law constant, k_H

Henry coefficient

Henry's law coefficient

Henry constant

For a gas B,

$$k_{H,B} = \lim_{x_B \rightarrow 0} (f_B / x_B) = (\partial f_B / \partial x_B)_{x_B \rightarrow 0}$$

where f_B is the fugacity of B.

Note 1: At low pressures, f_B becomes equal to the partial pressure p_B .

Note 2: Henry's law constant in terms of *mole fractions* has units Pa, but is sometimes expressed in terms of *molalities* or *amount concentrations*, with corresponding units Pa kg mol⁻¹, Pa m³ mol⁻¹, respectively.

Note 3: Henry's law constant is sometimes given as the reciprocal of the forms defined above, so its exact definition must always be given. It is recommended to use the definition above, and to refer to its reciprocal as a solubility constant.

See also *Henry's law*.

From [2,5].

higher-order system

multicomponent system

System containing more than three *components*.

See also *unary system, binary system, ternary system*.

immiscibility

Inability of two or more substances to form a homogeneous *mixture* or *solution*.

incongruent reaction

See *peritectic reaction*.

independent component

See *component*.

infinite dilution

Limiting composition or other variable in a *solution* obtained by extrapolating to a value of zero for the variable describing the composition of the solution.

infinite miscibility

miscibility in all proportions

Property of a *system* of forming a single *phase* at all relative proportions of its *components*.

See also *mutual solubility*.

initial complex method

See *wet residue method*.

ionic mole fraction, x_+ , x_-

ionic amount fraction

species mole fraction

species amount fraction

(a) For an ionized salt B in *solution*,

$$x_{+B} = \frac{v_{+B}x_B}{1 + \sum_{i=1}^s (v_i - 1)x_i}, x_{-B} = \frac{v_{-B}x_{+B}}{v_{+B}}$$

where the summation is over all s *solute components* i and $v_i = v_{+i} + v_{-i}$ is the sum of the stoichiometric numbers of the ions formed from salt i .

(b) For a single solvent A in an ionic solution,

$$x'_A = \frac{x_A}{1 + \sum_{i=1}^s (v_i - 1)x_i}$$

Note 1: These are generalizations of terms defined in [18], and are used in formulating fitting equations for *solubility* of salts, in defining *activity coefficients* on the *mole fraction* scale, and in discussing salt effects on solubilities of gases.

Note 2: Note that

$$\sum_{i=1}^s (x_{+i} - x_{-i}) + x'_A = 1$$

From [5,18].

ionic strength

Measure of effective *molality* or *amount concentration* of ionic species in *solution*:

(a) on molality basis: $I_m = \frac{1}{2} \sum z_i^2 m_i$

(b) on amount concentration basis: $I_c = \frac{1}{2} \sum z_i^2 c_i$

where z_i is the charge number of species i , and the summation is over all ionic species.

From [2].

Ising model

Theory of *coexistence curves* or other discontinuities in the properties of *phases* (such as order-disorder or magnetic transitions) in *binary systems*, based on a one-, two-, or three-dimensional statistical mechanical nearest-neighbor lattice theory.

Note: The theory predicts phase separation in a wide variety of systems, including binary liquid or solid systems that possess *critical solution points*.

From [19].

isobar

Line joining points of equal pressure on a *phase diagram*.

isopleth

Line joining points of equal composition on a *phase diagram*.

isotherm (solubility)

Line joining points of equal temperature on a *phase diagram*.

isothermal method

See *synthetic method*.

Jänecke coordinates

solute mole (or mass) fraction coordinates

Coordinates used mainly in representation of multicomponent *phase diagrams* that distinguish *solutes* and a single *solvent*. The *mole* or *mass fractions* of the s solutes are chosen as the primary composition variables and the mole or mass fraction of solvent as a secondary variable, so that the solute amount (mass) fractions may be represented, for example, in *ternary* and *quaternary systems*, as linear (ternary) or planar triangular or square planar (quaternary) diagrams, with the solvent amount or mass fraction along an axis perpendicular to the chosen diagram of solute variables. Quantitatively,

$$x_{s,B} = x_B / \sum_{i=1}^s x_i$$

where the summation is over the s solute substances. Note that $\sum_{i=1}^s x_{s,B} = 1$.

Note 1: The mole fraction of solvent component A in a mixture containing $p - s$ solvents (total species p) is replaced by a special case of the *solvent mole fraction* $x_{s,A} = x_A / \sum_{i=s+1}^p x_i$, which becomes infinite for pure solvent.

Note 2: This quantity can be scaled to a finite value by adding an arbitrary constant to the denominator.

See also *solvent mole (mass) fraction*.
From [5,20].

Kuenen coefficient, S

Volume V^g of an amount n_B^1 of a dissolved gas at a given *standard temperature* T^\ominus (usually 273.15 K) and given *standard pressure* p^\ominus (1 bar = 0.1 MPa or, in older literature, 1 atm) divided by the mass m^1 of the dissolving liquid containing an amount n_A of *solvent* at temperature T and the given pressure p^\ominus .

Note 1: There are two Kuenen coefficients, depending on whether the liquid is the *equilibrium solution* or the pure liquid, with mathematical definitions:

$$\begin{aligned} \text{Kuenen coefficient, solution reference} \quad S_B &= V^g(T^\ominus, p^\ominus, n_B^1)/m^1(T, p^\ominus, n_A, n_B^1) \\ \text{Kuenen coefficient, pure solvent reference} \quad S_B^* &= V^g(T^\ominus, p^\ominus, n_B^1)/m^1(T, p^\ominus, n_A) \end{aligned}$$

Note 2: The relations between the *molality* $m_B(p^\ominus)$ or *mole fraction* $x_B(p^\ominus)$ of dissolved gas and the Kuenen coefficients are

$$\begin{aligned} \frac{1}{x_B(p^\ominus)} &= 1 + \frac{1}{m_B(p^\ominus)M_A} = 1 + \frac{RT^\ominus Z_B^\ominus(T^\ominus)}{p^\ominus M_A S_B} \\ \frac{1}{x_B(p^\ominus)} &= 1 + \frac{1}{m_B(p^\ominus)M_A} = 1 + \frac{RT^\ominus Z_B^\ominus(T^\ominus)}{p^\ominus M_A S_B^*} \end{aligned}$$

where M_A is the molar mass the solvent and Z_B is the compression factor of the gas.

Note 3: The Kuenen coefficient and the related quantities for expression of gas solubility: *absorption coefficient*, *Bunsen coefficient*, and *Ostwald coefficient* appear frequently in the older literature of gas solubility determination. However, the modern practice, recommended here, is to express gas solubility as *molality*, *mole fraction*, or *mole ratio*.

From [5].

lower critical solution temperature

See *critical solution point*.

mass concentration, γ, ρ

mass density

Mass of a *constituent* in a *mixture* divided by the volume of the *mixture*.

From [2].

mass density, ρ

See *density*.

mass fraction, w

Mass of a particular *constituent* divided by the sum of the masses of all *system* constituents.

$$w_B = m_B / \sum_{i=1}^C m_i$$

Note 1: m is used here as a symbol for mass, not molality.

Note 2: *Solubility* is often expressed in units ppm, which is equivalent to the SI units mg/kg if the physical quantity involved is mass fraction, or mmol/mol if mole fraction, etc., or even mmol/L, etc., for aqueous solutions where the density of the solution is approximately 1 g/cm³. However, it is recommended that the term “parts per million, ppm” be avoided since, as noted, “parts” may be measured on any one of a mass, amount, or volume basis. If it is used, the physical quantity to which it refers must be specified.

From [2].

mass percent

Deprecated term that includes both a quantity and a unit. Replace by mass fraction expressed as percent.

Examples: Deprecated: the solubility of B is 2.5 mass %. Recommended: the solubility of B is $w_B = 0.025$, or $w_B = 2.5\%$, or (especially in table headings and labels on axes of plots) 100 w_B , with entry 2.5 in table or on axis.

mass ratio, ζ

Mass of one *constituent* A divided by the mass of a second constituent B in the same *system*.

$$\zeta_{A,B} = m_A/m_B$$

mass solubility, C_w

Obsolete term for *molality* of a *saturated solution* of a gas.

melt

Liquid state of *system* that is a solid at room temperature.

metastable state

metastability

State of a *system* in which a perturbation of any one of its defining variables may cause a change to a more stable state.

Note 1: A system in a metastable state is in a state of metastable *equilibrium*, and so can be described consistently by thermodynamic methods.

Note 2: Although a driving force for the transition of a metastable state to a stable state exists ($\Delta_{\text{trs}}G < 0$ at constant T and p) the transition is retarded, i.e., the transition to the more stable state does not occur significantly during the time of observation.

Modified from [1,11].

metatectic reaction

catatectic reaction

Isothermal reversible reaction of a solid *mixture phase* β which is transformed into a different solid phase α plus a liquid phase l during cooling of a *system*. For a *binary system*,



where the forward arrow indicates the direction of cooling. The *equilibrium* transformation occurs along the metatectic line characterized by the metatectic temperature. The metatectic composition and temperature, isobaric invariants of the system, define the metatectic point, which lies between the compositions of liquid l and solid phase α .

Note 1: From Greek μετα-, referring to position of melting relative to eutectectic and monotectic + -τηκτος, fusible.

Note 2: The alternate name *catatectic reaction*, from Greek κατα, down + -τηκτος, fusible has been suggested to emphasize the phenomenon of melting during cooling [20].

Note 3: Occasionally, a similar reaction takes place in the subsolidus region. Quite appropriately, it is called metatectoid reaction.

Example: system Fe + Zr [15].
From [16].

miscibility

Ability of two liquids to undergo spontaneous mixing to form a homogeneous *mixture*.
See antonym *immiscibility*.

miscibility gap

See *mutual solubility*.

mixture

Gaseous, liquid, or solid *phase* containing more than one substance, when all the substances are treated in the same way.
See also *solution*.
From [2,13].

molality, m, b

Amount of a *solute* divided by the mass of the *solvent*.
Modified from [1].

mole fraction, x

amount-of-substance fraction
amount fraction

Amount of substance of a *constituent* divided by the total amount of all constituents in a *mixture*.

Note: Usually, x is used for constituents in solid or liquid phases, y in gas phases.

From [1].

mole percent

Deprecated term that includes both a quantity and a unit. Replace by mole fraction expressed as percent.

Example: Deprecated: the solubility of B is 2.5 mole %. Recommended: the solubility of B is $x_B = 0.025$, or $x_B = 2.5\%$, or (especially in table headings and labels on axes of plots) $100 x_B$, with entry 2.5 in table or on axis.

mole ratio, r

amount ratio

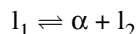
Amount of one *constituent* divided by the amount of a second constituent in the same *system*. For constituents 1 and 2,

$$r_{12} = n_1 / n_2$$

From [4].

monotectic reaction

Isothermal reversible reaction of a liquid *phase* to form a solid phase and a second liquid phase during cooling of a *system*. In a *binary system*,



where the forward arrow indicates the direction of cooling. The *equilibrium* transformation occurs along the monotectic line, characterized by the monotectic temperature. The monotectic composition and temperature, isobaric invariants of the system, define the monotectic point, which lies between the compositions of liquid l_2 and solid phase α .

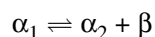
Note: From Greek $\mu\text{νο}\nu\text{ος}$ = one and $\tau\eta\kappa\tau\omicron\varsigma$ = fusible.

Examples: systems Pb + Zn [16], methanol + cyclohexane [22].

Modified from [1,12,16].

monotectoid reaction

Isothermal reversible reaction of a solid *phase* α_1 which is transformed into two different solid phases α_2 and β during the cooling of a *system*. In a *binary system*,



where the forward arrow indicates the direction of cooling. The *equilibrium* process occurs along the monotectoid line at the monotectoid temperature. The monotectoid composition and temperature, isobaric invariants of the system, define the monotectoid point, which lies between the compositions of phases β and α_2 .

Note 1: Derived from Greek, meaning “resembling a monotectic”.

Note 2: Because the monotectoid temperature is an isobaric invariant, the statement in [1,11], that it is the maximum temperature at which the monotectoid reaction can occur is incorrect.

Example: system Al + Zn [15].

Modified from [1,12,16].

multicomponent system

See *higher-order system*.

mutual solubility

In a *system* of two or more liquid or solid *components*, *solubility* of all components in all *phases*.

Note: If mutual solubility is limited over a range of temperature and composition, the liquids or solids are said to exhibit *partial miscibility* and the system possesses a *miscibility gap*.

non-saturating solute

Solute which forms an unsaturated solution.

Note: Together with the term *saturating solute* used to distinguish among solutes in *ternary* and *higher-order systems*.

number concentration, C

Number of entities (N) of a constituent in a *mixture* divided by the volume (V) of the mixture.

See also *amount concentration*.

From [1].

osmotic coefficient, φ_x, φ_m

Factor to correct for non-ideal behavior of the *solvent* in a *solution*.

(a) *Mole fraction* basis. For solvent A,

$$\varphi_{x,A} = (\mu_A - \mu_A^*)/RT \ln x_A$$

where μ_A^* is the standard chemical potential of A, i.e., the chemical potential of pure liquid A.

(b) *Molality* basis. For a solvent A in a solution of total molality $\sum m_B$,

$$\varphi_{m,A} = (\mu_A^* - \mu_A)/RTM_A \sum m_B$$

where M_A is the molar mass of the solvent.

Note 1: The coefficient φ_x was previously called the rational osmotic coefficient.

Note 2: For a single salt with sum of stoichiometric coefficients of its ions ν and molality m_B ,

$$\varphi_{m,A} = (\mu_A^* - \mu_A)/\nu RTM_A m_B$$

From [1,2], index B corrected from [1] and sign corrected from [2].

Ostwald coefficient, L

Volume V^g of an amount n_B^1 of a dissolved gas calculated at given temperature T and pressure p divided by the volume of the dissolving liquid of volume V^l and containing an amount n_A of *solvent* at the same temperature T and pressure p .

Note 1: There are two Ostwald coefficients, depending on whether the liquid is the *equilibrium solution* or the pure liquid, with mathematical definitions:

$$\text{Ostwald coefficient, solution reference} \quad L_B = V^g(T, p, n_B^1)/V^l(T, p, n_A, n_B^1) = c_B^l/c_B^g$$

$$\text{Ostwald coefficient, pure solvent reference} \quad L_B^* = V^g(T, p, n_B^1)/V^l(T, p, n_A)$$

Note 2: The relations between the *molality* $m_B(p)$ or *mole fraction* $x_B(p)$ of dissolved gas and the Ostwald coefficients are

$$\frac{1}{x_B(p)} = 1 + \frac{1}{m_B(p)M_A} = 1 + \frac{RTZ_B}{V_A p_B L_B}$$

$$\frac{1}{x_B(p)} = 1 + \frac{1}{m_B(p)M_A} = 1 + \frac{RTZ_B}{pV_{m,A}L_B^*}$$

where V_A , $V_{m,A}$ are the respective partial molar volume and molar volume of the solvent and Z_B is the compression factor of the gas.

Note 3: A discussion of the Ostwald coefficient from a historical perspective is available [22].

Note 4: The Ostwald coefficient and the related quantities for expression of gas solubility, the *absorption*, *Bunsen*, and *Kuenen coefficients*, appear frequently in the older literature of gas solubility determination. However, the modern practice, recommended here, is to express gas solubility as *molarity*, *mole fraction*, or *mole ratio*.

From [5].

Ostwald ripening

Dissolution of small crystals or *sol* particles and the redeposition of the dissolved species on the surfaces of larger crystals or sol particles.

Note: The process occurs because smaller particles have a higher surface energy, hence higher total Gibbs energy, than larger particles, giving rise to an apparent higher solubility.

From [24] as modified from [1].

partial miscibility

See *mutual solubility*.

partial pressure, p_B

In a *mixture* of ideal gases, $p_B = y_B p$, where y_B is the *mole fraction* of constituent B and p is the total pressure.

Note: In real (non-ideal) gases, there is a difficulty defining partial pressure [1,2].

percent, %

One part in a hundred parts.

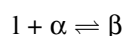
Example: The *mole fraction* $x = 2.8 \times 10^{-2} = 2.8 \%$.

From [1].

peritectic reaction

incongruent reaction

Isothermal, reversible reaction between two phases, a liquid and a solid, that results, on cooling of a *binary*, *ternary*, or *higher-order system* in one, two, ... ($n - 1$, where n is the number of *components*) new solid *phases*. For example, in a binary system



where the forward arrow indicates the direction of cooling. The *equilibrium* process occurs along the peritectic line, characterized by the peritectic temperature. The peritectic composition and temperature, isobaric invariants of the system, define the peritectic point, which lies between the compositions of phases l and α .

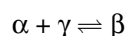
Note: From Greek περι-, around and -τηκτος, fusible.

Example: alloy system Cu + Zn [15], salt-water system Na₂SO₄ + H₂O.

Modified from [1,12,16].

peritectoid reaction

Isothermal, reversible reaction in the solid state, that, on cooling of a *binary*, *ternary*, or *higher-order system*, results in one, two, ... ($n - 1$) new solid *phases*. For a binary system.



where the forward arrow indicates the direction of cooling. The *equilibrium* process occurs at the peritectoid point, characterized by the peritectoid line at the peritectoid temperature. The peritectoid composition and temperature, isobaric invariants of the system, define the peritectoid point, which lies between the compositions of phases α and β .

Note 1: Derived from Greek, meaning “resembling a peritectic”.

Note 2: Metatectoid, meaning “resembling a metatectic”, is not an acceptable synonym for peritectoid.

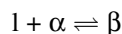
Example: systems Al + Cu [15], hexacosane (C₂₆H₅₄) + octacosane (C₂₈H₅₈) [25].

Modified from [1,12,16].

peritonic reaction

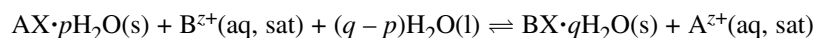
transition reaction (in phase equilibria)

Isothermal, isobaric reversible reaction between two phases, a saturated liquid and a solid, that results, on removal of the solvent *component* of a *ternary system* in one new solid *phase*. For example,



where the forward arrow indicates the direction of removal of the solvent component. The system is in *equilibrium* along the peritonic line, on which is found the peritonic composition or point, an isothermal, isobaric invariant of the system which lies between the compositions of phases l and α .

Example: In an ionic system,



The two salts may also contain the same ions.

Note 1: Named from a combination of eutonic and peritectic.

Note 2: The very general terms *transition point* or composition are deprecated, as they can refer to many other types of equilibria. Historically, the use of transition point in this case dates back to at least ref. [17].

Example: system KCl + MgCl₂ + H₂O

See also *dystonic reaction*, *eutonic reaction*, *transition point*.

permil, ‰

per mille

permille

promille

One part in a thousand parts.

Example: The *mole fraction* $x = 2.8 \times 10^{-3} = 2.8 \text{ ‰}$.

From [1].

See also *chlorinity*, *salinity*.

phase

System or portion of a system which is uniform in chemical composition and physical state.

Note: At *equilibrium*, all intensive variables (temperature, pressure, electric field, magnetic induction, chemical potential, etc.) are uniform within a phase.

Modified from [1,12].

phase diagram

Graphical representation, by use of points, lines, and surfaces, of the phases present at chemical *equilibrium* in unary, *binary*, *ternary*, and *higher-order systems* containing two or more *phases*.

Note: Phase diagrams may employ any pairs of the variables temperature, pressure, and compositions of various phases. Thus, temperature-composition and pressure-composition phase diagrams are possible, as well as diagrams showing only compositions under isothermal or isobaric conditions.

See also *isobar*, *isopleths*, *isotherm*.

phase rule

Gibbs' phase rule

Relation connecting number of possible stable *phases* P in an *equilibrium system* with the number of *components*, C , and the number of degrees of freedom, F , i.e., the number of variables that can be assigned free values:

$$F = C + 2 - P$$

Note 1: The phase rule as stated holds under the conditions: (a) negligible surface contributions (unless the curvature is constant); (b) uniform normal pressure (perpendicular to the phase surface) over all phases is the only external force; (c) interphase surfaces are deformable, heat-conducting, and permeable to all components.

Note 2: Sometimes, the phase rule is written as $F = (C - r) + 2 - P$ where r is the number of chemical reactions which can reach chemical equilibrium in the system. This form requires that C be the number of species assumed for the system, rather than the number of components.

Note 3: For the phase rule in the presence of surface phases, see [26].

Modified from [1,12,26].

plait point

See *critical solution point*.

polythermal method

See *synthetic method*.

Poynting correction, I_p

Factor used to convert experimentally determined *Henry's law constants* at the saturation vapor pressure of the solvent A, p_A^* , to a reference pressure p

$$I_p(p) = \int_{p_A^*}^p \frac{V_B^{\infty 1}}{RT} dp$$

$$k_{H,B}(p) = k_{H,B}(p_A^*) \exp[I_p(p)]$$

where $V_B^{\infty 1}$ is the partial molar volume of liquid B at infinite dilution in solvent A. The second equation gives the relation between the two *Henry's law constants*.

See *Henry's law constant*.

From [5].

precipitation

Formation of a solid material (a precipitate) from a liquid *solution* in which the material is present in amounts greater than its *solubility* in the liquid.

Note: The solid material may eventually sediment due to the action of gravity.

Modified from [1,12].

primary data

Data reported in peer-reviewed scientific reports of original research which allow an assessment of data quality.

Note: Primary data are distinguished from secondary data appearing in reviews, handbooks, compendia, etc. which hold the possibility of error and bias through transcription error, incomplete coverage of the primary literature, etc.

Raoult's Law

Fugacity (\tilde{p}_B) of a gaseous component (B) in equilibrium with a liquid or solid *mixture* containing B is directly proportional to the activity (a_B) of the component in the *mixture*

$$\tilde{p}_B = \tilde{p}_B^* f_B x_B$$

where f_A is the activity coefficient of A referenced to Raoult's law at mole fraction x_A and \tilde{p}_B^* is the fugacity of pure B.

Note: An ideal mixture is defined by replacing fugacities with *partial pressures* and setting the activity coefficient equal to unity

$$p_B = p_B^* x_B = y_B p$$

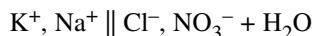
The total pressure, p , is then simply the sum of the partial pressures of all components.

See *activity coefficient*, *Henry's law*.

reciprocal salt system

System containing n ionic species with or without a single solvent. Because of electrical neutrality, the system has n components in an aqueous system with a single solvent and $n - 1$ components in a molten salt system.

Note 1: There is a special notation for reciprocal salt systems that involves use of double vertical bars. All ionic species are specified. For example,



denotes a four-component (quaternary) aqueous reciprocal salt system in which each cation can combine with each anion to produce anhydrous, hydrated, binary, or ternary solid components; i.e., the solution may become saturated with respect to any one of KCl, NaCl, KNO₃, NaNO₃, their hydrates, or anhydrous or hydrated binary compounds of the simple salts.

Note 2: Ternary aqueous systems containing a common ion can be considered as a limiting case of this class of system, where there is only one cation or one anion. For example,



reduced pressure, p_r

Pressure divided by the *critical pressure*.

reduced temperature, T_r

Temperature divided by the *critical temperature*.

reference data

Data that are critically evaluated and verified, obtained from an identified source, and related to a property of a phenomenon, body, or substance, or a *system of components* of known composition and structure.

relative activity

See *activity*.

retrograde solubility

- (1) *Solubility* that decreases with an increase in conditions such as temperature or added *component*, where an increase is expected as the usual case.
- (2) In ternary liquid systems with *coexisting phases*, where the *critical solution point* is not a maximum on a *ternary diagram*, passing from a homogeneous mixture in which the composition of a given component is greater than that of the critical mixture to a heterogeneous mixture and back to a homogeneous mixture by altering the relative amounts of the two other components.

From [27].

salinity, S

Mass of dissolved salts in sea water, brackish water, brine, or other saline solution divided by the mass of the solution.

Note 1: In practice, this quantity cannot be measured directly in sea water or other natural waters because of the difficulty of drying the salts from these waters. Salinity is usually calculated from another property (e.g., *chlorinity*, electrical conductivity) whose relationship to salinity is well known.

Note 2: In oceanography, where precise and reproducible determination of sea water density is of interest, practical salinity, S , is defined in terms of the ratio k_{15} of the electrical conductivity of the sea water sample at 15 °C and 1 atm (1.01325 kPa) to that of a potassium chloride (KCl) solution, in which the mass fraction of KCl is 32.4536×10^{-3} at the same temperature and pressure.

The Practical Salinity Scale, established in 1978, relates S to k_{15} by the equation

$$S/\text{g kg}^{-1} = \sum_{i=0}^5 a_i k_{15}^{i/2} \quad \text{range } 2 \leq S \leq 42$$

where $a_0 = 0.0080$, $a_1 = -0.1692$, $a_2 = 25.3851$, $a_3 = 14.0941$, $a_4 = 7.0261$, $a_5 = 2.7081$, $\sum_{i=0}^5 a_i = 35.0000$.

Especially before 1978, practical salinity was also determined from *chlorinity*, w_{Cl} , as $S = 1.80645 w_{\text{Cl}}$.

Note 3: Before 1978, the usual unit for S expressed as a *mass fraction* was *permil* (no longer recommended), now usually in units g kg^{-1} or expressed as g kg^{-1} without the units given explicitly.

Example: the practical salinity of a sample of artificial sea water is $S = 35.0000 \text{ ‰}$ or $35.0000 \text{ g kg}^{-1}$ or 35.0000×10^{-3} or 35.0000 .

See also *chlorinity*.

From [7,8].

salt effect (in solubility)

Change in *solubility* of a *solute* in aqueous solution on addition of a salt that does not possess a *common ion* with the original *solute*.

Note: If the solubility increases on addition of a salt, the addition is said to cause salting-in; if the opposite, it causes salting-out.

See also *Sechenov equation*.

saturated solution

Solution that has the same composition of a *solute* as one that is in *equilibrium* with undissolved solute at specified values of temperature and pressure.

Note: *Ternary* and *higher-order systems* can be saturated with respect to one *component* while being unsaturated with respect to another.

Modified from [1].

saturating solute

Solute that forms a saturated solution.

Note: Together with the term *non-saturating solute*, used to distinguish among solutes in *ternary* and *higher-order systems*.

saturation

State of a *saturated solution*.

Modified from [1].

saturation vapor pressure

Pressure exerted by a pure substance (at a given temperature) in a *system* containing only the vapor and condensed *phase* (liquid or solid) of the substance.

From [1].

scaling equation

Dimensionless equation representing *mutual solubilities* in a number of chemically related liquid *systems*. Each mutual solubility is subtracted from the solubility at the *critical solution point*, and the temperature is divided by the *critical solution temperature*.

Schreinemakers' method

See *wet residue method*.

Sechenov equation

Expression of the *salt effect* that relates the change in *solubility* of a nonelectrolyte (e.g., gas or organic liquid) to changing *ionic strength* of aqueous solutions,

$$\lg(s_0/s) = K_s I_s$$

where s_0 , s are the solubilities of nonelectrolyte in pure water and saline solution, respectively, K_s the Sechenov parameter (an empirical proportionality constant), and I_s the ionic strength of the saline solution.

Note 1: Positive values of the Sechenov parameter correspond to the commonly observed salting-out effect; negative values to the less common salting-in effect.

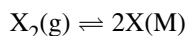
Note 2: Sechenov is the international and Setschenow the German transliteration of Сеченов.

From [5,28].

Sieverts' law

Solubility of a diatomic gas in a molten metal is proportional to the square root of the partial pressure.

Note 1: The law follows from the solubility constant for equilibrium dissolution of an ideal diatomic gas X_2 in a metal M to form an ideal solution of dissociated atoms:



for which, and for dilute solutions of the gas,

$$K_{s,x} = a(X,M)^2/a(X_2,g) \approx x(X,M)^2 p^0/p(X_2,g)$$

where $x(X, M)$ is the solubility of the gas in the molten metal expressed as a mole fraction of H-atoms. The solubility constant $K_{s,x}$ is called the *Sieverts constant*.

Note 2: Other forms of the solubility constant are common, especially in terms of amount concentrations or mass fractions (especially in metallurgical papers) instead of mole fractions.

See also *Henry's law constant*, *solubility constant*.

Expanded from [29].

smoothing equation

See *fitting equation*.

solid mixture

See *mixture*.

solid solution

See *solution*.

solubility, *s*

Analytical composition of a *mixture* or *solution* which is *saturated* with one of the *components* of the mixture or solution, expressed in terms of the proportion of the designated component in the designated mixture or solution.

Note 1: The definition refers to *constituents* B; i.e., s_B .

Note 2: Solubility may be expressed in any units corresponding to quantities that denote relative composition, such as *mass, number or amount concentration, molality, mass fraction, mole fraction, mole ratio*, etc.

Note 3: The mixture or solution may involve any physical state: solid, liquid, gas, vapor, supercritical fluid.

Note 4: The term “solubility” is also often used in a more general sense to refer to processes and phenomena related to *dissolution*.

Modified from [1,5].

solubility constant

Generalization of *solubility product* to include, for example, undissociated salt or uncharged cation-anion pair as *solute*, reaction between *solution* species and the cation or anion of the solid salt, and gas-solution equilibria.

Note 1: The solubility constant can also be considered in many cases as relating to a *solubility equilibrium* as described under *solubility product* plus one or more simultaneous homogeneous equilibria in solution.

Note 2: Examples and specialized notation for solubility constants are described in [30–34].

See also *solubility product*.

solubility parameter, δ

Parameter used in predicting the *solubility* of non-electrolytes (including polymers) in a given *solvent*. For a substance B,

$$\delta_B = (\Delta_{\text{vap}} E_{\text{m,B}} / V_{\text{m,B}})^{1/2}$$

where $\Delta_{\text{vap}} E_{\text{m}}$ is the molar energy of vaporization at zero pressure and V_{m} is the molar volume.

Note 1: For a substance of low molecular weight, the value of the solubility parameter can be estimated most reliably from the enthalpy of vaporization and the molar volume.

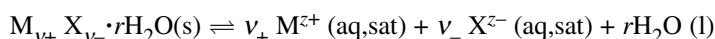
Note 2: The solubility of a substance B can be related to the square of the difference between the solubility parameters for supercooled liquid B and solvent at a given temperature, with appropriate allowances for entropy of mixing. Thus, a value can be estimated from the solubility of the solid in a series of solvents of known solubility parameter. For a polymer, it is usually taken to be the value of the solubility parameter of the solvent producing the solution with maximum intrinsic viscosity or maximum swelling of a network of the polymer. See [35] for the original definition, theory, and extensive examples.

Note 3: The SI units are $\text{Pa}^{1/2} = \text{J}^{1/2} \text{m}^{-3/2}$, but units used frequently are $(\mu\text{Pa})^{1/2} = (\text{J cm}^{-3})^{1/2}$ or $(\text{cal cm}^{-3})^{1/2}$, where $1 (\text{J cm}^{-3})^{1/2} \approx 2.045 (\text{cal cm}^{-3})^{1/2}$. The unit calorie is discouraged as obsolete.

Modified from [1,35].

solubility product, K_s , K_s^\ominus

Equilibrium constant for the dissolution process of an ionic solid or an addition compound that dissociates completely in solution; for example,



where a hydrated ionic solid (mole ratio water/salt = r) has been shown as a common example of an addition compound one part of which is an ionic solid. The equilibrium constant is

$$K_s = a_+^{v_+} a_-^{v_-} a_w^r$$

or

$$K_s = (\gamma_{\pm}/m^\ominus)^{\nu} (m_+)^{v_+} (m_-)^{v_-} \exp(-rM_w\phi_m\sum_i m_i)$$

where a_+ , a_- , and a_w are the respective cation, anion and water activities, $\nu = v_+ + v_-$ is the sum of the stoichiometric numbers and z_+ , z_- the charge numbers of the cation and anion, m molality, γ_{\pm} the mean ionic activity coefficient (referenced to molality), $m^\ominus = 1 \text{ mol kg}^{-1}$ the standard molality, M_w the molar mass of water and ϕ_m the osmotic coefficient (referenced to molality). The summation is over all species in solution.

Note 1: For the special case where there is no common cation or anion and no reaction with solution species and the cation or anion of the salt to form, e.g., an acid, base, or complex ion in the solution

$$K_s = (v_{\pm}\gamma_{\pm}m/m^\ominus)^{\nu} \exp(-r\nu M_w\phi_m)$$

where $v_{\pm} = (v_+^{v_+} v_-^{v_-})^{1/\nu}$ and m is the stoichiometric molality of the anhydrous salt, with $m_+ = v_+m$, $m_- = v_-m$.

Note 2: For the special case where a common anion, molality m_X , with balancing cations of molality m_N , exist in solution, but there is no reaction with solution species and the cation or anion of the salt

$$K_s = (\gamma_{\pm}/m^\ominus)^{\nu} m_+^{v_+} (v_-m + m_X)^{v_-} \exp[-rM_w(nm + m_N + m_X)\phi_m]$$

Note 3: Solubility products have been written here as dimensionless quantities, a practice that is not always followed but avoids extra symbols to make the solubility constant dimensionless when its use as the argument of a logarithm is required.

See also *solubility constant*.

Modified from [1].

solubilization

Process by which an agent increases the *solubility* or the rate of *dissolution* of a solid or liquid *solute*.

Note 1: The solute that is solubilized is called the solubilizate.

Note 2: Solubilization is sometimes used loosely to include processes caused by agents such as surfactants which hold a *component* in micelles or colloidal suspension rather than in *solution*.

Modified from entry “micellar solubilization” in [1].

solute

Minor component of a *solution* that is regarded as having been dissolved by the *solvent*.

Modified from [1].

solute mole (or mass) fraction

See *Jänecke coordinates*.

solution

Liquid or solid *phase* containing more than one substance, when, for convenience, one (or more) of the substances, called the *solvent*, is treated differently from the other substances, called *solutes*.

Note 1: When the sum of the *mole fractions* of the solutes is small compared with unity, the solution is called a dilute solution.

Note 2: A superscript ∞ attached to the symbol for a property of a solution denotes the property in the limit of *infinite dilution*.

See *mixture*.

From [2,13].

solvent

Major *component* of a *solution* that is regarded as having dissolved the *solute*.

Modified from [1].

solvent mole (mass) fraction, $x_{v,A}$ ($w_{v,A}$)

Mole or mass fraction of a *solvent* in a *solution* containing *s* *solute constituents* ($i = 1, 2, \dots, s$) and *p* solvent constituents ($i = s + 1, s + 2, \dots, p$). For a solvent A,

$$x_{v,A} = x_A / \sum_{i=s+1}^p x_i, \text{ where } \sum_{i=1}^p x_i = \sum_{i=1}^s x_i + \sum_{i=s+1}^p x_i = 1$$

and analogously for $w_{v,A}$, where the first and last summations are over all solvent constituents.

See also *Jänecke coordinates*.

From [5].

solvent volume fraction, ϕ_v

For a *solvent* A, *volume fraction* of A divided by the sum of the volume fractions of solvent in a *solution* containing both *s* solutes ($i = 1, 2, \dots, s$) and *p* solvents ($i = s + 1, s + 2, \dots, p$)

$$\varphi_{v,A} = \varphi_A / \sum_{i=s+1}^p \varphi_i$$

where the summation is over the p solvent *components* only.

Note: Used to express solvent composition for a system containing a solute in a mixed solvent.

See also *volume fraction*.

From [5].

solvomolality

See *aquamolality*.

species mole (amount) fraction

See *ionic mole (amount) fraction*.

spinodal curve

Boundary of separation between *metastable* and unstable *phases* on a temperature-composition or pressure-composition *phase diagram* for a liquid or solid *system* of two or more *components*.

See *spinodal decomposition*.

From [10,11].

spinodal decomposition

Mechanism by which a system (solid or liquid) consisting of two or more *components* in a *metastable* phase transforms into two stable phases.

Note 1: On a temperature-composition phase diagram for a liquid or solid *system* of two or more *components*, systems with compositions lying within the areas between the *spinodal* and *conodal curves* can undergo spinodal decomposition.

Note 2: The mechanism is considered to involve a clustering reaction in which the mixture separates spontaneously into two phases, starting with small fluctuations and proceeding with a decrease in the Gibbs energy without a nucleation barrier.

See *conodal curve*, *spinodal curve*.

Modified from [1,12].

standard amount concentration, c^\ominus

standard concentration

Chosen value of *amount concentration*.

Note: In principle, one may choose any value for the standard concentration, although the choice must be specified. The most common choice for standard concentration is $c^\ominus = 1 \text{ mol dm}^{-3}$, which is universally accepted.

Modified from [1,2].

standard molality, m^\ominus , m° , b^\ominus , b°

Chosen value of *molality*.

Note: In principle, one may choose any value for the standard molality, although the choice must be specified. The most common choice for standard molality is $m^\ominus = 1 \text{ mol kg}^{-1}$, which is universally accepted.

Modified from [1,2].

standard pressure, p^\ominus , p°

Chosen value of *pressure*.

Note: In principle, one may choose any value for the standard pressure, although the choice must be specified. In practice, the most common choice is $p^\ominus = 0.1 \text{ MPa} = 100 \text{ kPa}$ (= 1 bar). The value for $p^\ominus = 100 \text{ kPa}$ is the IUPAC recommendation since 1982, and is recommended for tabulating thermodynamic data. Prior to 1982, the standard pressure was usually taken to be $p^\ominus = 101\,325 \text{ Pa}$ (= 1 atm, called the *standard atmosphere*). In any case, the value for p^\ominus should be specified. The conversion of values corresponding to different p^\ominus is described in [36–38]. The newer value of p^\ominus , 100 kPa, is sometimes called the standard state pressure.

Modified from [1,2].

standard state

State of a *system* chosen as standard for reference by convention. Three standard states are recognized:

For a *gas phase*, it is the (hypothetical) state of the pure substance in the gaseous phase at the *standard pressure* $p = p^\ominus$, assuming ideal behavior.

For a *pure phase*, or a *mixture*, or a *solvent* in the liquid or solid state, it is the state of the pure substance in the liquid or solid phase at the standard pressure $p = p^\ominus$.

For a *solute in solution*, it is the (hypothetical) state of solute at the *standard molality* m^\ominus , standard pressure p^\ominus , or *standard concentration* c^\ominus and exhibiting infinitely dilute solution behavior.

Note: Either superscript, \ominus or \circ , is acceptable to designate standard state.

From [1].

supercritical fluid

State of a compound, *mixture* of fixed overall composition, or element above its *critical pressure* (p_c) and *critical temperature* (T_c).

From [1].

supersaturated solution

Solution that has a greater composition of a *solute* than one that is in *equilibrium* with undissolved solute at specified values of temperature and pressure.

See also *saturated solution*, *unsaturated solution*.

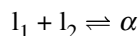
supersaturation

State of a *supersaturated solution*.

Modified from [1].

syntectic reaction

Isothermal reversible reaction of two liquid *phases* l_1, l_2 which are transformed into a solid phase α during the cooling of a *system*. For a *binary system*,



where the forward arrow indicates the direction of cooling. The equilibrium reaction occurs along the syntectic line, characterized by the syntectic temperature. The syntectic composition and temperature, isobaric invariants of the system, define the syntectic point, which lies between the composition of the two liquid phases.

Note 1: From Greek: $\sigma\upsilon\nu$ - = together and $-\tau\eta\kappa\tau\omicron\varsigma$ = fusible.

Note 2: Occasionally, a similar reaction takes place in the subsolidus region. Quite appropriately, it is called syntectoid reaction.

Note 3: Because the syntectic temperature is an isobaric invariant, the statement in [1,12] that it is the maximum temperature at which the syntectic reaction can occur is incorrect.

Example: system K + Zn [15].

Modified and corrected from [1,12,16].

synthetic method (in determination of solubility)

Class of experimental procedures for *solubility* determination in which a *solution* of known composition is prepared. Two major subclasses are recognized. In the isothermal method, one liquid *component* is titrated with a second liquid component at constant temperature until persistent turbidity is observed (i.e., to the *cloud point*). In the polythermal method, a *mixture* of known composition is heated above its solution temperature and monitored visually during cooling until turbidity (the cloud point) is observed.

system

Arbitrarily defined part of the universe, regardless of form or size.

Note: In the context of *solubility* phenomena, a system contains two or more *components* whose solubility is of interest.

Modified from [1].

ternary diagram

Gibbs' triangular representation

Triangular plot (usually an equilateral or right-angled triangle) whose vertices represent the pure *components* of a *ternary system* at constant temperature and pressure. Any point within the triangle represents the composition in terms of the two independent mole (or mass) fractions. Lines parallel to the sides of the triangle represent constant proportions of the respective components (*isopleths*).

Note 1: In an *isobaric* diagram, an axis perpendicular to the plane of the triangle may be added to represent temperature.

Note 2: In addition, any triangle of any shape, including any triangle within the main triangle, can be used to obtain the composition of the system represented by a point within the triangle in terms of the compositions represented by its vertices.

From [39].

ternary system

System containing three *components*.

See also *unary system, binary system, ternary system*.

thermodynamic component

See *component*.

tie-line

connodal

conodal

Straight line connecting compositions of independent coexisting *phases* in *equilibrium* on a *phase diagram*.

From [1,12].

transition point

See *peritonic reaction*.

unary system

System containing one *component*.

See also *binary system, ternary system, higher-order system*.

unsaturated solution

Solution that has a lower proportion of a *solute* than one that is in *equilibrium* with undissolved solute at specified values of temperature and pressure.

unsaturation

undersaturation

State of an *unsaturated solution*.

upper critical solution temperature

See *critical solution point*.

Van der Waals' equations

See *Gibbs–Kononov equations*.

volume fraction, φ

Volume of a *constituent* of a *mixture* divided by the sum of volumes of all constituents prior to mixing.

For a substance B,

$$\varphi_B = x_B V_{m,B}^* / \sum_{j=1}^C x_j V_{m,j}^*$$

where $V_{m,j}^*$ is the molar volume of the pure constituent *j*.

See also *solvent volume fraction*.

Extended from [1].

wet residue method

Schreinemakers' method

initial complex method

Method for determining composition of a solid *phase* in a *ternary system* at constant temperature and pressure by analysis of the total mixture of solid and liquid in *equilibrium*.

Note 1: The method relies on the fact that the wet residue lies on the *tie-line* connecting the solid phase and the *saturated* liquid phase. Equally well, the initial mixture of solid and liquid used in the *solubility* experiment can be used, when it is referred to as the “initial complex” method. In either case, two or more tie-lines intersect at the composition of the solid phase.

Note 2: The method is generally more reliable than isolation and analysis of the solid phase, especially when the solid phase is a hydrate.

From [40,41].

3. REFERENCES

1. IUPAC. *Compendium of Chemical Terminology*, 2nd ed. (the “Gold Book”), compiled by A. D. McNaught and A. Wilkinson, Blackwell Science, Oxford (1997). XML on-line corrected version: <<http://goldbook.iupac.org>> (2006–) created by M. Nic, J. Jirat, B. Kosata; updates compiled by A. Jenkins.
2. IUPAC Physical Chemistry Division. *Quantities, Units and Symbols in Physical Chemistry*, 3rd ed. (the “Green Book”), prepared for publication by E. R. Cohen, T. Cvitaš, J. G. Frey, B. Holmström, K. Kuchitsu, R. Marquardt, I. Mills, F. Pavese, M. Quack, J. Stohner, H. L. Strauss, M. Takami, A. J. Thor, RSC Publications, Cambridge (2007).
3. H. L. Clever, R. Battino. “Solubility of gases in liquids”, in *The Experimental Determination of Solubilities*, G. T. Hefter, R. P. T. Tomkins (Eds.), p. 104, John Wiley, Chichester (2003).
4. T. Cvitaš. *Metrologia* **33**, 35 (1996).
5. J. W. Lorimer. “Quantities, units and conversions”, in *The Experimental Determination of Solubilities*, G. T. Hefter, R. P. T. Tomkins (Eds.), pp. 1–15, John Wiley, Chichester (2003).
6. A. Bolz, U. K. Deiters, C. J. Peters, T. W. de Loos. *Pure Appl. Chem.* **70**, 2233 (1998).
7. E. L. Lewis. *IEEE J. Ocean. Eng.* **OE-5**, 3 (1980).
8. UNESCO. *The International System of Units in Oceanography. Technical Papers in Marine Science* 45 (1985); <www/unesdoc.unesco.org>.
9. E. C. W. Clarke, D. N. Glew. *Trans. Faraday Soc.* **62**, 539 (1966).
10. R. F. Weiss. *Deep-Sea Res. Oceanogr. Abs.* 721 (1970).
11. J. S. Rowlinson, F. L. Swinton. *Liquids and Liquid Mixtures*, 3rd ed., Sects. 4.9, 6.2, Butterworth Scientific, London (1982).
12. J. B. Clark, J. W. Hastie, L. H. E. Kihlberg, R. Metselaar, M. M. Thackeray. *Pure Appl. Chem.* **66**, 577 (1994).
13. M. L. McGlashan. *Chemical Thermodynamics*, pp. 35–36, 181–182, 261, Academic Press, New York (1979).
14. I. Prigogine, R. Defay (transl. D. H. Everett). *Chemical Thermodynamics*, pp. 71, 278, 373, Longmans, Green, London (1954).
15. T. B. Massalski, H. Okamoto, P. R. Subramanian, L. Kaprczak (Eds.). ASM International (corporate author). *Binary Alloy Phase Diagrams*, 2nd ed., ASM International (1990).
16. A. Prince. *Alloy Phase Equilibria*, pp. 43, 100, 109, Elsevier, Amsterdam (1966).
17. (a) N. S. Kurnakov, S. F. Zhemchuzhnii. *Zh. Russ. Fiz.-Khim. O-va, Chast Khim.* **51**, 1 (1920); (b) N. S. Kurnakov, S. F. Zhemchuzhnii. *Z. Anorg. Allg. Chem.* **140**, 149 (1924).

18. R. A. Robinson, R. A. Stokes. *Electrolyte Solutions*, 2nd ed., pp. 31–32, Butterworths, London (1959).
19. T. L. Hill. *Statistical Mechanics*, Chap. 7, McGraw-Hill, New York (1956).
20. E. Jänecke. *Z. Anorg. Chem.* **51**, 132 (1906).
21. S. Wagner, P. A. Rigney. *Met. Trans.* **5**, 2155 (1974).
22. D. Shaw, A. Skrzecz, J. W. Lorimer, A. Maczynski (Eds.). *IUPAC Solubility Data Series, Vol. 56, Alcohols with Hydrocarbons*, Oxford University Press (1994).
23. R. Battino. *Fluid Phase Equilib.* **15**, 231 (1984).
24. R. G. Jones, J. Alemán, A. V. Chadwick, J. He, M. Hess, K. Horie, P. Kratochvil, I. Meisel, I. Mita, G. Moad, S. Penczek, R. F. T. Stepto. *Pure Appl. Chem.* **79**, 1801 (2007).
25. F. Rajabalee, V. Métiraud, D. Mondieig, Y. Haget, H. A. J. Oonk. *Helv. Chim. Acta* **82**, 1916 (1999).
26. J. G. Kirkwood, I. Oppenheim. *Chemical Thermodynamics*, Sects. 9-1, 10-1, McGraw-Hill, New York (1961).
27. A. Findlay, A. N. Campbell. *The Phase Rule and its Applications*, pp. 221–222, Dover Publications, New York (1945).
28. J. Setschenow. *Z. Phys. Chem., Stoechiom. Verwandtschaftsl.* **8**, 657 (1891).
29. A. Sieverts. *Z. Elektrochem. Angew. Phys. Chem.* **16**, 707 (1910).
30. W. Feitknecht, P. Schindler. *Pure Appl. Chem.* **1**, 130 (1963). Sect. 2.2.
31. L. G. Sillén, A. E. Martell. *Stability Constants of Metal-Ion Complexes*, Special Publication No. 17, pp. xiii, xiv, The Chemical Society, London (1964).
32. L. G. Sillén, A. E. Martell. *Stability Constants of Metal-Ion Complexes*, Supplement No. 1, Special Publication No. 25, p. xvi, The Chemical Society, London (1971).
33. E. Högfeldt. *Stability Constants of Metal-Ion Complexes, Part A: Inorganic Ligands*, IUPAC Chemical Data Series, No. 21, p. xii, Pergamon Press, Oxford (1982).
34. IUPAC. *Compendium of Analytical Nomenclature. Definitive Rules 1997*, 3rd ed. (the “Orange Book”), prepared for publication by J. Inczédy, T. Lengyel, A. M. Ure, Blackwell Science, Oxford (1997). On-line ed.: <www.iupac.org/publications/analytical/compendium>. Chap. 3, Sect. 3.2.5.
35. J. H. Hildebrand, R. L. Scott. *The Solubility of Nonelectrolytes*, 3rd ed., Reinhold Publishing (1950); Dover Publications (1964), Chap. VII, p. 129; Chap. XXIII.
36. R. D. Freeman. *Bull. Chem. Thermodyn.* **27**, 523 (1982).
37. R. D. Freeman. *J. Chem. Eng. Data* **29**, 105 (1984).
38. R. D. Freeman. *J. Chem. Educ.* **62**, 681 (1985).
39. R. Haase, H. Schönert (transl. E. S. Halberstadt). *Solid-Liquid Equilibrium*, Chap. 5, Pergamon Press, Oxford (1969).
40. F. A. H. Schreinemakers. *Z. Phys. Chem.* **11**, 75 (1893).
41. (a) J. W. Lorimer. *Can. J. Chem.* **59**, 3076 (1981); (b) J. W. Lorimer. *Can. J. Chem.* **60**, 1978 (1982).

4. QUANTITIES, SYMBOLS, AND UNITS USED IN THIS GLOSSARY

4.1 Quantities, symbols, and units

Entries in the table are consistent with terminology, symbols, and units given in [2,5].

Note that use of a + sign as a separator between formulas or names of components of mixtures is contrary to use in [12], where a hyphen is used. The use here accords with the most prevalent current use in research journals in thermodynamics.

Name	Symbol	Definition	SI Unit
absolute activity	γ	$\gamma_B = \exp(\mu_B/RT)$	1
absorption coefficient (in gas solubility)	β^*	$\beta_B^* = V^g(T, p_A + p_B = p^\ominus, n_B^1)/V^l(T, p^\ominus, n_A)$	1
activity, relative activity	a_x	$RT \ln a_{x,B} = \mu_B(T, p, x) - \mu_B^\ominus(T, p)$	1
activity coefficient, ref. Henry, amount conc. basis	γ_c	$RT \ln(\gamma_{c,B} c_B/c^\ominus) = RT \ln a_B = \mu_B - \mu_{x,B}^\ominus$ $\mu_{c,B}^\ominus = \lim_{c_B \rightarrow 0} [\mu_B - RT \ln(c_B/c_B^\ominus)]$	1
activity coefficient, ref. Henry, molality basis	γ_m	$RT \ln(\gamma_{m,B} m_B) = RT \ln a_B = \mu_B - \mu_{m,B}^\ominus$ $\mu_{m,B}^\ominus = \lim_{m_B \rightarrow 0} [\mu_B - RT \ln(m_B/m_B^\ominus)]$	1
activity coefficient, ref. Henry, mole fraction basis	γ_x	$RT \ln(\gamma_{x,B} x_B) = RT \ln a_B = \mu_B - \mu_{x,B}^\ominus$ $\mu_{x,B}^\ominus = \lim_{x_B \rightarrow 0} [\mu_B - RT \ln(\gamma_{x,B} x_B)]$	1
activity coefficient, ref. Raoult, mole fraction basis	f	$RT \ln(f_B x_B) = RT \ln a_B = \mu_B - \mu_B^*$ μ_B^* : standard chemical potential of pure B	1
activity coefficient, infinite dilution	f^∞	$\ln f_B^\infty = \lim_{x_B \rightarrow 0} \left(\frac{\mu_B - \mu_B^*}{RT} - \ln x_B \right)$	1
amount concentration	c , [species]	$c_B = [\text{species B}] = n_B/V$	mol m ⁻³
amount of substance	n	(SI base unit)	mol
aquamolality	$m^{(C)}$	$m_B^{(C)} = m_B \bar{M}/M_C$	mol m ⁻³
Bunsen coefficient, pure solvent basis	α^*	$\alpha_B^* = V^g(T^\ominus, p^\ominus, n_B^1)/V^l(T, p^\ominus, n_A)$	1
Bunsen coefficient, solution basis	α	$\alpha_B = V^g(T^\ominus, p^\ominus, n_B^1)/V^l(T, p^\ominus, n_A, n_B^1)$	1
chemical potential	μ	$\mu_B = (\partial G/\partial n_B)_{T,p,n_i \neq n_B}$	J mol ⁻¹
chlorinity	w_{Cl}	(see main entry)	1
compression (compressibility) factor	Z	$Z = pV_m/RT$	1
density, mass density	ρ	$\rho = (\text{total mass})/V$	kg m ⁻³
energy of vaporization, molar	$\Delta_{\text{vap}} E_m$	$\Delta_{\text{vap}} E_m = E_m^g - E_m^l$	J mol ⁻¹
enthalpy, molar	H_m	H/n	J mol ⁻¹
enthalpy, partial molar	H_B	$H_B = (\partial H/\partial n_B)_{T,p,n_i \neq n_B}$	J mol ⁻¹

(continues on next page)

(Continued).

Name	Symbol	Definition	SI Unit
entropy, molar	S_m	S/n	$\text{J K}^{-1} \text{mol}^{-1}$
entropy, partial molar	S_B	$S_B = (\partial S/\partial n_B)_{T,p,n_i \neq n_B}$	$\text{J K}^{-1} \text{mol}^{-1}$
fugacity	f, \tilde{p}_B	$f_B = \lambda_B \lim_{p \rightarrow 0} (p_B/\lambda_B)_T$	1
gas constant	R	$R = 8.314\,472(15)$	$\text{J K}^{-1} \text{mol}^{-1}$
Gibbs energy, molar	G_m	$G_m = H_m - TS_m$	J mol^{-1}
Henry's law constant	k_H	$k_{H,B} = \lim_{x_B \rightarrow 0} (f_B/x_B) = (\partial f_B/\partial x_B)_{x_B \rightarrow 0}$	Pa
ionic strength, molality basis	I_m	$I_m = \frac{1}{2} \sum z_i^2 m_i$	mol kg^{-1}
ionic strength, amount conc. basis	I_c	$I_c = \frac{1}{2} \sum z_i^2 c_i$	mol m^{-3}
Kuenen coefficient, pure solvent basis	S^*	$S_B^* = V_B^g(T^\ominus, p^\ominus, n_B^1)/m^1(T, p^\ominus, n_A)$	$\text{m}^3 \text{kg}^{-1}$
Kuenen coefficient, solution basis	S	$S_B = V_B^g(T^\ominus, p^\ominus, n_B^1)/m^1(T, p^\ominus, n_A, n_B^1)$	$\text{m}^3 \text{kg}^{-1}$
mass	m	(SI base unit)	kg
mass concentration	γ, ρ	$\rho_B = m_B/V$	kg m^{-3}
mass fraction	w	$w_B = m_B/\sum_{i=1}^C m_i$	1
mass ratio	ζ	$\zeta_{A,B} = m_A/m_B$	1
molality	m, b	$m_B = n_B/M_A(n - \sum_B n_B)$	mol kg^{-1}
molar mass	M	$M_A = m_A/n_A$ (= mass/amount)	kg mol^{-1}
molar volume	V_m	$V_m = V/n$	$\text{m}^3 \text{mol}^{-1}$
mole (amount) fraction	x	$x_B = n_B/\sum_{i=1}^C n_i$	1
mole ratio	r	$r_{12} = n_1/n_2$	1
number density of entities, number concentration	C	$C_B = N_B/V$	m^{-3}
number of entities	N		1
number of phases	C		1
osmotic coefficient, mole fraction basis	φ_x	$\varphi_{x,A} = (\mu_A - \mu_A^*)/RT \ln x_A$	1

(continues on next page)

(Continued).

Name	Symbol	Definition	SI Unit
osmotic coefficient, molality basis	φ_m	$\varphi_{m,A} = (\mu_A^* - \mu_A)/RTM_A \sum m_B$	1
Ostwald coefficient, pure solvent basis	L^*	$L_B^* = V_B^g(T, p, n_B^1)/V^l(T, p, n_A)$	1
Ostwald coefficient, solution basis	L	$L_B = V_B^g(T, p, n_B^1)/V^l(T, p, n_A, n_B^1) = c_B^l/c_B^g$	1
Poynting correction	$I_p(p)$	$I_p(p) = \int_{p_A^*}^p \frac{V_B^{\infty 1}}{RT} dp$	1
pressure	p	(normal force)/area	Pa
pressure, partial	p_B	$p_B = y_B p$	Pa
salinity	S	(see entry)	1
solubility	s	composition of saturated solution or mixture	(various)
solubility parameter	δ	$\delta_B = (\Delta_{\text{vap}} E_{m,B}/V_{m,B})^{1/2}$	Pa ^{1/2}
solubility product	K_s	(see entry)	1
solute mole fraction; Jänecke mole fraction	x_s	$x_{s,B} = x_B / \sum_{i=1}^s x_i$	1
solvent mole fraction	x_v	$x_{v,A} = x_A / \sum_{i=s+1}^p x_i$	1
solvent volume fraction	φ_v	$\varphi_{v,A} = \varphi_A / \sum_{i=s+1}^p \varphi_i$	1
stoichiometric number (of a salt)	ν	$\nu = \nu_+ + \nu_-$	1
temperature (Celsius)	θ, t	$\theta/^{\circ}\text{C} = T/\text{K} - 273.15$	$^{\circ}\text{C}$
temperature, thermodynamic	T	(SI base unit)	K
volume	V		m ³
volume, partial molar	V_B	$V_B = (\partial V / \partial n_B)_{T,p,n_i \neq n_B}$	m ³ mol ⁻¹
volume fraction	φ	$\varphi_B = x_B V_{m,B}^* / \sum_{j=1}^C x_j V_{m,j}^*$	1

4.2 Subscripts and superscripts

4.2.1 Subscripts

A	general constituent, usually solvent
B	general constituent
c	critical state
<i>c</i>	concentration basis
<i>i</i>	general constituent
m	molar (divided by amount of substance)
<i>m</i>	molality basis
r	reference, reduced
sln	solution
<i>s</i>	saline solution
trs	transition
vap	vaporization
<i>v</i>	volume
<i>x</i>	mole fraction basis
+, −	positive, negative charge

4.2.2 Superscripts

g	vapor
l	liquid
α, β, γ	labels for phases
*	pure substance
\ominus, \circ	standard state
∞	infinite dilution
+, −	positive, negative charge

4.2.3 Other symbols

Δ	difference
Δ_{α}^{β}	change from phase α to phase β
	indicator of reciprocal salt system
\rightleftharpoons	equilibrium process
+	separator between components in mixture; e.g., Mg + Sn
%	percent
‰	permil