

SOLUBILITY DATA SERIES Volume 24 PROPANE, BUTANE AND 2-METHYLPROPANE



SOLUBILITY DATA SERIES

Editor-in-Chief A. S. KERTES

Volume 24

PROPANE, BUTANE AND 2-METHYLPROPANE

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Volume 24

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FOREWORD

If the knowledge is undigested or simply wrong, more is not better

How to communicate and disseminate numerical data effectively in chemical science and technology has been a problem of serious and growing concern to IUPAC, the International Union of Pure and Applied Chemistry, for the last two decades. The steadily expanding volume of numerical information, the formulation of new interdisciplinary areas in which chemistry is a partner, and the links between these and existing traditional subdisciplines in chemistry, along with an increasing number of users, have been considered as urgent aspects of the information problem in general, and of the numerical data problem in particular.

Among the several numerical data projects initiated and operated by various IUPAC commissions, the Solubility Data Project is probably one of the most ambitious ones. It is concerned with preparing a comprehensive critical compilation of data on solubilities in all physical systems, of gases, liquids and solids. Both the basic and applied branches of almost all scientific disciplines require a knowledge of solubilities as a function of solvent, temperature and pressure. Solubility data are basic to the fundamental understanding of processes relevant to agronomy, biology, chemistry, geology and oceanography, medicine and pharmacology, and metallurgy and materials science. Knowledge of solubility is very frequently of great importance to such diverse practical applications as drug dosage and drug solubility in biological fluids, anesthesiology, corrosion by dissolution of metals, properties of glasses, ceramics, concretes and coatings, phase relations in the formation of minerals and alloys, the deposits of minerals and radioactive fission products from ocean waters, the composition of ground waters, and the requirements of oxygen and other gases in life support systems.

The widespread relevance of solubility data to many branches and disciplines of science, medicine, technology and engineering, and the difficulty of recovering solubility data from the literature, lead to the proliferation of published data in an ever increasing number of scientific and technical primary sources. The sheer volume of data has overcome the capacity of the classical secondary and tertiary services to respond effectively.

While the proportion of secondary services of the review article type is generally increasing due to the rapid growth of all forms of primary literature, the review articles become more limited in scope, more specialized. The disturbing phenomenon is that in some disciplines, certainly in chemistry, authors are reluctant to treat even those limited-in-scope reviews exhaustively. There is a trend to preselect the literature, sometimes under the pretext of reducing it to manageable size. The crucial problem with such preselection — as far as numerical data are concerned — is that there is no indication as to whether the material was excluded by design or by a less than thorough literature search. We are equally concerned that most current secondary sources, critical in character as they may be, give scant attention to numerical data.

On the other hand, tertiary sources - handbooks, reference books and other tabulated and graphical compilations - as they exist today are comprehensive but, as a rule, uncritical. They usually attempt to cover whole disciplines, and thus obviously are superficial in treatment. Since they command a wide market, we believe that their service to the advancement of science is at least questionable. Additionally, the change which is taking place in the generation of new and diversified numerical data, and the rate at which this is done, is not reflected in an increased third-level service. The emergence of new tertiary literature sources does not parallel the shift that has occurred in the primary literature.

With the status of current secondary and tertiary services being as briefly stated above, the innovative approach of the *Solubility Data Project* is that its compilation and critical evaluation work involve consolidation and reprocessing services when both activities are based on intellectual and scholarly reworking of information from primary sources. It comprises compact compilation, rationalization and simplification, and the fitting of isolated numerical data into a critically evaluated general framework.

The Solubility Data Project has developed a mechanism which involves a number of innovations in exploiting the literature fully, and which contains new elements of a more imaginative approach for transfer of reliable information from primary to secondary/tertiary sources. The fundamental trend of the Solubility Data Project is toward integration of secondary and tertiary services with the objective of producing in-depth critical analysis and evaluation which are characteristic to secondary services, in a scope as broad as conventional tertiary services.

Fundamental to the philosophy of the project is the recognition that the basic element of strength is the active participation of career scientists in it. Consolidating primary data, producing a truly critically-evaluated set of numerical data, and synthesizing data in a meaningful relationship are demands considered worthy of the efforts of top scientists. Career scientists, who themselves contribute to science by their involvement in active scientific research, are the backbone of the project. The scholarly work is commissioned to recognized authorities, involving a process of careful selection in the best tradition of IUPAC. This selection in turn is the key to the quality of the output. These top experts are expected to view their specific topics dispassionately, paying equal attention to their own contributions and to those of their peers. They digest literature data into a coherent story by weeding out what is wrong from what is believed to be right. To fulfill this task, the evaluator must cover all relevant open literature. No reference is excluded by design and every effort is made to detect every bit of relevant primary source. Poor quality or wrong data are mentioned and explicitly disqualified as such. In fact, it is only when the reliable data are presented alongside the unreliable data that proper justice can be done. The user is bound to have incomparably more confidence in a succinct evaluative commentary and a comprehensive review with a complete bibliography to both good and poor data.

It is the standard practice that the treatment of any given solute-solvent system consists of two essential parts: I. Critical Evaluation and Recommended Values, and II. Compiled Data Sheets.

The Critical Evaluation part gives the following information:

- (i) a verbal text of evaluation which discusses the numerical solubility information appearing in the primary sources located in the literature. The evaluation text concerns primarily the quality of data after consideration of the purity of the materials and their characterization, the experimental method employed and the uncertainties in control of physical parameters, the reproducibility of the data, the agreement of the worker's results on accepted test systems with standard values, and finally, the fitting of data, with suitable statistical tests, to mathematical functions;
- (ii) a set of recommended numerical data. Whenever possible, the set of recommended data includes weighted average and standard deviations, and a set of smoothing equations derived from the experimental data endorsed by the evaluator;
- (iii) a graphical plot of recommended data.

The Compilation part consists of data sheets of the best experimental data in the primary literature. Generally speaking, such independent data sheets are given only to the best and endorsed data covering the known range of experimental parameters. Data sheets based on primary sources where the data are of a lower precision are given only when no better data are available. Experimental data with a precision poorer than considered acceptable are reproduced in the form of data sheets when they are the only known data for a particular system. Such data are considered to be still suitable for some applications, and their presence in the compilation should alert researchers to areas that need more work.

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The typical data sheet carries the following information:

components - definition of the system - their names, formulas and Chemical Abstracts registry numbers;

- reference to the primary source where the numerical information is (ii) reported. In cases when the primary source is a less common periodical or a report document, published though of limited availability, abstract references are also given;
- experimental variables;
- identification of the compiler; (iv)
- experimental values as they appear in the primary source. Whenever available, the data may be given both in tabular and graphical form. If auxiliary information is available, the experimental data are converted also to SI units by the compiler.

Under the general heading of Auxiliary Information, the essential experimental details are summarized:

- experimental method used for the generation of data; (vi)
- (vii) type of apparatus and procedure employed; (viii) source and purity of materials;
- - (ix) estimated error:
 - (x) references relevant to the generation of experimental data as cited in the primary source.

This new approach to numerical data presentation, formulated at the initiation of the project and perfected as experience has accumulated, has been strongly influenced by the diversity of background of those whom we are We thus deemed it right to supposed to serve. preface evaluation/compilation sheets in each volume with a detailed discussion of the principles of the accurate determination of relevant solubility data and related thermodynamic information.

Finally, the role of education is more than corollary to the efforts we are seeking. The scientific standards advocated here are necessary to strengthen science and technology, and should be regarded as a major effort in the training and formation of the next generation of scientists and engineers. Specifically, we believe that there is going to be an impact of our project on scientific-communication practices. The quality of consolidation adopted by this program offers down-to-earth guidelines, concrete examples which are bound to make primary publication services more responsive than ever before to the needs of users. The self-regulatory message to scientists of the early 1970s to refrain from unnecessary publication has not achieved much. A good fraction of the literature is still cluttered with poor-quality articles. The Weinberg report (in 'Reader in Science Information', ed. J. Sherrod and A. Hodina, Microcard Editions Books, Indian Head, Inc., 1973, p. 292) states that 'admonition to authors to restrain themselves from premature, unnecessary publication can have little effect unless the climate of the entire technical and scholarly community encourages restraint...' We think that projects of this kind translate the climate into operational terms by exerting pressure on authors to avoid submitting low-grade material. The type of our output, we hope, will encourage attention to quality as authors will increasingly realize that their work will not be suited for permanent retrievability unless it meets the standards adopted in this project. It should help to dispel confusion in the minds of many authors of what represents a permanently useful bit of information of an archival value, and what does not.

If we succeed in that aim, even partially, we have then done our share in protecting the scientific community from unwanted and irrelevant, wrong numerical information.

A. S. Kertes

PREFACE

The three gases, propane, butane and 2-methylpropane are rather unusual gases and possess rather unusual solubility characteristics. First of all, at ambient conditions these gases are well below their critical temperatures and, in fact, are closer in temperature to their normal boiling points than they are to their critical temperatures. The normal boiling points, and critical temperatures are respectively: for propane 231, 370 K, for 2-methylpropane 261, 408 K, and for butane 273, 425 K. Secondly, their solubilities are extremely high in non-polar solvents but, in contrast, they are relatively low in highly polar solvents such as water. The term "high solubility" has usually been reserved for solubilities in which the quantity of dissolved gas at a gas partial pressure of 101.325 kPa exceeds about 5 mole percent. In fact, particularly for butane and 2-methylpropane at low temperatures, solubilities in excess of 50 mole percent and even 80 mole percent solute in the saturated solution have been observed. In these cases the solvent becomes the minor component in the saturated solution, and the Ostwald coefficient expressing the solubility may be in the order of 500 volumes of gas to one volume of solvent1.

The solubilities of propane, butane and 2-methylpropane increase dramatically as the temperatures are reduced toward the respective boiling points of the liquefied gases. As a result, the temperature-solubility relation is more complex and is more difficult to represent mathematically than for most other gases. Further, as for vapor-liquid equilibria, the composition corresponding to pure gas is an extension of the solubility relation1. That is, if solubility experiments are performed at a constant total pressure of 101.325 kPa, then as the temperature is reduced toward the normal boiling point, the compositions of both the gas and liquid phases approach that of the pure gas. Thus the normal boiling point, corresponding to the composition of the pure liquefied gas can be considered as one point on the solubility curve for that particular gas in all solvents, provided that the solvents still exist as miscible liquids at the temperatures concerned. It is apparent that gas solubilities at 101.325 kPa cannot be measured for those solvents whose freezing point temperatures are higher than the normal boiling points of the liquefied gases.

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For the treatment of solubility data corresponding to a gas partial pressure of 101.325 kPa, true gas molar volumes are required. Particularly for butane and 2-methylpropane, the deviation from ideality is as high as 5 percent. To aid in the work of reviewing solubility data, the second virial coefficients for the three gases as obtained from Dymond and Smith² were fitted by simple exponential functions and found to describe that data well. In the truncated form, the virial equation of state is:

$$PV / (RT) = 1 + B/V$$
 (1)

The equation which may be used to successfully correlate virial coefficient data for many gases and vapors has the following form:

$$B = a T^b$$
 (2)

When Equation (1) is used in estimating the gas molar volume, a quadratic equation for molar volume results:

$$V = C/2 + 0.5 (C^2 + 4BC)^{0.5}$$
 (3)

$$C = RT/P \tag{4}$$

The resulting constants for the three cases for use in Equation (2), the percentage deviations in B and V, as well as the temperature ranges for which the equations apply, are shown in Table 1. Whereas the maximum deviation in B is 2.9 percent, the maximum deviation of the molar volume is 0.11 percent. It is noted that the correlation for the virial coefficients breaks down near the Boyle temperature and is useful only in the temperature range in which the second virial coefficients are negative. There are two advantages in using the above correlation for the second virial coefficients: interpolation to any arbitrary temperature is simplified, and the equation for the second virial coefficients can be easily incorporated in a computational sequence whereas tabulated information cannot.

A consistency check of the solubility data for high pressures was devised. It involves plotting the mole fraction solubility versus the partial pressure of solute on log scales. On such a graph the solubility - partial pressure relation is often nearly linear; a slope of unity is obtained if Henry's law is obeyed. Solubilities obtained at high pressures can be extrapolated to atmospheric pressure so that a comparison with solubilities actually measured at atmospheric pressure can be readily made. Equally useful is an extrapolation of solubility data obtained at one temperature to the higher pressure corresponding to the vapor pressure of pure liquefied solute gas. Interpolation between solubility isotherms

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Table 1: Calculation of Second Virial

Coefficients and Gas Molar Volumes

For	Propage.	B	=	-1 246	(108)	m-2.224	cm ³ /mole
roi	Propane:	D	-	-1.240	(TO)	1	cm / more

/K	B(ref.2)	B(calc.)	B, % Diff.	V(ref.2)	V(calc.)	V, % Diff.
240	-640	-634	1.0	19032	19039	0.04
300	-382	-386	1.0	24230	24226	0.02
350	-276	-274	0.8	28442	28444	0.01
400	-208	-203	2.2	32615	32619	0.01
500	-124	-123	0.1	40906	40906	-
550	- 97	-100	3.3	45036	45033	0.01

For Butane: $B = -7.985 (10^8) T^{-2.436} cm^3/mole$

250	-1170	-1151	1.7	19269	19269	0.11
300	-722	-738	2.2	23874	23857	0.07
360	-472	-473	0.3	29062	29061	-
400	-370	-366	1.0	32450	32454	0.1
500	-219	-213	2.9	40810	40816	0.02
560	-164	-161	1.6	45789	45792	0.01

For 2-Methylpropane: $B = -1.403 (10^9) T^{-2.542} cm^3/mole$

273.2	-900	-899	0.1	21475	21476	-
303.2	-687	-690	0.4	24170	24167	0.01
360.9	-441	-443	0.4	29170	29168	-
406.9	-326	-326	_	33058	33058	-
477.6	-218	-217	0.4	38973	38973	=
510.9	-184	-183	0.5	41740	41741	-

Gas molar volume, V, in $cm^3/mole$.

Gas constant taken as: $R = 82.06 \text{ cm}^3 \text{ atm/(mole K)}$

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also appears possible with reasonable accuracy. Refer to the section "Alkane solvents at high pressure" for an example of the solubility-pressure diagram based on data reported by Reamer and Sage³ for the solubility of propane in decane.

When solubility data at 101.325 kPa pressure were available over a temperature range, the solubility was usually expressed as a function of temperature using an equation having one of the following forms:

$$\ln x_1 = a + b / (T/K) \tag{5}$$

$$\ln x_1 = a + b \ln (T/K) \tag{6}$$

$$\ln x_1 = a + b / (T/K) + c \ln (T/K)$$
 (7)

The constants for the equations were determined by means of a regression analysis; then one of the equations was chosen on the basis of its being the best representation of the particular data. Smoothed values for mole fraction solubility as shown in some of the compiled sheets were obtained by means of the regression equation and may not be accurately extrapolated beyond the temperature range of the data on which the equation is based.

It is readily apparent from an examination of the pages of this volume, that in only a very few instances are data available indicating within narrow limits the solubility of any of the gases in a particular solvent. In many instances there is a wide discrepancy between data from two or more sources. In many other instances data are simply not available to draw any general conclusions. Perhaps a useful function of this compilation is to draw attention to the real shortage of accurate solubility data for propane, butane and 2-methylpropane in most solvents.

To permit maximum use of data as they become available, it is recommended that authors include an analysis of both the gas and liquid phases in future publications for solubilities of highly soluble gases. The vapor pressure of a volatile solvent containing a significant quantity of dissolved gas cannot usually be accurately determined by simple calculation. Nor can the true molar volume of gas saturated with solvent vapor be accurately calculated without auxiliary information. Finally, Henry's law cannot generally be expected to apply with good accuracy for gas solubilities as high as those for propane, butane and 2-methylpropane. If for any reason it is not possible to measure phase compositions, the raw data, at the actual conditions of measurement, should be included to permit useful comparisons by other workers who may be able to correct the

data for phase non-idealities at a later date. When only the results, extrapolated to a gas partial pressure of 101.325 kPa, are reported, it becomes impossible to make any subsequent corrections to the data. The gas molar volumes and solvent vapor pressures and densities that were used in the calculations would also be most helpful.

As may also be apparent, there is a considerable delay between the time that data from the technical literature are initially compiled and subsequently evaluated, and the time the volume is published in its final form. Hence, some data appearing in the very recent literature have not been included in this volume. Included in this volume are data appearing in the technical literature to the end of 1983. It has not been possible to process data from some few papers which contain solubilities of propane, butane or 2-methylpropane gases appearing in 1984.

The contributions and assistance of Professors R. Battino, H.L. Clever and C.L. Young as Compilers and/or Evaluators as well as collaborators is most gratefully acknowledged. The assistance of compilers, Dr. E. S. Thomsen and Dr. E.S. Rudakov is also acknowledged. The support of the IUPAC Commission on Solubility Data is most appreciated; without their initiative, guidance, and continued encouragement this volume would not have been possible. The painstaking assistance of Dr. B.S. Minhas and Mr. C.-F. Wong and typists C. Lachaine and A. Mainville is also acknowledged and much appreciated.

Walter Hayduk

Ottawa, Canada December, 1984

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THE SOLUBILITY OF GASES IN LIQUIDS

Introductory Information

C. L. Young, R. Battino, and H. L. Clever

INTRODUCTION

The Solubility Data Project aims to make a comprehensive search of the literature for data on the solubility of gases, liquids and solids in liquids. Data of suitable accuracy are compiled into data sheets set out in a uniform format. The data for each system are evaluated and where data of sufficient accuracy are available values are recommended and in some cases a smoothing equation is given to represent the variation of solubility with pressure and/or temperature. A text giving an evaluation and recommended values and the compiled data sheets are published on consecutive pages. The following paper by E. Wilhelm gives a rigorous thermodynamic treatment on the solubility of gases in liquids.

DEFINITION OF GAS SOLUBILITY

The distinction between vapor-liquid equilibria and the solubility of gases in liquids is arbitrary. It is generally accepted that the equilibrium set up at 300K between a typical gas such as argon and a liquid such as water is gas-liquid solubility whereas the equilibrium set up between hexane and cyclohexane at 350K is an example of vapor-liquid equilibrium. However, the distinction between gas-liquid solubility and vapor-liquid equilibrium is often not so clear. The equilibria set up between methane and propane above the critical temperature of methane and below the critical temperature of propane may be classed as vapor-liquid equilibrium or as gas-liquid solubility depending on the particular range of pressure considered and the particular worker concerned.

The difficulty partly stems from our inability to rigorously distinguish between a gas, a vapor, and a liquid; a subject which has been discussed in numerous textbooks. We have taken a fairly liberal view in these volumes and have included systems which may be regarded, by some workers, as vapor-liquid equilibria.

UNITS AND QUANTITIES

The solubility of gases in liquids is of interest to a wide range of scientific and technological disciplines and not solely to chemistry. Therefore a variety of ways for reporting gas solubility have been used in the primary literature. Sometimes, because of insufficient available information, it has been necessary to use several quantities in the compiled tables. Where possible, the gas solubility has been quoted as a mole fraction of the gaseous component in the liquid phase. The units of pressure used are bar, pascal, millimeters of mercury, and atmosphere. Temperatures are reported in Kelvins.

EVALUATION AND COMPILATION

The solubility of comparatively few systems is known with sufficient accuracy to enable a set of recommended values to be presented. This is true both of the measurements near atmospheric pressure and at high pressures. Although a considerable number of systems have been studied by at least two workers, the range of pressures and/or temperatures is often sufficiently different to make meaningful comparison impossible.

Occasionally, it is not clear why two groups of workers obtained very different sets of results at the same temperature and pressure, although both sets of results were obtained by reliable methods and are internally consistent. In such cases, sometimes an incorrect assessment has been given. There are several examples where two or more sets of data have been classified as tentative although the sets are mutually inconsistent.

Many high pressure solubility data have been published in a smoothed form. Such data are particularly difficult to evaluate, and unless specifically discussed by the authors, the estimated error on such values can only be regarded as an "informed guess".

Many of the high pressure solubility data have been obtained in a more general study of high pressure vapor-liquid equilibrium. In such cases a note is included to indicate that additional vapor-liquid equilibrium data are given in the source. Since the evaluation is for the compiled data, it is possible that the solubility data are given a classification which is better than that which would be given for the complete vapor-liquid data (or vice versa). For example, it is difficult to determine coexisting liquid and vapor compositions near the critical point of a mixture using some widely used experimental techniques which yield accurate high pressure solubility data. As another example, conventional methods of analysis may give results with an expected error which would be regarded as sufficiently small for vapor-liquid equilibrium data but an order of magnitude too large for acceptable high pressure gas-liquid solubility.

It is occasionally possible to evaluate data on mixtures of a given substance with a member of a homologous series by considering all the available data for the given substance with other members of the homologous series. In this study the use of such a technique has been limited.

The estimated error is often omitted in the original article and sometimes the errors quoted do not cover all the variables. In order to increase the usefulness of the compiled tables estimated errors have been included even when absent from the original article. If the error on any variable has been inserted by the compiler, this has been noted.

PURITY OF MATERIALS

The purity of materials has been quoted in the compiled tables where given in the original publication. The solubility is usually more sensitive to impurities in the gaseous component than to liquid impurities in the liquid component. However, the most important impurities are traces of a gas dissolved in the liquid. Inadequate degassing of the absorbing liquid is probably the most often overlooked serious source of error in gas solubility measurements.

APPARATUS AND PROCEDURES

In the compiled tables brief mention is made of the apparatus and procedure. There are several reviews on experimental methods of determining gas solubilities and these are given in References 1-7.

METHODS OF EXPRESSING GAS SOLUBILITIES

Because gas solubilities are important for many different scientific and engineering problems, they have been expressed in a great many ways:

The Mole Fraction, x(g)

The mole fraction solubility for a binary system is given by:

$$x(g) = \frac{n(g)}{n(g) + n(1)}$$

$$= \frac{W(g)/M(g)}{\{W(g)/M(g)\} + \{W(1)/M(1)\}}$$

here n is the number of moles of a substance (an amount of substance), W is the mass of a substance, and M is the molecular mass. To be unambiguous, the partial pressure of the gas (or the total pressure) and the temperature of measurement must be specified.

The Weight Per Cent Solubility, wt%

For a binary system this is given by

$$wt% = 100 W(g)/{W(g) + W(1)}$$

where W is the weight of substance. As in the case of mole fraction, the pressure (partial or total) and the temperature must be specified. The weight per cent solubility is related to the mole fraction solubility by

$$x(g) = \frac{\{wt\%/M(g)\}}{\{wt\%/M(g)\} + \{(100 - wt\%)/M(1)\}}$$

The Weight Solubility, $C_{\overline{W}}$

The weight solubility is the number of moles of dissolved gas per gram of solvent when the partial pressure of gas is 1 atmosphere. The weight solubility is related to the mole fraction solubility at one atmosphere partial pressure by

ial pressure by
$$x(g) \text{ (partial pressure 1 atm)} = \frac{C_w M(1)}{1 + C_w M(1)}$$

where M(1) is the molecular weight of the solvent.

The Moles Per Unit Volume Solubility, n

Often for multicomponent systems the density of the liquid mixture is not known and the solubility is quoted as moles of gas per unit volume of liquid mixture. This is related to the mole fraction solubility by

$$x(g) = \frac{n v^{O}(1)}{1 + n v^{O}(1)}$$

where $v^{\text{O}}(1)$ is the molar volume of the liquid component.

The Bunsen Coefficient, α

The Bunsen coefficient is defined as the volume of gas reduced to 273.15K and 1 atmosphere pressure which is absorbed by unit volume of solvent (at the temperature of measurement) under a partial pressure of 1 atmosphere. If ideal gas behavior and Henry's law are assumed to be obeyed, then

$$\alpha = \frac{V(g)}{V(1)} \quad \frac{273.15}{T}$$

where V(g) is the volume of gas absorbed and V(1) is the original (starting) volume of absorbing solvent. The mole fraction solubility x is related to the Bunsen coefficient by

$$x(g, 1 \text{ atm}) = \frac{\alpha}{\alpha + \frac{273.15}{T} \frac{v^{\circ}(g)}{v^{\circ}(1)}}$$

where $v^{O}(g)$ and $v^{O}(1)$ are the molar volumes of gas and solvent at a pressure of one atmosphere. If the gas is ideal,

$$x(g) = \frac{\alpha}{\alpha + \frac{273.15R}{v^{0}(1)}}$$

Real gases do not follow the ideal gas law and it is important to establish the real gas law used for calculating α in the original publication and to make the necessary adjustments when calculating the mole fraction solubility.

The Kuenen Coefficient, S

This is the volume of gas, reduced to 273.15K and 1 atmosphere pressure, dissolved at a partial pressure of gas of 1 atmosphere by 1 gram of solvent.