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Volume 9
ETHANE

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ETHANE

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INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION
COMMISSION ON SOLUBILITY DATA

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Volume 9

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Volumes in preparation

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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, thus obviously are superficial in treatment. Since they command a wide market, we believe that their service to 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 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.

The typical data sheet carries the following information:
(i) components - definition of the system - their names, formulas and Chemical Abstracts registry numbers;
(ii) reference to the primary source where the numerical information is 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;
(iii) experimental variables;
(iv) identification of the compiler;
(v) 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:

(vi) experimental method used for the generation of data;

(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, developed during our four years of existence, has been strongly influenced by the diversity of background of those whom we are supposed to serve. We thus deemed it right to preface the 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 15 years ago to refrain from unnecessary publication has not achieved much. The literature is still, in 1982, cluttered with poor-quality articles. The Weinberg report (in "Reader in Science Information", Eds. 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 data compiled in this volume for the solubility of ethane in liquids represent the result of an exhaustive literature search. The compilations and evaluations were made with great care in the interest of usefulness and accuracy. It is impossible however, to make this type of compilation both complete and fault-free. Readers and users of this volume are therefore kindly requested to bring to the attention of the Editor any errors or omissions they may find.

It is not possible to claim even for a single solvent, and definitely not for any class of solvents, that there are sufficient data of accuracy to a fraction of a percent so that further experimentation is no longer required, except perhaps for the solubility of ethane in water at atmospheric pressure and at low temperature. In all other cases data are too few and of accuracy too low, for many modern applications. Much of the data in this volume has been classified as *tentative* often only because comparable data have been lacking. When comparable data were available, differences frequently exceeded 2%. We may conclude that there is a need for more, as well as more accurate, solubility data.

The accuracy of solubility data is often limited by the ingenuity of the researcher in the design and construction of the solubility apparatus and the care during its operation. Almost as frequently the accuracy is further limited by the choice of basic data used to calculate the solubility, such as the gas molar volume, partial pressure and partial molal volume in solution in some cases, as well as the solvent or solution density and vapor pressure. In some instances compilers and evaluators have had to guess which data were used by the authors in their calculation of solubility. I wish to make a plea for inclusion of all the actual pertinent data used in the calculation of the gas solubility in all future publications.

Ethane behaves essentially as an ideal gas with deviations from ideality diminishing from approximately 1.0% at 273.15 K to 0.3% at 400 K (1,2,3). In most cases in this volume, the mole fraction

solubility was calculated on the basis of ethane being a perfect
gas. A notable exception is the solubility in water where the real
gas molar volumes were used. For essentially all the remaining data,
ideal ethane molar volumes were used in the conversion of solubilities
expressed in volumetric units to those expressed as mole fractions.
For correcting the solubilities for the non-ideality of ethane, molar
volumes may be obtained from the following equation utilizing the
compressibility factor, Z:

$$PV = Z\,R\,T$$

Suggested values of Z as a function of temperature (for atmospheric
pressure) as calculated from the second virial coefficients obtained
from the recent compilation by Dymond and Smith (3) are:

T/K	Z	T/K	Z
260	0.9886	300	0.9926
273.15	0.9901	325	0.9942
280	0.9908	350	0.9955
298.15	0.9925	400	0.9971

In general, the mole fraction solubility is increased as a result
of a correction for gas phase non-ideality.

Solvent or solution densities were frequently required for the
calculation of solubilities but were not usually available from the
original solubility papers. These density data were obtained from
various literature sources as required (4,5,6,7,8,9) or estimated by
comparison with those for homologous compounds or solutions.

The temperature coefficient of solubility at constant pressure
for most solvents was expressed as a linear function of the log of
the mole fraction solubility and the inverse of the absolute tempe-
rature. A regression line was used as a basis for the smoothed values
shown in the compiled sheets. Except for the solubility in water
for which a more complex function was used, the simple function was
sufficient to accurately represent the effect of temperature.

The contribution and assistance of Professors R. Battino, H.L.
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most gratefully acknowledged. The assistance of several other

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also acknowledged and much appreciated.

Walter Hayduk

Ottawa, Canada

May, 1982

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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 criti-
cal 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 scien-
tific and technological disciplines and not solely to chemistry. Therefore
a variety of ways for reporting gas solubility have been used in the pri-
mary 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 accur-
acy 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 suffi-
ciently 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 clas-
sified 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:

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

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

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

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

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

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

The Weight Solubility, C_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

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

where M(l) 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

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

where $v^o(l)$ 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

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

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

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

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

$$x(g) = \frac{\alpha}{\alpha + \dfrac{273.15R}{v^o(l)}}$$

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.

The Ostwald Coefficient, L

The Ostwald coefficient, L, is defined as the ratio of the volume of gas absorbed to the volume of the absorbing liquid, all measured at the same temperature:

$$L = \frac{V(g)}{V(l)}$$

If the gas is ideal and Henry's Law is applicable, the Ostwald coefficient is independent of the partial pressure of the gas. It is necessary, in practice, to state the temperature and total pressure for which the Ostwald coefficient is measured. The mole fraction solubility, x(g), is related to the Ostwald coefficient by

$$x(g) = \left[\frac{RT}{P(g) \ L \ v^O(l)} + 1 \right]^{-1}$$

where P is the partial pressure of gas. The mole fraction solubility will be at a partial pressure of P(g). (See the following paper by E. Wilhelm for a more igorous definition of the Ostwald coefficient.)

The Absorption Coefficient, β

There are several "absorption coefficients", the most commonly used one being defined as the volume of gas, reduced to 273.15K and 1 atmosphere, absorbed per unit volume of liquid when the total pressure is 1 atmosphere. β is related to the Bunsen coefficient by

$$\beta = \alpha(1 - P(l))$$

where P(l) is the partial pressure of the liquid in atmospheres.

The Henry's Law Constant

A generally used formulation of Henry's Law may be expressed as

$$P(g) = K_H x(g)$$

where K_H is the Henry's Law constant and x(g) the mole fraction solubility. Other formulations are

$$P(g) = K_2 C(l) \qquad \text{or} \qquad C(g) = K_c C(l)$$

where K_2 and K_c are constants, C the concentration, and (l) and (g) refer to the liquid and gas phases. Unfortunately, K_H, K_2 and K_c are all sometimes referred to as Henry's Law constants. Henry's Law is a *limiting law* but can sometimes be used for converting solubility data from the experimental pressure to a partial gas pressure of 1 atmosphere, provided the mole fraction of the gas in the liquid is small, and that the difference in pressures is small. Great caution must be exercised in using Henry's Law.

The Mole Ratio, N

The mole ratio, N, is defined by

$$N = n(g)/n(l)$$

Table 1 contains a presentation of the most commonly used inter-conversions not already discussed.

For gas solubilities greater than about 0.01 mole fraciton at a partial pressure of 1 atmosphere there are several additional factors which must be taken into account to unambiguously report gas solubilities. Solution densities or the partial molar volume of gases must be known. Corrections should be made for the possible non-ideality of the gas or the non-applicability of Henry's Law.

TABLE 1   Interconversion of parameters used for reporting solubility

$$L = \alpha(T/273.15)$$

$$C_w = \alpha/v_o\rho$$

$$K_H = \frac{17.033 \times 10^6 \rho(soln)}{\alpha\, M(l)} + 760$$

$$L = C_w\, v_{t,gas}\, \rho$$

where v_o is the molal volume of the gas in $cm^3 mol^{-1}$ at 0°C, ρ the density of the solvent at the temperature of the measurement, ρ_{soln} the density of the solution at the temperature of the measurement, and $v_{t,gas}$ the molal volume of the gas ($cm^3 mol^{-1}$) at the temperature of the measurement.

SALT EFFECTS

Salt effect studies have been carried out for many years. The results are often reported as Sechenov (Setchenow) salt effect parameters. There appears to be no common agreement on the units of either the gas solubility, or the electrolyte concentration.

Many of the older papers report the salt effect parameter in a form equivalent to

$$k_{scc}/mol\ dm^{-3} = (1/(c_2/mol\ dm^{-3}))\ log\ ((c_1^o/mol\ dm^{-3})/(c_1/mol\ dm^{-3}))$$

where the molar gas solubility ratio, c_1^o/c_1, is identical to the Bunsen coefficient ratio, α^o/α, or the Ostwald coefficient ratio, L^o/L. One can designate the salt effect parameters calculated from the three gas solubility ratios as k_{scc}, $k_{sc\alpha}$, k_{scL}, respectively, but they are identical, and $k_{scc}/dm^3\ mol^{-1}$ describes all of them. The superzero refers to the solubility in the pure solvent.

Recent statistical mechanical theories favor a molal measure of the electrolyte and gas solubility. Some of the more recent salt effects are reported in the form

$$k_{smm}/kg\ mol^{-1} = (1/(m_2/mol\ kg^{-1}))\ log\ ((m_1^o/mol\ kg^{-1})/(m_1/mol\ kg^{-1}))$$

In this equation the m_1^o/m_1 ratio is identical to the Kuenen coefficient ratio, δ_1^o/δ_1, or the solvomolality ratio referenced to water, $A_{\delta m}^o/A_{\delta m}$. Thus the salt effect parameters k_{smm}, k_{sms}, and $k_{smA_{\delta m}}$ are well represented by the $k_{smm}/kg\ mol^{-1}$.

Some experimentalists and theoreticians prefer the gas solubility ratio as a mole fraction ratio, x_1^o/x_1. It appears that most calculate the mole fraction on the basis of the total number of ions. The salt effect parameters

$$k_{scx}/dm^3\ mol^{-1} = (1/(c_2/mol\ dm^{-3}))\ log\ (x_1^o/x_1)$$

and

$$k_{smx}/kg\ mol^{-1} = (1/(m_2/mol\ kg^{-1}))\ log\ (x_1^o/x_1)$$

are both in the literature, but k_{scx} appears to be the more common.