

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:

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

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

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

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

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

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

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

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

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,

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

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 rigorous 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

$$P(g) = K_2 C(l) \quad \text{or} \quad C(g) = K_C C(l)$$

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 fraction 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

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

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

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

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

where v_o is the molal volume of the gas in $\text{cm}^3 \text{mol}^{-1}$ 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 $v_{t,\text{gas}}$ the molal volume of the gas ($\text{cm}^3 \text{mol}^{-1}$) 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

$$k_{\text{SCC}}/\text{mol dm}^{-3} = (1/(c_2/\text{mol dm}^{-3})) \log ((c_1^0/\text{mol dm}^{-3})/(c_1/\text{mol dm}^{-3}))$$

where the molar gas solubility ratio, c_1^0/c_1 , is identical to the Bunsen coefficient ratio, α^0/α , or the Ostwald coefficient ratio, L^0/L . One can designate the salt effect parameters calculated from the three gas solubility ratios as k_{SCC} , $k_{\text{SC}\alpha}$, k_{scL} , respectively, but they are identical, and $k_{\text{SCC}}/\text{dm}^3 \text{mol}^{-1}$ 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

$$k_{\text{Smm}}/\text{kg mol}^{-1} = (1/(m_2/\text{mol kg}^{-1})) \log ((m_1^0/\text{mol kg}^{-1})/(m_1/\text{mol kg}^{-1}))$$

In this equation the m_1^0/m_1 ratio is identical to the Kuenen coefficient ratio, δ_1^0/δ_1 , or the solvomolality ratio referenced to water, $A_{\delta m}^0/A_{\delta m}$. Thus the salt effect parameters k_{Smm} , k_{Sms} , and $k_{\text{sm}A_{\delta m}}$ are well represented by the $k_{\text{Smm}}/\text{kg mol}^{-1}$.

Some experimentalists and theoreticians prefer the gas solubility ratio as a mole fraction ratio, x_1^0/x_1 . It appears that most calculate the mole fraction on the basis of the total number of ions. The salt effect parameters

$$k_{\text{scx}}/\text{dm}^3 \text{mol}^{-1} = (1/(c_2/\text{mol dm}^{-3})) \log (x_1^0/x_1)$$

and

$$k_{\text{smx}}/\text{kg mol}^{-1} = (1/(m_2/\text{mol kg}^{-1})) \log (x_1^0/x_1)$$

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

The following conversions were worked out among the various forms of the salt effect parameter from standard definitions of molarity, molality, and mole fraction assuming the gas solubilities are small.

$$k_{\text{smc}} = (c_2/m_2) k_{\text{scc}} = (c_2/m_2) k_{\text{sccm}} + F_{1m}$$

$$k_{\text{sccm}} = k_{\text{scc}} - F_{1c} = (m_2/c_2) k_{\text{smc}} - F_{1c} = (m_2/c_2) k_{\text{smm}}$$

$$k_{\text{scx}} = (m_2/c_2) k_{\text{smx}} = (m_2/c_2) k_{\text{smm}} + F_{2c}$$

$$k_{\text{smm}} = k_{\text{smx}} - F_{2m} = (c_2/m_2) k_{\text{scx}} - F_{2m}$$

$$k_{\text{smx}} = (c_2/m_2) k_{\text{scx}} = (c_2/m_2) k_{\text{scc}} + F_{3m}$$

$$k_{\text{scc}} = k_{\text{scx}} - F_{3c} = (m_2/c_2) k_{\text{smx}} - F_{3c}$$

where

$$F_{1m} = (1/m_2) \log [(\rho^\circ/\rho) (1000 + m_2 M_2)/1000]$$

$$F_{1c} = (m_2/c_2) F_{1m}$$

$$F_{2m} = (1/m_2) \log [(1000 + \nu m_3 M_3)/1000]$$

$$F_{2c} = (m_2/c_2) F_{2m}$$

$$F_{3m} = (1/m_2) \log [(1000\rho + (\nu M_3 - M_2) c_2)/1000\rho^\circ]$$

$$F_{3c} = (m_2/c_2) F_{3m}$$

The factors F_{1m} , F_{1c} , F_{2m} , F_{2c} , F_{3m} , and F_{3c} can easily be calculated from aqueous electrolyte data such as weight per cent and density as found in Volume III of the International Critical Tables. The values are small and change nearly linearly with both temperature and molality. The factors normally amount to no more than 10 to 20 per cent of the value of the salt effect parameter.

The symbols in the equations above are defined below:

| Component | Molar Concentration $c/\text{mol dm}^{-3}$ | Molal Concentration $m/\text{mol kg}^{-1}$ | Mole Fraction x | Molecular Weight $M/\text{g mol}^{-1}$ |
|----------------|--|--|-------------------------|--|
| Nonelectrolyte | c_1°, c_1 | m_1°, m_1 | x_1°, x_1 | M_1 |
| Electrolyte | c_2 | m_2 | x_2 | M_2 |
| Solvent | c_3 | m_3 | x_3 | M_3 |

The superscript "°" refers to the nonelectrolyte solubility in the pure solvent. The pure solvent and solution densities are $\rho^\circ/\text{g cm}^{-3}$ and $\rho/\text{g cm}^{-3}$, respectively. They should be the densities of gas saturated solvent (water) and salt solution, but the gas free densities will differ negligibly in the ρ°/ρ ratio. The number of ions per formula of electrolyte is symbolized by ν .

The following table gives estimated errors in k_{scc} for various salt concentrations and a range of random errors in the gas solubility measurement

| $c_2/\text{mol dm}^{-3}$ | Error in $k_{\text{scc}}/\text{dm}^3 \text{mol}^{-1}$ ^a | | | | |
|--------------------------|--|-------|-------|-------|--------|
| | Random Error in gas solubility Measurement | | | | |
| | ±2% | ±1% | ±0.5% | ±0.1% | ±0.05% |
| 1 | ±18% | ±9% | ±5% | ±1.5% | ±1% |
| 0.1 | ±175% | ±87% | ±43% | ±9% | ±4% |
| 0.05 | ±350% | ±174% | ±87% | ±17% | ±9% |
| 0.01 | ±1750% | ±870% | ±435% | ±87% | ±43% |

^a Based on a k_{scc} value of 0.100.

AQUAMOLAL OR SOLVOMOLAL, $A_{\Delta m}$ or $m_i^{(\Delta)}$

The term aquamolal was suggested by R. E. Kerwin (9). The unit was first used in connection with D₂O and H₂O + D₂O mixtures. It has since been extended in use to other solvents. The unit represents the numbers of moles of solute per 55.51 moles of solvent. It is represented by

$m_i^{(\Delta)}/\text{mol kg}^{-1} = (n_i M_2/w_2)(w_2/M_0) = m_i(M_2/M_0)$ where an amount of n_i of solute i is dissolved in a mass w_2 of solvent of molar mass M_2 ; M_0 is the molar mass of a reference solvent and $m_i/\text{mol kg}^{-1}$ is the conventional molality in the reference solvent. The reference solvent is normally water.

TEMPERATURE DEPENDENCE OF GAS SOLUBILITY

In a few cases it has been found possible to fit the mole fraction solubility at various temperatures using an equation of the form

$$\ln x = A + B / (T/100K) + C \ln (T/100K) + DT/100K$$

It is then possible to write the thermodynamic functions $\Delta\bar{G}_1^\circ$, $\Delta\bar{H}_1^\circ$, $\Delta\bar{S}_1^\circ$ and $\Delta\bar{C}_{P1}^\circ$ for the transfer of the gas from the vapor phase at

101,325 Pa partial pressure to the (hypothetical) solution phase of unit mole fraction as:

$$\Delta\bar{G}_1^\circ = -RT - 100 RB - RCT \ln (T/100) - RDT^2/100$$

$$\Delta\bar{S}_1^\circ = RA + RC \ln (T/100) + RC + 2 RDT/100$$

$$\Delta\bar{H}_1^\circ = -100 RB + RCT + RDT^2/100$$

$$\Delta\bar{C}_{P1}^\circ = RC + 2 RDT/100$$

In cases where there are solubilities at only a few temperatures it is convenient to use the simpler equations

$$\Delta\bar{G}_1^\circ = -RT \ln x = A + BT$$

in which case $A = \Delta\bar{H}_1^\circ$ and $-B = \Delta\bar{S}_1^\circ$

REFERENCES

1. Battino, R.; Clever, H. L. *Chem. Rev.* 1966, *66*, 395.
2. Clever, H. L.; Battino, R. in *Solutions and Solubilities*, Ed. M. R. J. Dack, J. Wiley & Sons, New York, 1975, Chapter 7.
3. Hildebrand, J. H.; Prausnitz, J. M.; Scott, R. L. *Regular and related Solutions*, Van Nostrand Reinhold, New York, 1970, Chapter 8.
4. Markham, A. E.; Kobe, K. A. *Chem. Rev.* 1941, *63*, 449.
5. Wilhelm, E.; Battino, R. *Chem. Rev.* 1973, *73*, 1.
6. Wilhelm, E.; Battino, R.; Wilcock, R. J. *Chem. Rev.* 1977, *77*, 219.
7. Kertes, A. S.; Levy, C.; Markovits, G. Y. in *Experimental Thermochemistry* Vol. II, Ed. B. Vodar and B. LeNaindre, Butterworth, London, 1974, Chapter 15.
8. Long, F. A.; McDevit, W. F. *Chem. Rev.* 1952, *51*, 119.
9. Kerwin, K. E., Ph.D. Thesis, University of Pittsburgh 1964.

Revised: April 1982 (F.B., H.I.C.)