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Invited Review

Some Aspects of the Solubility of Gases in Liquids

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Summary. *Henry*'s law constants may usually be used to calculate solubilities of gases at low pressures. If experimental measurements are unavailable values of *Henry*'s law constants may be estimated by various methods. Several of these methods depend upon quantitative structure-property relationships. A method developed by *Hine* and *Mookerjee* depends on the assumption that each bond of a particular type makes approximately the same contribution to the molar free energy change when different organic gases are dissolved in water. The solubility of gases and also the rate at which gases dissolve in cloud droplets is important for the understanding of processes which occur in the atmosphere. A simple model for the uptake of gases by water is based on an analogy with the behaviour of an electric circuit containing resistances in series and in parallel. This model is important for the interpretation of experimental measurements of rates of gas uptake.

Keywords. Ecology; Semiempirical calculations; Thermodynamics; *Henry*'s law; Atmosphere.

Introduction

The IUPAC Solubility Data Commission was established in 1979 to compile and evaluate solubility data in all media for gases, liquids, and solids. The data obtained are published as volumes in the IUPAC Solubility Data Series. At the present time 77 volumes have been published of which 21 are volumes containing data for gases. Early volumes were published by Pergamon Press and later volumes by Oxford University Press. The most recent volumes have been published in the *Journal of Physical and Chemical Reference Data*. *Professor H. Gamsjäger* has served as a very competent Secretary of this Commission since 1996.

The solubility of a gas depends on its partial pressure and on the temperature as well as on the nature of the liquid phase. For most gas–liquid systems there tends to

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Dedicated to Prof. *Heinz Gamsjäger*

be a linear variation of solubility with partial pressure as the partial pressure approaches zero. The limiting ratio of pressure to solubility or the ratio of solubility to pressure is the *Henry*'s law constant. The constant can also be expressed as the ratio of molar concentrations in the liquid and gas phase. For many purposes the relationship can also be taken to be linear at low finite partial pressures. *Henry*'s law constants can therefore be used to calculate solubilities at low partial pressures. Solubility at a constant partial pressure may either decrease or increase with increase in temperature. The mole fraction solubilities in water at constant partial pressure of some gases have been found to pass through minima with increase in temperature. The minimum for the solubility of nitrogen in water occurs at about 370 K at a partial pressure of nitrogen of 1.013 bar. The minimum for hydrogen is at about 327 K and that for hydrogen sulfide is at about 450 K [1]. In this paper no differentiation is made between gases and species which are often referred to as vapours.

Prediction of the Solubility of Gases

Despite the inclusion of the solubilities of a wide range of gases in volumes of IUPAC Solubility Data Series and the extensive experimental solubility data throughout the rest of the chemical literature there is considerable interest in the prediction of solubility from other chemical and physical properties. There are two reasons for this. One is the desire to find which properties of molecules determine solubility. The other is the need to predict solubilities of gases for which no reliable direct measurements are available. Data for the solubilities of trace quantities of organic vapours in water is of particular importance in environmental chemistry.

Numerous papers have been published describing methods of predicting the solubility of gases [2–12]. The following factors which would be expected to influence solubility have been listed by *Cronin* [2]: volatilisation, size, entropy, H-bonding, enthalpy of solvation, and intrinsic hydrophobicity. These are not entirely independent parameters.

Monte Carlo simulation methods and molecular dynamics methods have been used. Both methods have limited application because of the approximate nature of predicted intermolecular force fields of complex molecules. Calculations of the solubility of inert gases from molecular dynamics have been published by *Swope* and *Andersen* [13] and by *Watanabe* and *Andersen* [14]. Monte Carlo predictions of the *Henry*'s law constants of methane, ethane, butane, hexane, cyclohexane, and benzene have been published [16–20] but application of the technique to more complex molecules is not possible at present [15]. There have been numerous attempts to derive simpler models which can be used to predict *Henry*'s law constants for a wide range of compounds.

Henry's law constants of gases which also exist as pure liquids or solids at the temperature of interest may often be calculated from the vapour pressure of the pure solid or liquid and the solubility of the solid or liquid. If an aqueous solution of a compound is in equilibrium with the solid or liquid compound then the fugacity of the compound in the gas phase over the solution can be assumed to be equal to the fugacity in the gas phase over the pure compound provided the solubility of water in the pure compound is low. It is usually possible to assume that the fugacity is approximately equal to the vapour pressure. This provides a good method of estimating a ratio of vapour pressure, p, over concentration in an aqueous phase, c_w. If vapour pressures and concentrations are fairly low this ratio may be equated with a *Henry*'s law constant, k_H, in units of pressure divided by the concentration in the aqueous layer, *i.e.* $k_H = p/c_w$. This is often the most reliable method of predicting *Henry*'s law constant for solution in water provided reliable solubility and vapour pressure data are available.

Quantitative Structure-property Relationships

Many methods of correlating physical properties of molecules depend on quantitative structure-property relationships (QSPR). Most of the models for prediction of *Henry*'s law constants depend upon the assumption that the free energy change on dissolution is a linear function of other molecular properties. Such an assumption is called a linear solvation energy relationship (LSER). There is a logarithmic relationship between the ratio of concentrations in the two phases and the free energy change when molecules are dissolved. In the case of aqueous solutions an LSER can be written in the form of Eq. (1) where c_w/c_g is the ratio of molar concentrations in aqueous and gas phases.

$$\log(c_w/c_g) = aA + bB + cC + \cdots + xX \tag{1}$$

This ratio is a form of *Henry*'s law constant. A is the value of property **A**, B is the value of property **B**, X the value of property **X**, *etc*. The different properties are often called descriptors. The parameters a, b, c, *etc.* are coefficients associated with the properties under consideration. For an ideal model these coefficients would be the same for each compound, *i.e.* for compounds 1, 2, 3, *etc.* $\log(c_w/c_g)_1 = aA_1 + bB_1 + cC_1 + \ldots + xX_1$, $\log(c_w/c_g)_2 = aA_2 + bB_2 + cC_2 + \ldots + xX_2$, *etc.* If N compounds were under consideration then N simultaneous equations could be written. This usually would be much greater than the number of coefficients a, b, c, *etc.* In practice, however, the exact values of the coefficients will not be the same for all the compounds. The better the model the less variation from compound to compound. Computer programs are available for input of experimental values of c_w/c_g together with values of the various properties A, B, C, *etc.* These programs give the best values of a, b, c, *etc.*, which correspond to the best fit between values to values of c_w/c_g from Eq. (1) and experimental values of c_w/c_g. Equation (1) can then be applied to a compound for which no experimental value of c_w/c_g is available.

Simple properties common to a large group of compounds are the numbers of each sort of atom in a molecule of the compound. It would be possible to associate each type of atom, **X**, with a value of X and make the number of these atoms in the molecule the value of X. However, such a model would not give satisfactory predictions. There would be no differentiation between different compounds with the same empirical formula.

Various LSER models have been developed to predict solubilities of organic compounds in water. In one of the models developed by *Hine* and *Mookerjee* [5] it was assumed that each type of bond of a particular type makes approximately the same contribution to the solubility of an organic compound in water. In some cases the bonds in a functional group were treated as single contributions. For instance the bonds in the cyano group (–CN), the nitro group (–NO_2) and the carbonyl group (–CO–) were each treated as a single entity. The contribution of –C–CO– therefore included the contribution of the double bond and that of –C–CN the contribution of the triple bond. Carbon atoms involved in ethenic double bonding, ethynic triplebonding, and in aromatic bonding were differentiated from one another and given the symbols C_d, C_t, and C_{ar}. It was assumed that the contribution of a C_d–X (*e.g.* C_d–H) bond included a quarter of the contribution of the –C=C– bond and that of a C_t–X bond half a –C≡C– bond. The C_{ar}–H contribution did not allow for C_{ar} to C_{ar} bonds. Separate allowance was made for them.

Henry's law constants were expressed as the ratio of the molar concentration in the aqueous phase to that in the gas phase, c_w/c_g. Average bond contributions, based on 263 solubilities from direct measurements, were expressed as contributions to log (c_w/c_g). *Hine* and *Mookerjee* also developed a similar model based on an estimation of the contribution of each group to the solubility rather than the contribution of each bond [5].

Meylan and *Howard* [6] developed *Hine* and *Mookerjee*'s bond contribution model. Some of the experimental data used by *Hine* and *Mookerjee* were replaced by more reliable data and new data were added so that values log (c_w/c_g) at 298.2 K for 345 compounds were available. As before, certain groups were treated as though they were single atoms. Certain types of compounds such as cyclic monoethers showed a systematic error. These were compensated by correcting factors. In the case of cyclic monethers the correcting factor was $+0.90$.

The model was tested using a second set of values of log (c_w/c_g) for 74 compounds, none of which had been used in determination of the bond contributions. The experimental data in this validation set correlated with the predicted values with a correlation coefficient (r^2) of 0.965, and a standard deviation of 0.457. This standard deviation in logarithmic values corresponds to a factor of 2.86 as far as values of k_H are concerned. The values of *Henry*'s constant in the form c_w/c_g for compounds in the validation set span over a range of ten orders of magnitude. It must be borne in mind that this, and similar models, are only useful in predicting the order of magnitude of *Henry*'s constant. They do not give precise values.

The predicted value of the ratio of c_w/c_g for methyl benzoate agrees very closely with the experimental value. The value for an aromatic C–H bond is -0.1543, that for an aromatic C–CO is 1.2387. Other bonds in the molecule make a characteristic contribution to the value of log (c_w/c_g) as indicated below. On the basis of this model the value of log (c_w/c_g) for methyl benzoate, $C_6H_5COOCH_3$, is predicted (CO–O 0.00714, C–O 1.0855, C–H -0.1197, C_{ar}–C_{ar} 0.2638) to be 2.8478. There are no correcting factors and hence the predicted value of log (c_w/c_g) is 2.8478. The value based directly on experimental data is 2.838. The difference between these logarithmic values is 0.0098. This corresponds to 2% difference between predicted and experimental values of c_w/c_g.

The predicted value for 3-hexanol, CH_3–CH_2–CH_2–CH(OH)–CH_2–CH_3, shows poor correlation with an experimental value. It can be estimated (C–C -0.1163, O–H 3.2318) as 3.3427; correcting factor -0.20. Thus, the predicted value of log (c_w/c_g) is 3.1427 and that based directly on experimental data is 2.757 with a difference of 0.3857. This corresponds to an error in c_w/c_g by a factor of

2.43 i.e. an error of 143%. In this case the method gives the right order of magnitude of the solubility. This may be satisfactory for some applications.

Meylan and *Howard* improved the model which they first published. It is now incorporated in the program *HENRYWIN* © published by Syracuse Research Corporation [28]. The group contribution model of *Hine* and *Mookerjee* has also been incorporated into the program. There is now a choice of estimation methods. Contributions for more types of bond and a greater variety of groups have been included. *Meylan* and *Howard* also extended the correction factor list. The bond contribution method is more widely applicable but the group method can be better when contributions for each fragment of the molecule are known. Structures are input using the *SMILES* notation.

Many of the data in the database were measured at 25°C and predicted values of c_w/c_g correspond to this temperature. The data base supplied with *HENRYWIN 3*© also contains equations for variation of *Henry*'s constant with temperature based on experimental measurements over a temperature range for 297 compounds. Where possible, equations for variation of c_w/c_g with temperature were taken directly from the literature. In other cases data were fitted to equations of the type $\ln (c_w/c_g) = A - B/(T/\mathrm{K})$, where A and B are constants. The equations were correlated with chemical structure. Similar classes of compounds were found to have similar values of the constant B with similar slopes when experimental values of $\log (c_w/c_g)$ were plotted against $1/(T/\mathrm{K})$. Average values of B were then evaluated for each class of compound – general aliphatic, general aromatic ester, nitrate, *etc*. The program can now be used to estimate values of c_w/c_g in the temperature range 273.15 to 323.15 K. The calculated values for 2-methylpropane and values based on direct experiment are shown in Fig. 1.

A variety of other quantitative structure property relationship studies have been published [3, 7–12]. Most of these have involved correlation with physical properties in addition to structural properties. Most have involved the derivation of linear solvation energy relationships for $\log (c_w/c_g)$. Although some have given more reliable correlations with certain groups of compounds none is as convenient to use as the ones published by *Meylan* and *Howard*.

Abraham et al. [11] derived Eq. (2) for the solubility of gases, where R_2 = excess molar refraction calculated from the experimental molar refraction,

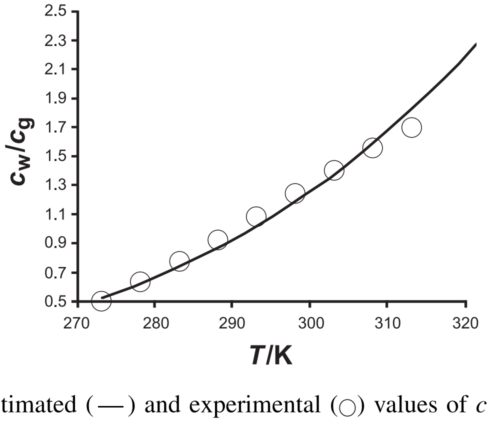

Fig. 1. Comparison of estimated (—) and experimental (○) values of c_w/c_g for 2-methylpropane

$\pi^H{}_2$ = dipolarity/polarizability determined experimentally, $\sum \alpha^H{}_2$ = the effective hydrogen-bond acidity, $\sum \beta^H{}_2$ = the effective hydrogen-bond basicity, and V_x = the *McGowan* characteristic volume [21] calculated from tabulated atomic increments.

$$\log(c_w/c_g) = -0.994 + 0.557\,R_2 + 2.549\pi^H{}_2 + 3.813\sum \alpha^H{}_2 + 4.841\sum \beta^H{}_2 - 0.869\,V_x \tag{2}$$

For a group of 408 gaseous compounds the standard deviation of values of $\log(c_w/c_g)$ was 0.15. This method suffers from the disadvantage that experimentally determined data are required. This limits its applicability for prediction.

Katritzky and *Mu* [10] used the 408 compounds investigated by *Abraham et al.* with the elimination of sulfur hexafluoride and triethyl phosphate. They investigated the applicability of more than 600 descriptors related to the structures and physical properties of molecules. Not only were the number of atoms of bonds of different types taken into account but geometrical and topological factors were also included. A variety of quantum mechanical descriptors such as energy levels were also included. They chose the most significant five descriptors to give Eq. (3),

$$\begin{aligned}\log(c_w/c_g) = {} & (2.65 \pm 0.22) + (42.37 \pm 1.11)HDCA(2) \\ & + (0.65 \pm 0.02)[N(\mathrm{O}) + 2N(\mathrm{N})] + (-0.16 \pm 0.02)(E_{\mathrm{HOMO}} - E_{\mathrm{LUMO}}) \\ & + (0.12 \pm 0.01)PCWT^{\mathrm{E}} + (0.82 \pm 0.06)N_{\mathrm{rings}}\end{aligned} \tag{3}$$

HDCA(2) is a hydrogen bonding related descriptor defined by Eq. (4), where q_D is the partial charge on the hydrogen bonding donor atom or atoms (H) and S_D is the exposed surface of this atom or atoms and S_{tot} is the total surface area of the molecule.

$$HDCA(2) = \sum \frac{q_D\sqrt{S_D}}{\sqrt{S_{tot}}} \tag{4}$$

$N(\mathrm{O}) + 2N(\mathrm{N})$ is a linear combination of the number of nitrogen atoms $N(\mathrm{N})$ and the number of oxygen atoms $N(\mathrm{O})$. N_{rings} is the number of rings. (E_{HOMO}–E_{LUMO}) is the energy gap associated with the dispersion energy of polar solutes in solution [22, 23]. $PCWT^{\mathrm{E}}$ is the partial charge weighted topological electronic index discussed by *Osmialowski et al.* [24]. This is defined by Eq. (5), where q_i and q_j are the *Zefirov* partial charges of the bonded atoms [25], $Q_{\min}$ is the more negative partial charge, and r_{ij} is the corresponding bond length. The standard deviation was 0.52.

$$PCWT^E = \frac{1}{Q_{\min}} \sum_{i<j} \frac{|q_i - q_j|}{r_{ij}^2} \tag{5}$$

English and *Carroll* [27] recently published two linear regression models. They investigated the use of descriptors to account for the influences on the solubility in water at 298.15 K of connectivity, charge distribution, charged surface area, hydrogen bonding characteristics, and nature of groups. For the first model an optimum group of ten descriptors was chosen. Twelve descriptors were used for the second model. These descriptors took into account effects due to hydrogen bonding. These linear models were developed using experimental data for 303 gases and tested with the remaining 54 gases.

Use of Neural Networks

The methods described above depend on the assumption that there are linear relationships between physical properties and solubility. There is no provision for non linear relationships between values of c_w/c_g and properties of molecules. Artificial neural networks have found wide applications in many other branches of chemistry [26]. It is possible to apply artificial neural networks to the prediction of the solubility of gases but little work has been published. *Sixt* [12] has described the effect of inputting fifteen descriptors into a 15-10-1 network using a Stuttgart Neural Network Simulator. The model was developed with a data set which contained 305 compounds and it was tested with 76 compounds. The test data gave a standard deviation of 0.31. For thiobencarb, methylparathion, and 2,3,6-trichloroanisol there were large discrepancies between measured and predicted values of $\log k_H$. Differences in values of $\log(c_w/c_g)$ were 1.66, 1.07, and 1.01.

English and *Carroll* [27] developed two models based on neural networks using the same experimental data and the same groups of ten or twelve descriptors which they used for developing their linear models. The neural models were tested with the 54 compounds used to test the linear models. In each case the neural versions of the models performed better than the corresponding linear versions. The models which used twelve descriptors performed significantly better than the models based on ten descriptors. The neural model using twelve descriptors gave a standard deviation of 0.237 in units of $\log_{10}$. This corresponds to an error in the *Henry*'s law constant by a factor of 1.73.

Some Recent Studies of Dissolution Processes

Reliable solubility data is essential for many aspects of research and of industry. In the case of gases one important field is that of atmospheric chemistry. There is need for reliable data for trace gases in order to understand and predict their behaviour towards cloud droplets. For this purpose what is needed is the ratio of solubility of the gas in aqueous media to the partial pressure of the gas. Since partial pressures are usually very low this can be equated to a *Henry*'s law constant which is the limiting value of this ratio. This ratio is essentially an equilibrium property. The rate at which this equilibrium is reached is often of practical importance. This is especially true in the case of atmospheric chemistry.

At high altitudes free radicals such as OH exist in the gaseous phase. Important reactions involving these and other stable or unstable species occur in the gas phase, liquid phase, or on the surface of solids such as ice particles. Reliable data for solubility and rate of solution in water and aqueous solutions of a wide range of compounds are requirements for generation of effective models of the behaviour of the atmosphere.

Gas molecules diffuse towards a liquid–gas interface and collide with the interface. Some rebound from the interface, others reversibly pass into the interface. There they may reversibly diffuse into the bulk of the liquid and, in the case of

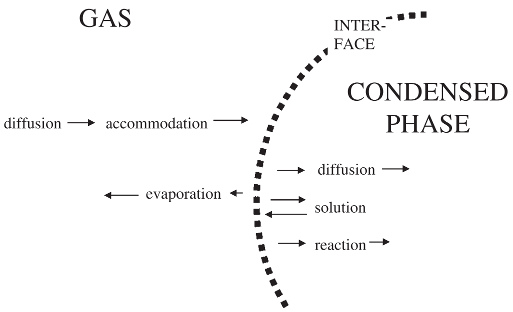

Fig. 2. The interaction of gas molecules with liquid droplets

reactive gases, react in the liquid phase. Cloud droplets have compositions, which vary depending on the altitude and conditions of formation. Various solutes are likely to be present at low concentrations in water at low altitudes in the troposphere. The liquid phase is largely concentrated sulphuric acid at very high altitudes. Reactions may occur after dissolution of a gas in a cloud droplet. There may be solvation, ionisation, or other chemical reactions. The process of absorption of a gas molecule by a cloud droplet can be thought of as involving various stages. These are 1) diffusion of the gas to the interface; 2) accommodation of the gas at the interface; 3) dissolution; 4) diffusion into the bulk of the liquid. They are described more extensively in various publications [29–31]. Depending on the nature of the gas this may be followed by reaction within the body of the droplet. Reaction can also occur in the interfacial region.

Dissolution and accommodation at the interface are both reversible processes. Gas molecules can evaporate and diffuse back into the bulk of the gas phase. The overall process can be represented as shown in Fig. 2.

The mass accommodation coefficient, α, is a measure of the rate at which molecules cross the interface, in one direction, from the gas to the liquid phase. It is defined as shown in Eq. (6).

$$\alpha = \frac{\text{number of gas molecules passing through the interface into the liquid phase}}{\text{number of gas molecules which collide with the interface with the liquid}} \tag{6}$$

It is sometimes called the sticking coefficient. Experimental measurements range from 1×10^{-7} to unity but are always subject to some degree of uncertainty because of difficulties of measurement. However, it is the order of magnitude which is of interest in particular cases. The uptake coefficient, γ, is a measure of the net rate of disappearance of gas from the gas phase. It differs from the accommodation coefficient in that it is a measure of the overall loss of molecules of a particular gas from the gas phase. This includes loss due to diffusion into the body of the droplet and loss by any chemical reaction in the liquid. It is defined as given in Eq. (7) and the value of γ also lies between 0 and 1.

$$\gamma = \frac{\text{number of gas molecules removed by the condensed phase in unit time}}{\text{number of gas molecules striking the interface in unit time}} \tag{7}$$

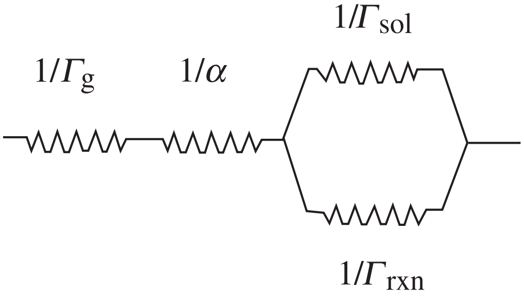

Fig. 3. The analogy between absorption processes and electrical circuits

The overall rate of uptake depends on all these processes illustrated in Fig. 2. Rigorous mathematical analyses have been published [32, 33]. Often a simple mathematical model can be useful in interpreting the overall process [32]. The different stages in the uptake of a gas, which influence the overall rate of uptake, are analogous to electrical resistances which control the rate of flow of electricity as illustrated in Fig. 3. As an approximation it can be assumed that a steady state is reached. This model is especially useful for interpreting the rate of absorption of gases which react in the liquid phase.

The rate at which molecules of a gas are removed from the gas phase depends on 1) rate of diffusion to the surface which is dependent on the gas transport coefficient Γ_{g}; 2) rate of passage through the interface which is dependent on a coefficient α; 3) rate of diffusion into the bulk of the liquid which is dependent on a coefficient Γ_{sol}; 4) rate of any subsequent reaction in the liquid phase which is dependent on a coefficient Γ_{rxn}. Processes 1) and 2) take place sequentially, but processes 3) and 4) take place simultaneously. The reciprocals of Γ_{g}, α, Γ_{sol}, and Γ_{rxn} are a measure of resistances to the overall removal of gas from the gas phase. The overall dissolution process is analogous to a system of four electrical resistances with two connected in series and two in parallel as shown in Fig. 3.

The proportion of gas molecules hitting the surface which disappear from the gas phase is given by the accommodation coefficient γ. Eq. (8) analogous to that for a system of electrical resistances in series and parallel can be written:

$$\frac{1}{\gamma} = \frac{1}{\Gamma_{\mathrm{g}}} + \frac{1}{\alpha} + \frac{1}{\Gamma_{\mathrm{sol}} + \Gamma_{\mathrm{rxn}}} \tag{8}$$

The coefficients Γ_{g}, Γ_{sol}, and Γ_{rxn} are defined so as to represent rates rather than probabilities. Unlike γ and α they can have values greater than unity. When Γ_{g} and $(\Gamma_{\mathrm{sol}} + \Gamma_{\mathrm{rxn}})$ become very large the value of γ approaches that of α. The gas transport coefficient, Γ_{g}, is given approximately by Eq. (9).

$$\frac{1}{\Gamma_{\mathrm{g}}} = \frac{\bar{c}d}{8D_{\mathrm{g}}} - \frac{1}{2} \tag{9}$$

The droplets are assumed to be spherical with diameter d. D_{g} is the gas diffusion coefficient and $\bar{c}$ the mean molecular velocity. The term $1/2$ allows for the effect on the collision rate when there is net gas uptake at the surface. It can be neglected if the droplet size is large enough.

Provided there is no chemical reaction to remove absorbed species the droplets eventually become saturated and the rate of desorption becomes equal to the rate of absorption. The net amount of gas absorbed then decreases with time. The solubility limited uptake coefficient, Γ_{sol}, therefore decreases the time of exposure to the gas. In this model the coefficient is given by Eq. (10), where k_H is the *Henry*'s law solubility (molar concentration/pressure), R the gas constant, T the temperature, t the time of exposure to the gas of the particular sample of condensed phase under consideration, D_{l} the diffusion coefficient of the gas in the condensed phase, and $\bar{c}$ the mean molecular velocity. The coefficient is a pure number with a value which may be greater than unity.

$$\Gamma_{sol} = \frac{4k_H RT}{\pi^{1/2}\bar{c}}\left(\frac{D_l}{t}\right)^{1/2} \tag{10}$$

The reactive uptake coefficient, Γ_{rxn}, for a non-reversible reaction is given by Eq. (11).

$$\Gamma_{\mathrm{rxn}} = \frac{4k_{\mathrm{H}}RT}{\bar{c}}(D_{\mathrm{l}}k_1)^{1/2} \tag{11}$$

The constant k_1 is the first order rate constant of the reacting gas. When there is a second order reaction with a component X other than water which is also present in the droplet this term is replaced by k_2 [X] where k_2 is the second order rate constant. Reaction occurs in a surface layer whose thickness is approximately $(D_{\mathrm{l}}\ k_1)^{1/2}$. The radius of the condensed phase must be greater than this if the equation above is to hold. This coefficient is also a pure number which can have any value.

There are several methods of measuring uptake coefficients. In some cases accommodation coefficients may be calculated from measured uptake coefficients. In some cases measurements also yield values of *Henry*'s law constants of gases which are unstable in aqueous solution.

Usually, methods involve the following: 1) Measurement of the rate at which a gas under test is removed from the gas phase to the liquid phase. This usually requires analysis of the gas phase and measurement of the rate of movement of the liquid and the gas phases. 2) Measurement or estimation of the surface area of the liquid. When water is in the form of droplets it is essential that these are of uniform size and the diameters can be measured. 3) Estimation of the rate of diffusion of gas to the liquid surface so that the rate at which gas molecules under test reach the liquid surface may be calculated. 4) Measurement of the time during which any part of the liquid phase is in contact with the gas under test.

Examples of Methods of Measuring Uptake Coefficients

Many different techniques have been used to measure uptake coefficients. Some measurements depend on the interaction of bubbles of gas of uniform size with liquid in a vertical or horizontal tube. Others involve interaction between bubbles of a gas with a vertical column of liquid. Absorption of gas by an aerosol of the liquid under test has also been measured. Three of the many methods are summarised below.

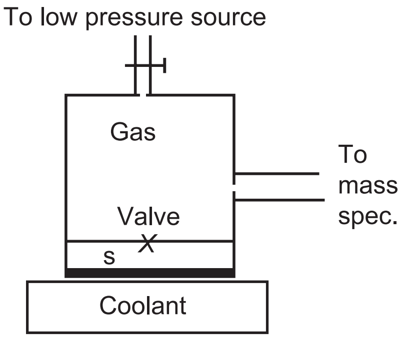

Fig. 4. Diagram of a *Knudsen* cell reactor

Knudsen Cell

Knudsen [36] studied the behaviour of gaseous molecules emerging through a small orifice into a small evacuated vessel in the early nineteen hundreds. Under these conditions the mean free path is large so that most of the gas molecules reach the walls of the evacuated vessel or any liquid present without colliding with other gas molecules. Calculation of the collision rate on the walls can then be very reliable.

Golden [34] has described a form of *Knudsen* cell reactor consisting essentially of two chambers separated by a valve, as shown in Fig. 4. In one of the chambers a liquid surface, S, can be prepared and cooled to low temperatures if stratospheric conditions need to be reproduced. The system operates at low pressures. Gas under test can be introduced into the upper chamber. Traces of this gas leak through a small orifice and are monitored by a mass spectrometer. When the valve between the chambers is opened the mass spectrometer signals caused by the gas under test are reduced. This is due to absorption and perhaps reaction at the liquid surface under test. Products of reaction can also be monitored by the mass spectrometer.

The rate at which molecules under test are lost to the surface under test is measured by the difference between the number of molecules per second reaching the mass spectrometer before the valve is opened (F^0) and the number per second after opening (F) *i.e.* (F^0–F). Because diffusion effects due to gas–gas collisions are negligible the collision frequency with the surface under test can be calculated very accurately.

Wetted Wall Flow Tube

The inside wall of a vertical tube is completely covered with a slow moving film of water or aqueous solution. Carrier gas flows through the tube over the liquid surface. Samples of gas under test can be injected into the carrier gas stream. Changes in concentration of this gas at different carrier gas flow rates are monitored by optical methods or by mass spectrometry. The uptake coefficient can be calculated for the rate of removal of the gas under test if a value of the gas-phase diffusion coefficient is known. The method is suitable for values of an uptake coefficient of about 10^{-6} to about 10^{-1}.

Cavity Resonance

Reid has reported that the chemistry of microdrops can be investigated by making use of cavity resonances [35]. The chemical composition of a droplet can be probed at different distances from its surface by using laser light of different wavelengths. This gives a method of investigating mass accommodation and chemical reaction in the interfacial region.

The investigation of the dissolution of gases in liquids may be one of the oldest branches of chemistry. However, there is still great scope for reliable experimentation and theoretical studies in the field. Many experimental solubility data need to be verified using modern techniques. There are still many data which need to be compiled and evaluated in a systematic manner. There is, thus, scope for many more volumes in the IUPAC Solubility Data Series devoted to further compilation and evaluation of experimental data for gases.

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