The Solubility of Gases in Water–Alcohol Mixtures

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1 Introduction

Since the beginning of the nineteenth century the solubility of a large number of gaseous solutes in a great variety of liquid solvents has been investigated. The measurements of solubility have found an increasing variety of applications in pure and applied science during the twentieth century. It could be argued that an accurate knowledge of solubility is fundamental to any research on physiological or environmental systems as it is to a large number of industrial processes, and to many analytical techniques. It is also obvious that particular interest exists in solvents which are water-based. This interest may stem from considerations about the use and protection of the hydrosphere on the global scale of this planet, or from desires to know much more on a molecular scale about the structure and interactions which exist in water, especially in its liquid state.

This review deals with an interesting class of mixed solvents, water mixed with monohydric alcohols. When a gas dissolves into such a solvent, the molecules of the gas become involved in all the interactions present in the solvent, and act as a probe of the local structure of that solvent, revealing how it changes as the components and the conditions are altered. To obtain information about this structure and its changes, enthalpy and entropy changes during the solubility process have been calculated from the solubility measurements and their temperature dependance. The differences in these thermodynamic parameters for different gases, different alcohols, and different temperatures have been interpreted by reference to intermolecular bonding and order–disorder transitions.

The first comprehensive review of gas–liquid solubilities was by Markham and Kobe[1] in 1941, to be followed by reviews by Battino *et al.*[2–4] in 1966, 1973, and 1976, keeping the scientific community informed about what systems had been studied, developments which had taken place in techniques of measurement, and about the accuracy and reliability of results. In 1974 the International Union of Pure and Applied Chemistry initiated the Solubilty Data Project, by means of which information on solubilities scattered throughout the scientific journals of the world would be collected, classified, and critically evaluated. Over fifty volumes of carefully indexed and evaluated data have already been published, about one third of which deal with individual gaseous solutes in all liquid solvents. They are the authoritative sources of solubility data, for present and future generations of scientists.[5]

Probably the earliest quantitative studies on the solubility of gases in liquids were made by William Henry[6] in 1803. From his work, which really was very limited in scope (five gases dissolved in water at a single temperature, and pressures of one, two, and three atmospheres) the well-known Henry's law was formulated. It is of course a limiting law, applying only to gases at low pressure and where no chemical interactions occur between solute and solvent molecules. It has been used to define an ideal gas–liquid solution. It has a limited usefulness under appropriate conditions.

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2 Experimental Methods for Measurement of Gas Solubility

Henry's method, shaking a fixed amount of solvent in contact with a gas and measuring the change in the volume of the gas at constant pressure, was developed and improved by Bunsen[7] and Ostwald,[8] before the end of last century. Numerous modifications and adaptations were made thereafter, noteworthy among them being the van Slyke apparatus[9] which has been widely used for the analysis of gases extracted from physiological specimens, and the Orsat and Haldane gas analysers[10] used especially for the analysis of flue gases before the advent of gas chromatography. Titration methods were also used from time to time, one of the commonest being that of Winkler for the determination of oxygen dissolved in water,[11] a method replaced only recently by the deployment of an oxygen electrode.

In the pioneering phase of gas solubility work, the precision of the measurement was about 2—5%. The methods were all of the batch-shake type. Even allowing for the lack of facilities for precise measurements and for thorough purification of components, the main source of error in these measurements was failure to reach equilibrium between the two phases. Unsaturation of the solvent by solute is common when shaking is used to mix the phases, and also when a gas is bubbled through a solvent. However, under certain conditions of prolonged shaking, supersaturation may occur.

Modern methods of solubility measurement can achieve a very high precision and accuracy, of the order of 0.04%. To achieve this kind of precision, the following factors must be taken into account:

(a) The purity of the solute gas. Ultra high purity grade gases better than 99.999 mol% have been used recently, although 99.9 mol% purity is more usual.

(b) The purity of the solvent. Repeated distillations, or if appropriate, reverse osmosis, ion exchange, and ultrafiltration have been used to achieve high purity. A method of checking the maintenance of purity standards is essential, *e.g.* conductivity of water, density or refractive index of mixed solvents. In addition an extremely important quality of the solvent is its freedom from previously dissolved gases. Methods of degassing are based upon refluxing, freeze–thaw cycling, and low pressure pumping. After degassing, the maximum residual dissolved gas can be less than 10^{-3} percent of its saturation solubility in the liquid at room temperature.

(c) Equilibrium between the gas and solution phases. To achieve equilibrium in batch methods, free from unsaturation or supersaturation, a time period of between 16 and 48 hours is required during which the solvent is swirled, shaken, or pumped in contact with the gas.

(d) Control of temperature Accurate thermostats capable of maintaining $\pm$ 0 002 K have been used for highest quality work A control of at least $\pm$ 0 05 K is necessary for all reliable gas solubility measurements since temperature affects both the volume of the gas to be measured and the vapour pressure of the solvent, as well as the actual solubility itself

(e) Calibration of temperature readings Devices such as thermocouples, resistance thermometers, or mercury in glass thermometers need to be checked periodically against standards such as triple-point-of-water cells

(f) Calibration of equipment for measuring volume and/or pressure Gas-lubricated piston pressure gauges can be used as primary standards

(g) Calculation of results Ideality cannot be assumed for gases or for solutions, so real gas corrections have to be applied if PVT measurements are used Fugacities and mole fractions have to be calculated from relevant data

(h) Definition of units of solubility In the literature there is a proliferation of different units for solubility measurements They are interconvertible only when all the appropriate conditions are recorded For example, the Bunsen coefficient is defined as the volume of gas reduced to STP absorbed by unit volume of solvent, at the temperature of the measurement, under a partial pressure of 1 atmosphere The Ostwald coefficient is defined as the ratio of the volume of gas absorbed to the volume of liquid absorbing it at a specified temperature and total pressure Henry's constant is the ratio of the fugacity of the gas in the gas phase to its mole fraction in the solution phase Frequently gas solubilities are quoted as molar concentrations (mol dm^{-3}) or as mole fractions, both of which are to be commended as units, but either of which is meaningful only when the temperature and partial pressure conditions are specified

The apparatus and calculations used by Rettich, Battino, and Wilhelm to measure the solubility of methane and ethane[12] and nitrogen[13] in water exemplify best practice taking account of all the above factors As a result these measurements are the most reliable yet to be obtained, and are unlikely to be improved upon significantly in the near future Their apparatus was developed from that of Benson and Krause[14] which introduced a substantial improvement in the attainment of equilibrium between the gas and its solvent by pumping to recycle the solvent over a spherical surface in contact with the gas phase, for periods of time of 20—44 hours Before this, the design of Cook and Hanson[15] was regarded the best for achieving saturation especially for gases of low solubility It employed a repeated cycle of shaking and measurement of volume until equilibrium was reached An alternative method of equilibration based on rapid then slow stirring and swirling was the basis of an apparatus used by Ben Naim and co-workers for their measurements of solubility of gases in water + alcohol mixtures [16]

An altogether different type of apparatus for the measurement of gas solubilities employs not single batches but a continuous flow of solvent In terms of precision it bridges the gap between the earlier and the very modern batch methods just described, and routinely gives a precision of 0 5—1% The method was devised by Morrison,[17] adapted by Clever *et al* [18] and developed and used widely by Cargill *et al* [19] to measure the solubility of several gases in water-based solvents, at partial pressures around 1 atmosphere Solubility values obtained ranged from 10 to 50000 cm^3 (STP) kg^{-1} (4 × 10^{-4} to 2 3 mol dm^{-3})

The essence of this technique is to cause a thin film of solvent to flow slowly and smoothly down the walls of a glass tube, about 60 cm in length, enclosing a fixed quantity of gas at known temperature and constant pressure (Figure 1) Over a period of 30—180 minutes the mass of solvent passing through the tube and the accompanying volume change of the gas are continuously recorded Solvent is degassed by boiling under reflux and is pumped at a steady rate to the top of the absorption tube Equilibrium is established very rapidly within the mobile thin film of solvent coating the inner walls of the absorption tube Fresh solvent is continuously exposed to the gas, and repeated measurements of changes in mass and volume over the period of a single experiment maximize reliability and minimize the influence of random errors Temperature is controlled by a thermostatted water bath, and measurements have been made between 275 and 350 K of the solubility of gases in solvents which have water as their main components

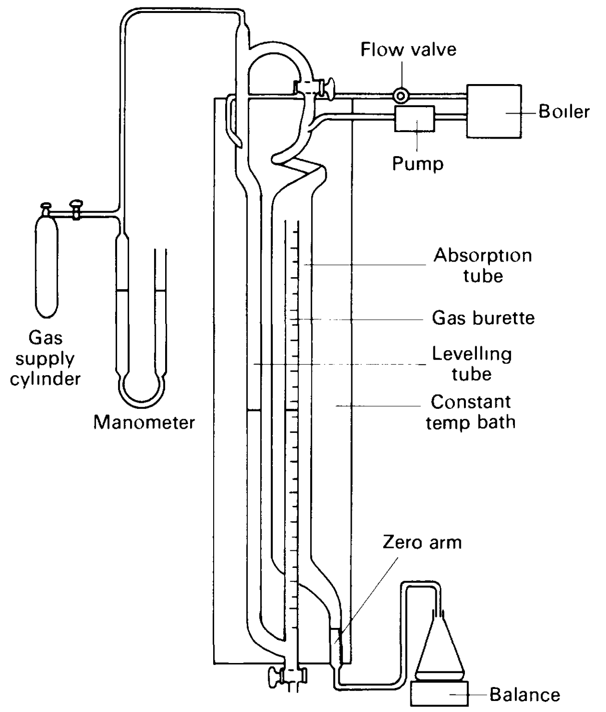


Figure 1 Flowing film technique for measuring solubility of gases in liquids

3 Characteristics of Liquid Solvents

Of the three main states of matter, the liquid state remains the one which is least understood and most difficult to model in a satisfactory manner The liquid most difficult of all to model is our commonest one, water A more difficult task still is to develop a model to account for all types of aqueous solutions A full analysis of solvent–solvent and solute–solvent molecular interactions is required Extensive computer power has recently been applied to this analysis for water itself, using Monte Carlo simulations The earlier scaled particle theory of Pierotti,[20] modified in several ways by subsequent researchers, has been quite successful when applied to dilute solutions of non-polar substances in water [21]

All models and theories need to be formulated from and tested by reliable data obtained from experiments One source of such data is measurement of the solubility of gases in the liquids in their pure state, and with small amounts of miscible co-solvents present, coupled with calculations of the thermodynamic properties of the equilibrium The most revealing parameters capable of structural interpretation in such studies are the changes in standard values of partial molar enthalpy, entropy, and heat capacity when a gas dissolves into the liquid These parameters can be derived from solubility data if they have been measured accurately over a range of temperatures, as will be shown in the next section

For water as solvent, this type of investigation was begun by Eley more than fifty years ago [22] It has been developed and modified continuously through the work and ideas notably of Frank and Evans[23] – water contains 'clusters' of hydrogen-bonded molecules, code-named 'icebergs', Nemethy and Scheraga [24] – structure is temporary and changing, 'flickering clusters', and Ben Naim[25] – there is a dynamic equilibrium between some bonded and non-bonded water molecules, with hydrophobic interactions between solute particles being important Other scientists such as Bernal[26] have favoured continuum rather than mixture theories of water structure, based on the concept of strained and bent hydrogen bonds Continuum theories have been well developed recently by computer simulations

Whatever the model or theory, the need has always been for more and better data to advance our understanding The advent of substantial computing power has not changed this need, although it has improved the rigour with which models can be tested Against this background we will consider an analysis of an important range of solvents, the water–alcohol mixtures, and the results obtained when several gases were dissolved into them

4 Thermodynamics of the Gas Solubility Equilibrium

If the solubility of a gas can be measured over a temperature range of 30–60 K with sufficient accuracy, and the solubility expressed as mol fraction x of the gas in the solution phase, then the data fit an equation of the following type, due to Clarke and Glew [27]

$$\ln x = A + B/T + C\ln T + DT \qquad (1)$$

From data of the highest quality, the coefficients A, B, C, and D can be evaluated with confidence For poorer quality data the coefficient D may be in doubt It is, however, several orders of magnitude lower than the others, and the fourth term in the equation is sometimes omitted

It is now straightforward to calculate thermodynamic functions from equation 1 We begin by stating the chemical potential (μ) of the gas in the two phases which are in equilibrium, and define convenient standard states

For gas in the gas phase at fugacity f

$$\mu_{(g)} = \mu^{\ominus} + RT\ln f$$

For gas in solution phase at activity a

$$\mu_{(sln)} = \mu^{\ominus} + RT\ln a$$

At equilibrium, $\mu_{(sln)} = \mu_{(g)}$

hence $\quad \mu^{\ominus}_{(sln)} + RT\ln a = \mu^{\ominus}_{(g)} + RT\ln f$

or $\quad \Delta\mu^{\ominus} = RT\ln(f/a) \qquad (2)$

Now for the vast majority of gas solubility studies at low partial pressure (around 1 bar) and ambient temperatures, partial pressure (p) of the gas may be substituted for its fugacity, and unless the gas is highly soluble its mole fraction (x) in solution may be substituted for its activity

Then $\quad \Delta\mu^{\ominus} = RT\ln p - RT\ln x$

Furthermore, we may select $p = 1$ atm and simplify the equation to read

$$\Delta G^{\ominus} = -RT\ln x \qquad (3)$$

and consider the changes in partial molar thermodynamic functions for the transfer of the gas from the vapour phase at 101 325 Pa partial pressure to the (hypothetical) solution phase of unit mol fraction For these conditions therefore we have, from equations 1 and 3

$$\Delta G^{\ominus} = -RAT - RB - RCT\ln T - RDT^2 \qquad (4)$$

Next, $\Delta\bar{S}^{\ominus} = -\partial\Delta\bar{G}^{\ominus}/\partial T$

so $\quad \Delta\bar{S}^{\ominus} = RA + RC\ln T + RC + 2RDT \qquad (5)$

Also, $\Delta\bar{H}^{\ominus} = \Delta\bar{G}^{\ominus} + T\Delta\bar{S}^{\ominus}$

so $\quad \Delta H^{\ominus} = -RB + RCT + RDT^2 \qquad (6)$

Finally $\Delta\bar{C}_p^{\ominus} = \partial\Delta H^{\ominus}/\partial T$

so $\quad \Delta\bar{C}_p^{\ominus} = RC + 2RDT \qquad (7)$

When these thermodynamic functions are used to interpret mechanisms of and structural changes during a solubility, at least two things have to be borne in mind (i) All such functions are bulk properties of the system and may be arrived at from different structural models and assumptions However the thermodynamic properties have a permanent value just because they do not depend on which model of structure is 'correct' Obviously any acceptable model must be consistent with the thermodynamic properties (ii) In comparing and contrasting the values of thermodynamic parameters, as is done next, error limits in the values are important Thus the error in the $\Delta G^{\ominus}$ values will be small – similar to the error in the measurement of the solubility which may be 0 05—0 5%, or even less in the best work The differentiation step used to obtain $\Delta\bar{S}^{\ominus}$ and $\Delta\bar{H}^{\ominus}$ leads to a possible error maybe two or three times greater, whilst the second differentiation to obtain $\Delta C_p^{\ominus}$ may lead to significantly greater errors Because of this, $\Delta C_p^{\ominus}$ values are not often used on their own in structural interpretations Comparisons between $\Delta\bar{H}^{\ominus}$ values and $\Delta\bar{S}^{\ominus}$ values for different conditions or different systems are the reliable indicators of structural changes in the solvent

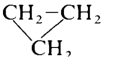
5 Analysis of Water–Alcohol Solvents

The solubilities of eleven gases in different alcohol–water mixtures have been measured over the temperature ranges 4—65 °C at partial pressures between 0 75 and 1 bar These systems are summarized in Table 1, and they afford an excellent opportunity to monitor the effects of the three components of the systems on each other, and to search for common features The results of these investigations will be considered in two parts

(i) analysis of similarities between the different systems, which are revealed in the patterns and trends of the solubility and its thermodynamic parameters over the range of solvent composition studied,

(ii) analysis of the differences between different gases, revealed in the magnitudes of these thermodynamic parameters

Table 1 Gas – solvent systems studied

	Solvent water mixed with		
Solute gas	CH_3OH	C_2H_5OH	$(CH_3)_3COH$
Helium		[a]	[a]
Argon		[b]	[b]
Hydrogen		[c]	
Oxygen			
Carbon dioxide		[d]	
$CH_3CH_2CH_2CH_3$		[f]	[g]
$CH_3CH_2CH_3$		[f]	[g]
$CH_3CH{=}CH_2$		[f]	
		[f]	
$(CH_3)_3CH$		[f]	
$(CH_3)_4C$		[f]	

R W Cargill *J Chem Soc Faraday Trans I* 1978 **74** 1444 R W Cargill and T J Morrison *J Chem Soc Faraday Trans I* 1975 **71** 618 R W Cargill *J Chem Soc Faraday Trans I* 1976 **72** 2296 R W Cargill and D E MacPhee *J Chem Research* 1981 (S) 232 (M) 2743 R W Cargill *J Chem Research* 1982 (S) 230 (M) 2313 R W Cargill and D E MacPhee *J Chem Soc Research* 1986 (S) 276 (M) 2301 [g] R W Cargill and D E MacPhee *J Chem Soc Faraday Trans I* 1989 **85** 2665

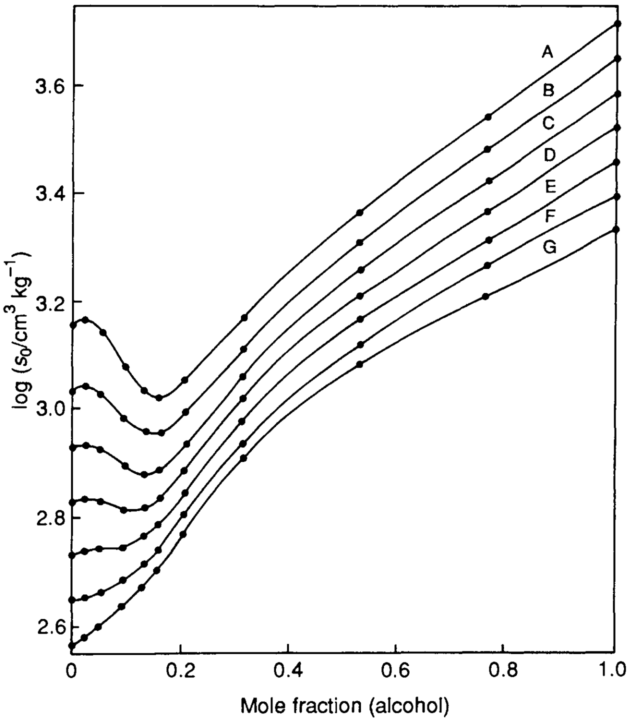


Figure 2 Solubility isotherms of carbon dioxide in water–ethanol mixtures. A = 4.7, B = 12.6, C = 21.0, D = 29.9, E = 39.4, F = 49.5, G = 60.2 °C.

5.1 Similarities between Water–Alcohol Solvents

For an analysis of the similarities between the systems, we look first at a typical set of isotherms on Figure 2, showing how the solubility of a gas is changed by the addition of increasing amounts of an alcohol. The unit of solubility used, s_0 is defined as the volume of gas (at STP) which dissolves into 1 kg of the solvent under a partial pressure of 1 atm, assuming ideality of the gas and of the solution. From s_0 the mole fraction x may be derived to use in equation 3.

At temperatures between 4 and 30 °C, there is first a small increase in solubility followed by a larger decrease to a minimum, then a gradual and more linear change as the mole fraction of alcohol, $x_2 \rightarrow 1$. At higher temperatures these extrema are increasingly smoothed out.

Now two important points emerge when all of the systems in Table 1 are scrutinized.

(i) For a given alcohol, this pattern of Figure 2 is shown by all of the gases studied. The isotherms are displaced on the vertical axis, or show different gradients, but the pattern is uniform.

(ii) For a given gas, the different alcohols give the same pattern with only the positions of the extrema displaced on the horizontal axis of x_2, the mole fraction of alcohol.

These comparisons can be made more clearly when changes in standard thermodynamic functions are calculated as in Section 4, to sort out some of the contributions to the solubility process. Thus isotherms of $\Delta\bar{G}^\ominus$, $\Delta\bar{H}^\ominus$, $\Delta\bar{S}^\ominus$, and $\Delta\bar{C}_p^\ominus$ may be compared for different gas–water–alcohol systems, as on Figure 3. When

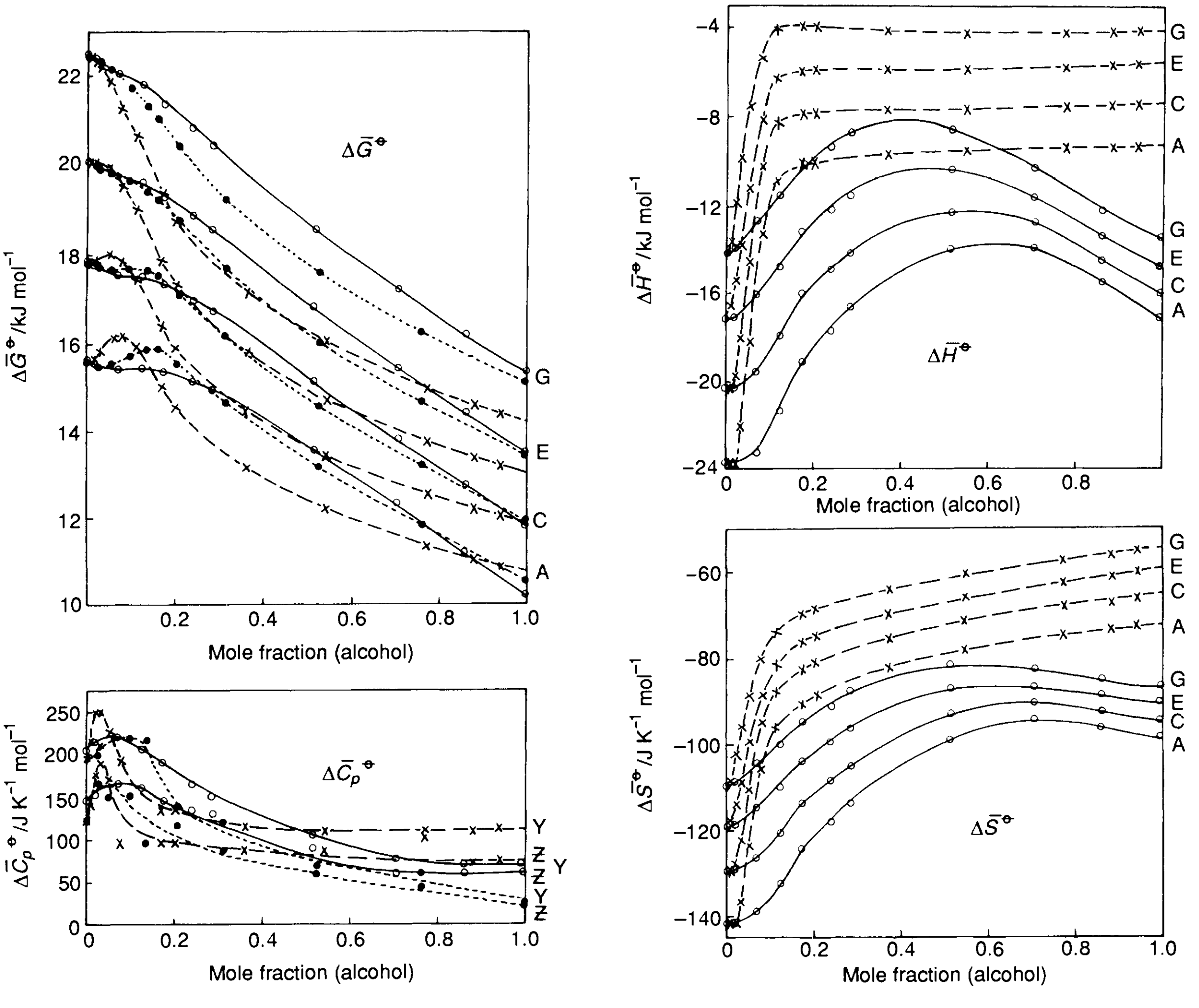


Figure 3 Thermodynamic parameters for solubility of carbon dioxide into water–methanol (full lines), water–ethanol (short dashed lines), and water–t-butyl alcohol (broken lines) mixtures. A = 4.7, C = 21.0, E = 39.4, G = 60.2, Y = 10—25, Z = 30—50 °C.

(Reproduced by permission from *J. Chem. Research (M)*, 1982, 2313.)

this is done, *e g* for the carbon dioxide aqueous alcohol system, the effects of methyl alcohol, ethyl alcohol, and t-butyl alcohol on the factors governing the solubility of a gas in water are evidently very similar Less of the alcohol with the bulkier alkyl group is required to produce the same effect as an alcohol with a smaller alkyl group, and this has been found for whatever gas has been used as solute

A closer analysis of the $\Delta\bar{H}^{\ominus}$ and $\Delta\bar{S}^{\ominus}$ graphs is fruitful in the light of proposals[23 24] that the H-bonded 'structure' of water is what governs the solubility of a non-polar gas into it, and that this 'structure' is dynamic, and modified when gas molecules are introduced 'Structure' is also modified by the addition of alcohol to water, and Ben-Naim[25] has suggested that in the temperature range up to 30 °C, very small amounts of alcohol added to water shift its equilibrium towards more structured forms and so the solubility of a gas is increased Then as more alcohol is added, the 'structure' is progressively destroyed by the extra amounts of alcohol, so that the solubility decreases to a deeper minimum After this it rises in a near linear fashion to its value in the pure alcohol

Thus with reference to Figure 4 where ethanol is the co-solvent, it is now proposed that on the $\Delta\bar{H}^{\ominus}$ and $\Delta\bar{S}^{\ominus}$ isotherms, the main shoulder at $x_2 \sim 0\ 2$, marks the transition between a solubility which is governed by the special structural features of water to one controlled by no such special structural effects, but rather by more regular and monotonous intermolecular forces This is indicated by the relatively large change in $\Delta\bar{H}^{\ominus}$ and $\Delta S^{\ominus}$ as $x_2 = 0$—0 2, and the relatively small change in $\Delta\bar{H}^{\ominus}$ and $\Delta S^{\ominus}$ as $x_2 = 0\ 2$—1 0 A consequence of this hypothesis is that the position of this shoulder on an isotherm is very important, since it marks the point where the added ethanol has removed the unique 'structure' from water The position on the horizontal axis (x_2) shows the different amounts of ethanol to be added at the different temperatures in order to remove this 'structure' These positions show an expected temperature dependence in that at higher temperature where less hydrogen-bonded water will be present, x_2 for the shoulder is also smaller Quantitative analysis of this, however, is difficult because the graphs do not give exact enough values of x_2

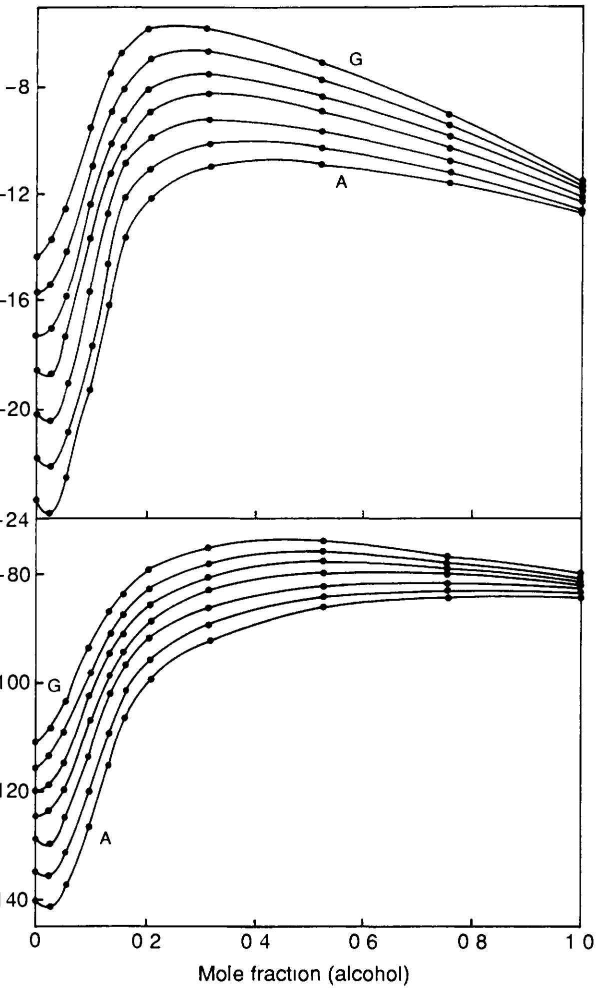


Figure 4 $\Delta H^{\ominus}$ and $\Delta\bar{S}^{\ominus}$ for solubility of carbon dioxide in water ethanol mixtures at 4 7 (A), 12 6, 21 0, 29 9, 39 4, 49 5, 60 2 °C (G)
(Reproduced by permission from *J Chem Research (M)*, 1981, 2743)

The positions on the vertical axis may be analysed in more detail We make use of the idea that the values of $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$, both of which are negative quantities, indicate the increase in the equilibrium amount of hydrogen-bonded structure in the solvent caused by the gas dissolving into it

In pure water, the numerical values of $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ are at their greatest, ignoring meantime the very small changes at low temperature for $x_2 < 0\ 02$ This is because the solvent (water) possesses special structural features (due to hydrogen bonding) which are exploited by the non-polar solute At the shoulder of the graph, the smaller numerical values of $\Delta\bar{H}^{\ominus}$ and $\Delta S^{\ominus}$ correspond to those for a gas dissolving into water which has had its special structural features removed (by the alcohol) Now standard values of the $\Delta\bar{H}^{\ominus}$ and $\Delta S^{\ominus}$ functions have been calculated throughout, so it is proposed that the difference between the $\Delta\bar{H}^{\ominus}$ or $\Delta\bar{S}^{\ominus}$ values at $x_2 = 0$ and at the shoulder of the curve will give a measurement of the amount of structure which was present in the water to begin with, and this difference does not depend on the standard state which was chosen

To clarify the analysis of this hypothesis, the 2-structure model of water[23 24] will be used For example, the $\Delta H^{\ominus}$ for the solution of a gas in water is considered to have two components,

(1) $\Delta H_u^{\ominus}$, for 'unstructured' (monomeric) water,
(2) $\Delta\bar{H}_c^{\ominus}$, for 'clustered' (H-bonded) water
and so $\Delta\bar{H}^{\ominus} = \Delta\bar{H}_u^{\ominus} + \Delta\bar{H}_c^{\ominus}$

Now if water has become totally unstructured at an isotherm shoulder, due to the addition of an alcohol, the measured $\Delta H^{\ominus}$ there will be the value of $\Delta H_u^{\ominus}$ component for water at that temperature So the $\Delta H_c^{\ominus}$ component for water itself at that temperature will be given by $\Delta\bar{H}^{\ominus}$ at $x_2 = 0$ minus $\Delta H^{\ominus}$ at the shoulder,

i e $$\Delta H^{\ominus} = \Delta\bar{H}_0^{\ominus} - \Delta\bar{H}_u^{\ominus}$$

An exactly similar analysis may be applied to $\Delta\bar{S}^{\ominus}$ isotherms to give values of $\Delta S_c^{\ominus}$

Values of $\Delta\bar{H}_c^{\ominus}$ and $\Delta\bar{S}_c^{\ominus}$ for the 'clustered' component of water at different temperatures obtained in this way with five gaseous solutes and ethanol as co-solvent are presented in Table 2 From this table it is evident that the absolute values of $\Delta\bar{H}_c^{\ominus}$ and $\Delta\bar{S}_c^{\ominus}$ depend upon which gas is dissolving into the water However the values for each gas can also be expressed on a relative scale if we take the value at 4 7 °C for reference, say as 100% The relative percentages are shown on Table 2 in italics, and it is clear that at a given temperature they show a very marked similarity, (a) for the $\Delta\bar{H}^{\ominus}$ and the $\Delta\bar{S}^{\ominus}$ functions, and (b) for each gas in the table The same quantitative comparisons and similarities are found when the data are analysed for these gases with t-butyl alcohol as co-solvent It is therefore proposed that these figures measure the relative change in the structure of water between 4 7 and 60 2 °C as encountered by the different gas molecules dissolving into it, and that they could provide a temperature coefficient for the mole fraction of 'clusters' in liquid water

5.2 Differences between the Gaseous Solutes

The second part of this analysis concerns the differences between the various gases It requires a closer scrutiny of the relative percentages in Table 2 generated by the different gases, and a consideration of similar data for the hydrocarbon gases, which are now given in Table 3 (For 2-methylpropane and 2,2-

Table 2 $\Delta\bar{H}_c^\ominus$ and $\Delta\bar{S}_c^\ominus$ for solution of gases into 'clustered' component of water (*with relative percentages in italics*)

	$-\Delta\bar{H}_c^\ominus$/kJ mol^{-1}				$-\Delta\bar{S}_c^\ominus$/J K^{-1} mol^{-1}			
Solute gas	4.7 °C	21.0 °C	39.4 °C	60.2 °C	4.7 °C	21.0 °C	39.4 °C	60.2 °C
Helium	13 *(100)*	11.5 *(88)*	10 *(77)*	9 *(69)*	48 *(100)*	44 *(92)*	40 *(83)*	33 *(69)*
Argon	16 *(100)*	14 *(87)*	12 *(75)*	10 *(63)*	62 *(100)*	54 *(87)*	50 *(81)*	40 *(64)*
Hydrogen	12 *(100)*	10.5 *(88)*	8.5 *(71)*	7 *(58)*	50 *(100)*	42 *(84)*	36 *(72)*	28 *(56)*
Oxygen	16 *(100)*	13.5 *(84)*	10.5 *(66)*	8.5 *(53)*	63 *(100)*	53 *(84)*	45 *(71)*	33 *(52)*
Carbon dioxide	12 *(100)*	10 *(83)*	9 *(75)*	8 *(67)*	42.5 *(100)*	37 *(87)*	34 *(80)*	30.5 *(72)*
Average %	*(100)*	*(86)*	*(73)*	*(62)*	*(100)*	*(87)*	*(77)*	*(63)*

Table 3 $\Delta\bar{H}_c^\ominus$ and $\Delta\bar{S}_c^\ominus$ for solution of gases into 'clustered' component of water (*with relative percentages in italics*)

	$-\Delta\bar{H}_c^\ominus$/kJ mol^{-1}				$-\Delta\bar{S}_c^\ominus$/J K^{-1} mol^{-1}			
Solute gas	4.7 °C	21.0 °C	39.4 °C	60.2 °C	4.7 °C	21.0 °C	39.4 °C	60.2 °C
Butane	38.8 *(100)*	30 *(77)*	20 *(51)*	9.4 *(24)*	148 *(100)*	118 *(80)*	85 *(57)*	53 *(36)*
Propane	34.7 *(100)*	26.8 *(77)*	19.4 *(56)*	12 *(35)*	130 *(100)*	103 *(79)*	77 *(59)*	55 *(42)*
Propene	27.6 *(100)*	20.6 *(75)*	15.2 *(55)*	9.4 *(34)*	97 *(100)*	77 *(79)*	60 *(62)*	43 *(44)*
Cyclopropane	20.8 *(100)*	16.4 *(79)*	12.2 *(59)*	7.7 *(37)*	80 *(100)*	65 *(81)*	52 *(65)*	37 *(46)*
2-Methylpropane		28.3 *(89)*	24.1 *(76)*	18 *(57)*		112 *(81)*	97.5 *(70)*	80 *(58)*
2,2-Dimethylpropane		26 *(89)*	20.6 *(70)*	14.3 *(49)*		105 *(89)*	87 *(74)*	68 *(58)*

dimethylpropane, data were not obtained at 4.7 °C because of their higher boiling points. The percentages entered in Table 3 for these two gases were calculated on an arbitrary scale, but one which is consistent with trends and values shown on Figure 5).

For these hydrocarbon gases, two points now emerge: (i) there is a greater divergence between the relative percentages for different gases this time; and (ii) these percentages are generally lower than those for the non-hydrocarbons. It is proposed that these lower percentages and the differences between them are due to hydrophobic interactions which are specific to certain types of molecules. Hydrophobic interaction (HI) leads to a reduction in the 'structure' of water, is greater at high temperature, and is greater for molecules of increasing size and departure from spherical shape. These factors will now be used to explain the data from Table 3, first graphically to reveal trends, and then numerically to calculate quantities.

A graphical display of the temperature dependence of the relative $\Delta\bar{H}_c^\ominus$ and $\Delta\bar{S}_c^\ominus$ values on the percentage scale, taken from Tables 2 and 3, is given on Figure 5 for all of the gases. The gradients of the lines sort the gases into an order of hydrophobicity if we accept the above proposal that the greater decrease in the $\Delta\bar{H}_c^\ominus$ or $\Delta\bar{S}_c^\ominus$ values indicate greater HI. Generally the smaller decreases are shown by the non-hydrocarbon gases. Also the monatomic helium and argon have less HI than the diatomic hydrogen and oxygen gases, and the smaller molecule of each pair has the smaller HI. For carbon dioxide, the HI appears to be small for the size and shape of its molecule, and this may be due to the small but significant amount of ionic species generated in this solution.

For the hydrocarbon gases the order of the HI obtained from the graph can again be rationalized in terms of molecular size and shape. Of the linear hydrocarbons, the longer C_4 chain of butane shows the greatest HI, followed by the C_3 chain of propane. Then the unsaturated propene has a little less HI. Cyclopropane shows significantly less HI, its molecule being more compact than that of propane. The branched chain

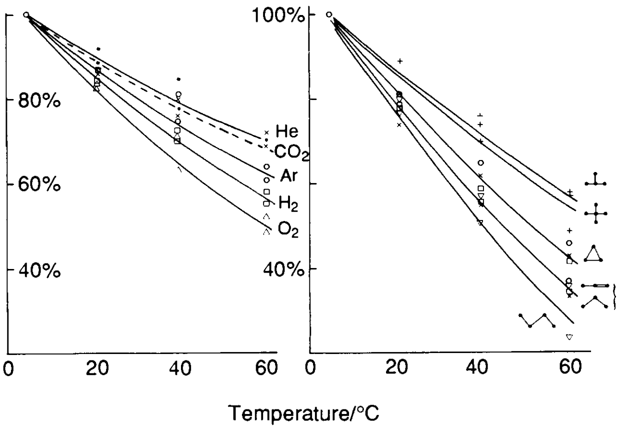


Figure 5 Percentage decrease in $\Delta\bar{H}_c^\ominus$ and $\Delta\bar{S}_c^\ominus$ values for different gases in water. (Pairs of identical symbols at a given temperature give values derived from $\Delta\bar{H}_c^\ominus$ and $\Delta\bar{S}_c^\ominus$ for a particular gas.)

molecules of $(CH_3)_3CH$ and $(CH_3)_4C$ approximate more closely to sphericity than any of the others, and this is probably why their hydrophobic interactions are much smaller, of the same order as those of hydrogen and argon

A quantitative and detailed analysis of the HI itself may be made by assuming that the reduction in $\Delta\bar{H}_c^\ominus$ between 5 and 60 °C is due to (a) a temperature effect and (b) a hydrophobic effect If the data for helium may be taken to be free from HI effects, as the above analysis would indicate and as other workers have assumed,[29] they will represent the temperature effect only The HI effect for any other gas may then be found by subtracting the percentage data for helium from those of the gas in question, to obtain on a relative percentage scale the extra reduction in the 'structure' of water due to the HI of that gas From this the enthalpy and the entropy changes due to the HI alone can be calculated Comparison between gases will give the contributions made to this interaction by different parts of molecules

For each of the four hydrocarbon gases which showed significant HI, Table 4 has collected data for percentage reductions in $\Delta\bar{H}_c^\ominus$ and $\Delta\bar{S}_c^\ominus$ (from Table 3) with the percentage values for helium (from Table 2) now subtracted from them These percentages on Table 4 represent the reduction in the structure of water due to the HI of each gas at the stated temperature If each of these percentages is then multiplied by the appropriate $\Delta\bar{H}_c^\ominus$ or $\Delta\bar{S}_c^\ominus$ value at 4 7 °C we obtain values of $\Delta\bar{X}_c^\ominus$ which are due to the HI alone These quantities are designated $\delta\Delta\bar{H}_c^\ominus$ and $\delta\Delta\bar{S}_c^\ominus$, the contributions each gas makes to the enthalpy and entropy of solution respectively, by virtue of its HI They demonstrate the extent to which the HI has raised the value of $\Delta\bar{H}^\ominus$ and $\Delta\bar{S}^\ominus$ for the solubility of the gas in water above what would be expected for a corresponding non-hydrophobic solute The values are given on Table 5, and two detailed calculations may be made in conclusion

(i) For propane and butane, quantitative comparison shows the increment in $\Delta\bar{H}^\ominus$ due to the HI for a CH_2 group Thus subtraction of the values for propane from the corresponding values for butane gives these $\Delta\bar{H}^\ominus$ increments at 294, 312, and 333 K as 0 5, 2 7, and 4 0 kJ mol^{-1} respectively Abraham[29] calculated this quantity to be 1 2—1 8 kJ mol^{-1} at 298 K Similarly, $T\Delta\bar{S}^\ominus$ contributions per CH_2 group are 0 2, 2 3, and 4 6 kJ mol^{-1} at 294, 312, and 333 K respectively Abraham's value at 298 K is 0 4—1 kJ mol^{-1}

(ii) The values for propane and propene may be compared in the same way to find the effect of replacing a single bond by a double bond in a molecule This evidently reduces the HI, and the decrement in $\Delta\bar{H}^\ominus$ due to HI for this substitution at 294, 312, and 333 K is 0 2, 1 2, and 3 8 kJ mol^{-1} respectively The corresponding $T\Delta\bar{S}^\ominus$ decrements are 1 3, 2 8, and 3 6 kJ mol^{-1} respectively

Whilst the precision of these figures is low due to large possible errors during subtractions, the contributions made by parts of a molecule to the HI have been estimated These estimates seem to be reasonable, and their temperature dependence is consistent with the model

Table 4 Differences between relative percentages in Table 3 and percentage values for helium on Table 2

Solute gas	for $\Delta(\Delta\bar{H}^\ominus)/\%$ 21 0 °C	39 4 °C	60 2 °C	for $\Delta(\Delta\bar{S}^\ominus)/\%$ 21 0 °C	39 4 °C	60 2 °C
Butane	11	26	45	12	26	33
Propane	11	21	39	13	24	27
Propene	13	22	35	13	21	25
Cyclopropane	9	18	32	11	18	23

Table 5 Calculated hydrophobic contributions to enthalpy and entropy of solution of selected hydrocarbon gases

Solute gas	$\delta\Delta\bar{H}^\ominus$/kJ mol^{-1} 21 0 °C	39 4 °C	60 2 °C	$\delta\Delta\bar{S}^\ominus$/J K^{-1} mol^{-1} 21 0 °C	39 4 °C	60 2 °C
Butane	4 3	10 0	17 5	17 8	38 5	48 8
Propane	3 8	7 3	13 5	17 0	31 2	35 1
Propene	3 6	6 1	9 7	12 6	22 3	24 2
Cyclopropane	1 9	3 7	6 7	8 8	16 0	18 4

We may now return briefly to the statement made at the end of Section 5 1 regarding a temperature coefficient for 'clusters' in water If we may safely assume that helium is a gas from which HI is absent, then the relative percentage figures for this gas are the ones which give the best values of the temperature coefficients for structure in water The small HI present in the other gases in Table 2 will have provided some contribution to the decrease in structure which was derived from the solubility measurements Thus, using the data for helium, it is proposed that the equilibrium amount of 'structured' water decreases by about 10% between 5 and 21 °C, between 21 and 40 °C, and between 40 and 60 °C From this it is estimated that the mole fraction of 'clusters' in water decreases from around 0 75 to around 0 52 between 5 and 60 °C

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