Low-Pressure Solubility of Gases in Liquid Water

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I. Introduction

Aqueous solutions of gases reveal many peculiarities generally not observed in other liquids.[1-9] For example, most gaseous solutes show a partial molar entropy and enthalpy of solution that are substantially lower than for other solvents, and the partial molar heat capacity is anomalously large. All these phenomena (and several other properties of aqueous solutions) have made water a particularly interesting liquid for studies in gas solubility. Furthermore, since water forms the basis of all biologically important systems, it is unique and thus deserves special attention. Indeed, the solubility of gases in this liquid has been the subject of innumerable investigations. Experimental data are so abundant, that in our preceding review[10] on gas solubility, water was deliberately omitted.

There are so many facets of gas solubility in water, both experimental and theoretical in nature, that we are limiting the present study to the low-pressure region, that is, to partial gas pressures *not* exceeding a few atmospheres. In addition, the upper temperature limit was set at 100 °C. (For an excellent review on the solubility of O_2, N_2, H_2, He, and CH_4 in water, see Himmelblau.[11] A short review article on gas solubility in water is the one by Miller and Hildebrand.[12]) Although these limitations may appear to be arbitrary, the reason will become apparent in the next section. Simply stated, it is connected with the difficulties encountered in the thermodynamic analysis of high-pressure equilibrium data. On the one hand, the mathematical formalism becomes increasingly complex; on the other hand, many of the necessary data are not available and have to be estimated by empirical correlation schemes. High-pressure vapor-liquid equilibria data are intrinsically important to the chemical engineer (see, for example, the excellent article by Prausnitz[13]); nevertheless, we thought it advisable to concentrate on the above-stated region of pressure and temperature, where (a) most of the data are reliable and of high precision, (b) we benefit from generally accepted and well-defined approximations to the thermodynamically exact relations, and (c) inaccuracies in some of the necessary semiempirical relations have no effect or a very small effect on the results.

The number of gases considered exceeds by far the number studied in ref 10. Solubility data will be reported for some 61 substances (including air), several of which have normal boiling points only slightly below room temperature (25 °C). Extreme cases are ethylamine (16.6 °C), neopentane (9.5 °C), ethylacetylene (8.1 °C), dimethylamine (7.4 °C), vinylacetylene (5.1 °C), and methyl bromide (3.6 °C). The other solutes have boiling points which are below 0 °C. It is with this reservation in mind that we use the expression "gas". Thus, we will *not* report data on substances having normal boiling points above 298.15 K, nor will we treat systems where the *dominant* feature is a chemical reaction (e.g., ionization reaction) between the gas and water, as is the case with HCl, SO_3, etc.

Roughly speaking, these gases may be divided into two groups: one whose members react chemically with water, and the other whose members do not. Some implications of this division will be discussed at the end of the next section. A solvent is never a substance which merely acts as an inert receptacle for a gas—there is *always* interaction. Only in such cases where this interaction is strong enough to produce new chemical species is it labeled "chemical". Obviously there is no sharp boundary, and this classification is to be taken as a mere heuristic convenience to interpret solubility data.

The emphasis in this review will be placed on reporting critically evaluated numerical results on equilibrium solubilities of various gases in water and on the thermodynamics connected with them. No effort was spent to completely review the vast literature on the theory of gas solubility in general, and on the theory of aqueous solutions in particular, although we endeavored to include most of the significant recent contributions. Necessarily, the selection of the theoretical studies which have an immediate bearing on the present problem is somewhat subjective and by no means exhaustive. We have also omitted a detailed description of methods and apparatus, since this topic

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was extensively covered in ref 14 and recently in the chapter by Clever and Battino[15] in the Weissberger series.

One additional aspect will be treated in detail: since water represents a particularly fortunate case where differences in isotopic composition have a considerable impact on the physical behavior of the solvent, we also report solubilities in "heavy water" D_2O. Unfortunately, the number of gases investigated is rather small. Additional experimental studies on gas solubility in deuterium oxide would be highly desirable.

We will also report work concerning the solubility of mixtures of gases in water, an area which has not attracted a great many investigators. Because of the biological importance of water as *the* life-sustaining liquid, several selected ecologically and biologically significant systems will be discussed. Lastly, in connection with the development of new theories concerning the structure of aqueous solutions, a few results on gas solubility in binary liquid mixtures containing water will be considered.

II. Thermodynamics

A. Basic Considerations

Consider a vapor phase (superscript V) and a homogeneous liquid phase (superscript L) in thermodynamic equilibrium. For any component i the chemical potential in both phases must be equal:

$$\mu_i^{\mathrm{V}} = \mu_i^{\mathrm{L}} \tag{1}$$

Connection with the observable variables total pressure P, mole fraction composition y_i of vapor, and x_i of liquid, respectively, is usually established with the aid of the two auxiliary functions: the vapor-phase fugacity coefficient ϕ_i, and the liquid-phase activity coefficient γ_i.

$$\begin{aligned}\mu_i^{\mathrm{V}}(T,P,y_i) &= \mu_i^{*\mathrm{V}}(T) + RT\ln P + RT\ln y_i + RT\ln\phi_i\\ &= \mu_i^{*\mathrm{V}}(T) + RT\ln f_i \end{aligned}\tag{2a}$$

$$\begin{aligned}\mu_i^{\mathrm{L}}(T,P,x_i) &= \mu_i^{\circ\mathrm{L}}(T,P) + RT\ln x_i + RT\ln\gamma_i\\ &= \mu_i^{\circ\mathrm{L}}(T,P) + RT\ln a_i \end{aligned}\tag{2b}$$

Here, $f_i\,(=Py_i\phi_i)$ and $a_i\,(=x_i\gamma_i)$ are the vapor-phase fugacity and the liquid-phase activity, respectively. The quantities $\mu_i^{*\mathrm{V}}(T)$ and $\mu_i^{\circ\mathrm{L}}(T,P)$ denote chemical potentials referring to conveniently chosen standard states. [Throughout this paper standard chemical potentials which depend only on temperature are denoted by a superscript asterisk, and those depending on both temperature and pressure are denoted by a superscript circle. Partial molar quantities (with the exception of the chemical potential) are indicated by a horizontal bar on top.] For the vapor phase, this is generally the ideal gas state at the same temperature and pressure P = 1 atm.[†] For the liquid phase of solutions of gases (where the pure component "gas" is often supercritical), most frequently the so-called unsymmetric convention for normalization of activity coefficients is adopted.[15a] Thus for a binary system:

$$\text{for solvent } (i = 1)\text{: } \gamma_1 \rightarrow 1 \text{ as } x_1 \rightarrow 1 \tag{3a}$$

$$\text{for solute } (i = 2)\text{: } \gamma_2 \rightarrow 1 \text{ as } x_2 \rightarrow 0 \tag{3b}$$

The standard state potential of the subcritical component (solvent) is the potential of the pure liquid at system temperature and pressure.[16] On the other hand, the activity coefficient of the solute is taken as approaching unity at infinite dilution. Hence $\mu_2^{\circ\mathrm{L}}$ can be interpreted as the chemical potential of pure solute in a hypothetical liquid state corresponding to extrapolation from infinite dilution (which serves as reference state) to x_2 = 1 along a line where γ_2 = 1, that is, along the Henry's law line. In physical terms, it might be regarded as a hypothetical state in which the mole fraction of solute is unity (pure solute), but some thermodynamic properties are those of the solute 2 in the reference state of infinite dilution in solvent 1 (e.g., partial molar heat capacity). Since from the context it should always be clear whether the superscript circle denotes "standard state" or "pure substance", no further distinction is introduced. Substituting from eq 2a,b into eq 1, we obtain after rearrangement

$$\frac{\phi_2 y_2 P}{\gamma_2 x_2} = \frac{f_2}{\gamma_2 x_2} = H_{2,1}(T,P) \text{ with}$$

$$H_{2,1}(T,P)/\mathrm{atm} = \exp\,(\Delta\mu_2^{\circ}/RT) \tag{4}$$

where $\Delta\mu_2^{\circ}(T,P) = \mu_2^{\circ\mathrm{L}} - \mu_2^{*\mathrm{V}}$ is the standard change of the partial molar Gibbs energy upon solution. The quantity $H_{2,1}(T,P)$ is called the Henry's law constant of substance 2 in solvent 1. Its value depends strongly on the nature of the solvent. Clearly, this well-defined and experimentally accessible quantity may be evaluated (at saturation pressure of the solvent, $P_{1\sigma}$) by extrapolating to $x_2 = 0$ a plot of (f_2/x_2) vs. x_2:

$$\lim_{x_2 \to 0}\,(f_2/x_2) = H_{2,1} \tag{5}$$

In general, the effect of pressure on Henry's law constant, as on other properties of condensed phases, is rather small. From its definition it follows that $(\partial \ln H_{2,1}/\partial P)_T = \overline{V}_2^{\circ\mathrm{L}}$, and hence

$$\begin{aligned}\ln H_{2,1}(T,P) &= \ln H_{2,1}(T,P_{1\sigma}) + \int_{P_{1\sigma}}^{P} \frac{\overline{V}_2^{\circ\mathrm{L}}}{RT}\,\mathrm{d}P\\ &\cong \ln H_{2,1}(T,P_{1\sigma}) + \frac{\overline{V}_2^{\circ\mathrm{L}}(P - P_{1\sigma})}{RT}\end{aligned}\tag{5a}$$

with $\overline{V}_2^{\circ\mathrm{L}}$ being the partial molar volume of component 2 at infinite dilution, which may be assumed, as a first approximation, to be independent of pressure.[13,18-20]

B. Some Useful Approximations

In low-pressure gas solubility work, it is frequently possible to adopt various approximations in evaluating the functions of eq 4 and eq 5 without seriously reducing numerical accuracy. Several of these approximations will be discussed in this section.

1. Liquid Phase

Empirically it is well established that for a sparingly soluble gas the solubility is proportional to its vapor-phase fugacity (partial pressure)

$$f_2 = Kx_2 \tag{6}$$

provided the gas pressure is not too large. The significance of the proportionality constant K is immediately revealed by comparison with eq 4: $K = \gamma_2 H_{2,1}$. At a given temperature and pressure, $H_{2,1}$ is independent of composition. Thus the constancy of K requires constancy of γ_2, which is, in fact, the essential feature of Henry's law. Since the activity coefficient has been normalized to 1 for $x_2 \rightarrow 0$, eq 6 is tantamount to stating that for the particular system the plot of fugacity vs. x_2 may be replaced by its tangent at infinite dilution (see eq 5).

2. Vapor Phase

a. Estimation of Fugacity Coefficient ϕ_2. At moderate vapor densities the equation of state may be approximated by the virial expansion truncated after the second virial coefficient B,[21,21a] in which case[17,22]

$$\ln \phi_i = \frac{2}{V^{\mathrm{V}}} \sum_j y_j B_{ij} - \ln\,(PV^{\mathrm{V}}/RT) \tag{7a}$$

[†] Throughout this paper Å = 0.1 nm, atm = 1.01325 × 10^5 Pa, bar = 10^5 Pa, Torr = atm/760, and cal = 4.184 J. All molar quantities are based on the relative atomic weights table 1971 as issued by IUPAC, *Pure Appl. Chem.*, **30**, 637 (1972).

For component 2 in a binary mixture, eq 7a becomes

$$\ln \phi_2 = \frac{2}{V^v}(y_2B_{22} + (1 - y_2)B_{12}) - \ln (PV^v/RT) \qquad (7b)$$

Here, B_{22} refers to the pure gaseous component, B_{12} is the second virial cross coefficient, and V^v is the molar volume of the gaseous mixture. Although B_{11} does not appear explicitly in eq 7b, its value is required for calculating V^v. Application of eq 7b requires extensive data in the single-phase vapor region. Unfortunately, for many cases of practical interest, these are not available, and thus one must resort to some convenient correlation scheme for computing B_{12}. Whereas for nonpolar gaseous mixtures several powerful correlation techniques[23-26] have been proposed, it is difficult to establish correlations for the second mixed virial coefficient of binary systems containing one or two strongly polar components.[27-30,33,35-37] Except for the last (Tsonopoulos[37]), all suffer from the disadvantage that unless some additional experimental information is available, their predictive accuracy is rather low. However, recently Hayden and O'Connell[38] have proposed a generalized method for predicting second pure-component and mixed virial coefficients which is based on the bound-pair formalism of Stogryn and Hirschfelder.[39] Only critical properties and some molecular parameters of the pure compounds are required. From the extensive comparison presented it appears that, particularly for highly complex systems (chemical association), the method is superior to existing correlations.

For many purposes one may rely upon a frequently used approximation commonly known as the Lewis fugacity rule, which should be useful up to pressures of the order of 5–10% of the critical:

$$\phi_2 = \phi_2^\circ, \text{ at same } T \text{ and } P \qquad (8)$$

where ϕ_2° denotes the fugacity coefficient of pure gaseous solute. In other words, the rule assumes that at constant T and P the fugacity coefficient is independent of composition. Generally it appears that for many gases at temperatures below the normal boiling temperature of water, and pressures of the order of a few atmospheres, the fugacity correction is rather small and often negligible.

b. Estimation of Vapor-Phase Mole Fraction y_2. With the usual simplifying assumptions, the mole fraction of solvent in the gaseous phase at low pressures may be calculated from the vapor pressure of the liquid[40] via Raoult's law, i.e.,

$$y_2 = 1 - y_1 \simeq [P - (1 - x_2)P_{1\sigma}]/P \qquad (9)$$

For the solvent water, x_2 is in general negligibly small and hence

$$y_2 \simeq (P - P_{1\sigma})/P \qquad (10)$$

Assuming an ideal vapor phase and replacing the fugacity by the partial pressure P_2 of solute may often yield satisfactory results, provided P_2 is small, the solubility of gas in the liquid sufficiently low, and the temperature well below the critical temperature of the solvent. (Just what "small" and "low" means depends on the gas and, of course, on the solvent involved. In general, $P_2 \sim 1$ atm or less, and $x_2 \lesssim 10^{-3}$ will suffice as necessary prerequisites.) Under these circumstances, the solution may be regarded as being effectively infinitely dilute. These approximations lead to the most familiar and simplest form of Henry's law,

$$P_2/x_2 = H_{2,1} \qquad (11)$$

C. Pressure Dependence

The pressure dependence of various quantities such as Henry's law constant $H_{2,1}$ has already been anticipated in the preceding sections[18-20,42] (cf., for example, eq 5a). In general, some information on the partial molar volumes in the liquid mixture and/or at infinite dilution is required. Similarly, the pressure dependence of the liquid-phase activity coefficient is given by

$$\left(\frac{\partial \ln \gamma_2}{\partial P}\right)_{T,x_2} = \frac{\bar{V}_2^{L} - \bar{V}_2^{\circ L}}{RT} \qquad (12)$$

where $\bar{V}_2^L$ is the partial molar volume of gas in the solution under consideration, and $\bar{V}_2^{\circ L}$ is the partial molar volume at infinite dilution. At low pressures, $H_{2,1}$ and a fortiori γ_2, are weakly dependent on pressure. Thus, for many practical purposes one may assume that the former depends only on T, and the latter only on T and composition.

In high-pressure solubility work,[43-46] effective thermodynamic analysis of solubility data requires separation of the effects of pressure from those of composition. This is best achieved by defining adjusted activity coefficients[13,17] at some arbitrary reference pressure P^r. In engineering applications, it is probably most convenient to use $P^r = P_{1\sigma}$, because it is the pressure at which $H_{1,2}$ is evaluated (cf. eq 5). However, other meaningful choices are possible (a careful discussion of this problem is presented in ref 13, 17, and 43). For the gaseous component, the pressure-independent activity coefficient is

$$\gamma_2(T,P_{1\sigma}) = \frac{f_2}{x_2H_{2,1}(T,P_{1\sigma})}\exp\left[\int_P^{P_{1\sigma}} \frac{\bar{V}_2^L}{RT}\,dP\right] \qquad (13)$$

It can be shown that this and the analogously defined activity coefficient $\gamma_1(T,P_{1\sigma})$ satisfy the isothermal, isobaric Gibbs–Duhem equation.[13]

D. Temperature Dependence

The temperature dependence of the Henry's law constant is obtained by differentiating eq 4,

$$\left(\frac{\partial \ln H_{2,1}}{\partial T}\right)_P = -\frac{\bar{H}_2^{\circ L} - H_2^{*V}}{RT^2} = -\frac{\Delta\bar{H}_2^\circ}{RT^2} \qquad (14)$$

where H_2^{*V} is the molar enthalpy of component 2 in the ideal gaseous phase, and $\bar{H}_2^{\circ L}$ is the partial molar enthalpy of the solute in liquid solution at infinite dilution. The quantity $\Delta\bar{H}_2^\circ = \bar{H}_2^{\circ L} - H_2^{*V}$ is commonly called the standard enthalpy change on solution, or the "enthalpy of solution". Conversely, the quantity $-\Delta\bar{H}_2^\circ$ is the standard enthalpy change resulting from evaporation of 1 mol of the solute from an infinitely dilute solution at constant temperature and pressure.

The corresponding (partial molar) standard entropy change (the ideal gas standard is at 1 atm pressure) is obtained by straightforward thermodynamics:

$$-\left(\frac{\partial(T \ln H_{2,1})}{\partial T}\right)_P = \Delta\bar{S}_2^\circ/R = (\bar{S}_2^{\circ L} - S_2^{*V})/R$$
$$= (\Delta\bar{H}_2^\circ - \Delta\mu_2^\circ)/RT = \Delta\bar{H}_2^\circ/RT - \ln H_{2,1} \qquad (15)$$

with S_2^{*V} being the standard molar entropy of solute in the ideal gas phase, and $\bar{S}_2^{\circ L}$ is the partial molar entropy of the gas in the hypothetical liquid standard state $x_2 = 1$. (For the sake of brevity, the adjectives "partial", "molar", or "standard", or any suitable combination therefrom will occasionally be omitted; that is, similar to $\Delta\bar{H}_2^\circ$, the quantity $\Delta\bar{S}_2^\circ$ will often be called "entropy of solution".)

The temperature dependence of $\Delta\bar{H}_2^\circ$ yields direct information on the partial molar heat capacity change upon solution:

$$\left(\frac{\partial\Delta\bar{H}_2^\circ}{\partial T}\right)_P = \Delta\bar{C}_{P2}^\circ = \bar{C}_{P2}^{\circ L} - C_{P2}^{*V} \qquad (16)$$

The quantity $\Delta\bar{C}_{P2}^\circ$ represents the difference in the partial molar heat capacity of the solute in aqueous solution at infinite dilution to that in the ideal gas state.

Equation 2b may be differentiated with respect to T at constant pressure and composition, yielding for the temperature dependence of the activity coefficient

$$\left(\frac{\partial \ln \gamma_2}{\partial T}\right)_{P,x_2} = \frac{\bar{H}_2^{\circ\mathrm{L}} - \bar{H}_2^{\mathrm{L}}}{RT^2} \tag{17}$$

Here, $\bar{H}_2^{\mathrm{L}}$ refers to the partial molar enthalpy of gas in the solution where the activity coefficient is γ_2. A general expression for the enthalpy change occurring on dissolving a gas in a liquid at a given composition was first derived by Sherwood and Prausnitz.[47] In the following we will outline the derivation (although in a slightly different manner) and discuss some implications of its use in an approximate form.

For any variation which maintains equilibrium

$$\mathrm{d}(\mu_i^{\mathrm{V}}/T) = \mathrm{d}(\mu_i^{\mathrm{L}}/T) \tag{18}$$

Under isobaric conditions, expansion in terms of the variables T, $\ln x_i$, and $\ln y_i$, respectively, yields

$$-\frac{\bar{H}_i^{\mathrm{V}}}{T^2}\mathrm{d}T + \left(\frac{\partial(\mu_i^{\mathrm{V}}/T)}{\partial \ln y_i}\right)_{T,P}\mathrm{d}\ln y_i = -\frac{\bar{H}_i^{\mathrm{L}}}{T^2}\mathrm{d}T + \left(\frac{\partial(\mu_i^{\mathrm{L}}/T)}{\partial \ln x_i}\right)_{T,P}\mathrm{d}\ln x_i \tag{19}$$

From eq 2a and 2b we obtain

$$\left(\frac{\partial(\mu_i^{\mathrm{V}}/T)}{\partial \ln y_i}\right)_{T,P} = R\left(\frac{\partial \ln f_i}{\partial \ln y_i}\right)_{T,P} = R\left[1 + \left(\frac{\partial \ln \phi_i}{\partial \ln y_i}\right)_{T,P}\right] \tag{20a}$$

$$\left(\frac{\partial(\mu_i^{\mathrm{L}}/T)}{\partial \ln x_i}\right)_{T,P} = R\left(\frac{\partial \ln a_i}{\partial \ln x_i}\right)_{T,P} = R\left[1 + \left(\frac{\partial \ln \gamma_i}{\partial \ln x_i}\right)_{T,P}\right] \tag{20b}$$

Substitution into eq 19 and rearrangement yields

$$-\frac{\bar{H}_i^{\mathrm{L}} - \bar{H}_i^{\mathrm{V}}}{RT^2}\mathrm{d}T = \left[1 + \left(\frac{\partial \ln \phi_i}{\partial \ln y_i}\right)_{T,P}\right]\mathrm{d}\ln y_i - \left[1 + \left(\frac{\partial \ln \gamma_i}{\partial \ln x_i}\right)_{T,P}\right]\mathrm{d}\ln x_i \tag{21}$$

a result which is perfectly general. In order to actually apply eq 21, several reasonable simplifying assumptions are introduced.

At moderate vapor densities eq 7b applies, in which case for component 2

$$\left(\frac{\partial \ln \phi_2}{\partial \ln y_2}\right)_{T,P} = y_2\frac{2B_{22} - 2B_{12}}{V^{\mathrm{V}}} - \frac{y_2}{V^{\mathrm{V}} + 2B}\left(\frac{\partial B}{\partial y_2}\right)_{P,T}\left[1 + \frac{2}{V^{\mathrm{V}}}(y_2B_{22} + y_1B_{12})\right] \tag{22}$$

Under the provision $1/(V^{\mathrm{V}} + 2B) \approx 1/V^{\mathrm{V}}$ and $2(y_2B_{22} + y_1B_{12})/V^{\mathrm{V}} \ll 1$, eq 22 simplifies to[47]

$$\left(\frac{\partial \ln \phi_2}{\partial \ln y_2}\right)_{P,T} = -2y_1y_2\frac{\delta B}{V^{\mathrm{V}}} \tag{23}$$

where $\delta B = 2B_{12} - B_{11} - B_{22}$.

In order to evaluate the composition dependence of the activity coefficient, consider an isothermal variation along an equilibrium path:

$$\left(\frac{\partial(\mu_2^{\mathrm{V}}/T)}{\partial \ln y_2}\right)_{T,P}\mathrm{d}\ln y_2 + \left(\frac{\partial(\mu_2^{\mathrm{V}}/T)}{\partial \ln P}\right)_{T,y_2}\mathrm{d}\ln P = \left(\frac{\partial(\mu_2^{\mathrm{L}}/T)}{\partial \ln x_2}\right)_{T,P}\mathrm{d}\ln x_2 + \left(\frac{\partial(\mu_2^{\mathrm{L}}/T)}{\partial \ln P}\right)_{T,x_2}\mathrm{d}\ln P \tag{24}$$

After insertion of the results of eq 20a and 20b, and taking into account that $[\partial(\mu_2^{\mathrm{L}}/T)/\partial \ln P]_{T,x_2} = \bar{V}_2^{\mathrm{L}}P/T$ and $[\partial(\mu_2^{\mathrm{V}}/T)/\partial \ln P]_{T,y_2} = R[1 + (\partial \ln \phi_2/\partial \ln P)_{T,y_2}]$, the following expression is obtained:

$$\left(\frac{\partial \ln \gamma_2}{\partial \ln x_2}\right)_{T,P} = \left[1 + \left(\frac{\partial \ln \phi_2}{\partial \ln y_2}\right)_{T,P}\right]\left(\frac{\partial \ln y_2}{\partial \ln x_2}\right)_T + \left[1 + \left(\frac{\partial \ln \phi_2}{\partial \ln P}\right)_{T,y_2} - \frac{P\bar{V}_2^{\mathrm{L}}}{RT}\right]\left(\frac{\partial \ln P}{\partial \ln x_2}\right)_T - 1 \tag{25}$$

where the pressure dependence of the fugacity coefficient is given by

$$\left(\frac{\partial \ln \phi_2}{\partial \ln P}\right)_{T,y_2} = -\frac{V^{\mathrm{V}} + B}{V^{\mathrm{V}}(V^{\mathrm{V}} + 2B)} \times \left[-2(y_2B_{22} + y_1B_{12}) + \frac{BV^{\mathrm{V}}}{V^{\mathrm{V}} + B}\right] \tag{26}$$

Again, with $1/(V^{\mathrm{V}} + B) \simeq 1/V^{\mathrm{V}}$ and $(V^{\mathrm{V}} + B) \simeq (V^{\mathrm{V}} + 2B)$, a simpler version of eq 26 is obtained:

$$\left(\frac{\partial \ln \phi_2}{\partial \ln P}\right)_{T,y_2} = \frac{\delta B(y_2^2 - 2y_2 + 1) + B_{22}}{V^{\mathrm{V}}} \tag{27}$$

Derivatives at constant temperature only, that is, the quantities $(\partial \ln y_2/\partial \ln x_2)_T$ and $(\partial \ln P/\partial \ln x_2)_T$, may be extracted from phase equilibrium data. The enthalpy change upon solution can now be calculated by inserting eq 23 and 25 in conjunction with eq 27 into eq 21. However, several approximations to this fairly complex relation are feasible. In particular, at low vapor densities, terms of the order $1/V^{\mathrm{V}}$ may be neglected and in addition, for small solubilities, one may assume that Henry's law in the simple version eq 11 holds. Then

$$-\frac{\bar{H}_2^{\mathrm{L}} - \bar{H}_2^{\mathrm{V}}}{RT^2} \simeq -\frac{\bar{H}_2^{\circ\mathrm{L}} - \bar{H}_2^{*\mathrm{V}}}{RT^2} = -\frac{\Delta\bar{H}_2^{\circ}}{RT^2} = \left(\frac{\partial \ln H_{2,1}}{\partial T}\right)_P \tag{28}$$

A much more convenient approximate relation which is applicable in most cases of practical interest, that is, where data at *constant partial gas pressure* are reported, may be derived in an analogous manner:[47]

$$\frac{\Delta\bar{H}_2^{\circ}}{RT^2} = \left(\frac{\partial \ln x_2}{\partial T}\right)_{P_2} \tag{29}$$

E. Chemical Effects

There are not many studies of the effect of "chemical forces" on gas solubility, primarily because of the inherent difficulty of characterizing them in a quantitative way. However, qualitatively, one may say that deviations from Henry's law even at low solute concentrations may often be a result of chemical effects. The failure of Henry's law is then due to the coupling of an additional chemical equilibrium in the liquid phase to the conventional vapor–liquid equilibrium. The solubility of SO_2 in water may serve as an example:

$$SO_2(\mathrm{g}) \underset{}{\overset{1}{\rightleftharpoons}} SO_2(\mathrm{dissolved}) \overset{2}{\rightleftharpoons} H^+ + HSO_3^-$$

Clearly, Henry's law concerns only equilibrium 1, but *not* 2. Thus, one has to use corrected mole fractions x_{SO_2} referring only to dissolved SO_2 which is still in a molecular (nonionized) state.[48]

Generally, in cases where independent measurements on the coupled chemical equilibrium have been reported, incorporation of corrected concentrations is possible. However, quite often, this additional information is lacking, in which case linearization of solubility data may still be achieved by devising a reasonably simple model for the second (chemical) equilibrium. Some representatives of both groups have been discussed in detail by Prausnitz.[17,49]

A valuable study is Burgess and Germann's work on hydrogen sulfide–water mixtures.[50] In particular, they present analytical equations for the temperature ranges from the hydrate point to

100 °C (range 1), and from 100 to 171 °C (range 2), and for the pressure range 0.6895 to 2.7579 MPa. For example, the equation governing solubility in range 1 is of the form

$$\ln x_{H_2S} = A + BP - CP^2 + DP^3 - ET + FT^2 + GT^3 \quad (30)$$

For range 2, mixed terms in P and T appear. Most of the calculated values were within 1% of those obtained by Selleck et al.[51] For the hydrate temperature, $t_H/°C$, as a function of pressure, Burgess and Germann give

$$t_H/°C = 9.3987 \ln(145.038P/\mathrm{MPa}) - 24.85 \quad (31)$$

Recently, Edwards, Newman, and Prausnitz[52] investigated the thermodynamics of aqueous solutions containing one or more volatile weak electrolytes, such as ammonia, carbon dioxide, hydrogen sulfide, etc. Their molecular thermodynamics approach gave satisfactory results in the range 0 to 100 °C and for liquid-phase concentrations less than 2 M and ionic strength not more than 0.5 M. Equilibrium compositions of multisolute systems can also be predicted using binary parameters only. Agreement with data on two ternary systems (NH_3-H_2S-H_2O and NH_3-CO_2-H_2O) was good.

F. Units of Gas Solubility

There are numerous ways of expressing the solubility of a gas in a liquid. The more popular of these along with interconversion formulas have been presented in ref 10, 14, and 15. However, in these articles ideality of the gas phase was assumed. Thus, by way of example, we will present a more generally applicable relation between Ostwald coefficient, $L = v_2^V/v_1^L$, and mole fraction where v_2^V denotes the volume of pure gas absorbed by the volume v_1^L of pure solvent at the given pressure and temperature. To the extent that $V_2^{oV} = RT/P_2 + B_{22}$ (V_2^{oV} denotes the molar volume of pure gaseous solute) is a valid approximation to the equation of state eq 7c in ref 21, we obtain

$$n_2^L = v_2^V/V_2^{oV} = v_2^V/(RT/P_2 + B_{22}) \quad (32)$$

and consequently

$$x_2 = \left[\frac{n_1^L}{n_2^L} + 1\right]^{-1} = \left[\frac{1}{V_1^{oL}L}\left(\frac{RT}{P_2} + B_{22}\right) + 1\right]^{-1} \quad (33)$$

For $B_{22} \ll RT/P_2$, this reduces to[53]

$$x_2 = [RT/(V_1^{oL}LP_2) + 1]^{-1} \quad (34)$$

Wilhelm and Battino[53] also present approximate corrections for determining the Ostwald coefficient of highly soluble gases using an apparatus of the Morrison and Billet type[54] (cf. also Hayduk[55]). Similar relations may be easily derived for the Bunsen coefficient, etc.

III. Data Reduction and Results

A. Curve Fitting

Three review articles,[11,14,56] *Chemical Abstracts*, the literature, and other sources,[57,58] were searched for data of reasonable accuracy. We went as far back as Bunsen's work[59-62] in the 1850's. We have hard copy on hand for all of the articles containing data used in this review. Unless the data used from one source were so precise as to warrant independent treatment, all experimental data for a particular gas were handled as a group. The reported data were converted where required to Ostwald coefficients, mole fractions at 1 atm partial pressure of gas, and Kelvin temperatures. Corrections for nonideality and chemical effects were *not* made. Along with identifying information, these reduced data were punched onto Hollerith cards, and all subsequent data handling was done with the cards. All the data for each gas were submitted to an initial screening using a scattergram program with a plotting routine. Data which were grossly out of line were discarded after double-checking the original paper for its level of precision and the reliability of the work.

The final fitting and selection of data were done using a least-squares program modified from one available from the Quantum Chemistry Program Exchange—QCPE Program 230, FITIT (available from Indiana University Chemistry Department). The temperature dependence of the solubility was then accounted for by fitting to an expression of the form[5,63,63a]

$$R \ln x_2 = A + BT^{-1} + C \ln (T/K) + DT \quad (35)$$

where the inclusion of the fourth term[64,65] depended on the overall precision and the number of points. An alternative expression for the variation of the logarithm of the Henry's law constant with temperature was given by Franks et al.,[66] who represent it in terms of a polynomial in T. The disadvantages of the approach of Franks et al. have been discussed.[63] For a discussion of a general unbiased approach to the problem of representing equilibrium data of high accuracy, see the article by Clarke and Glew[67] and the condensed treatment by Bolton.[68] They recommend the form used in eq 35. However, Peterson and Krause[69] have criticized the Clarke and Glew form as not being unique to the problem. Benson and Krause[70] (with whom Parker collaborated) recommend the form $\ln x_2 = a_0 + a_1T^{-1} + a_2T^{-2} + \ldots$ as providing the best fit with the least number of constants for their high-precision data. The advantage of eq 35 over polynomial fits[10] with an equal number of coefficients is that it correctly correlates solubility and temperature with a significantly smaller standard deviation. Its merits in gas solubility work have been amply discussed by Alexander et al.[63] Weiss[71] uses a form similar to eq 35 but uses $T/100$ rather than T as the independent variable so as to diminish the magnitude of the coefficients. Occasionally, we encountered systems for which only very limited or somewhat less accurate data were available, and in those cases we used the simple relation[10]

$$RT \ln x_2 = B + AT \quad (36)$$

B. Results

Table I lists the constants of eq 35 and 36, respectively, for solubilities in water; Table II gives the corresponding coefficients for "heavy water", D_2O. In order to distinguish between the two sets of constants corresponding to these two equations, the numbers for A and B of eq 36 have been italicized in the tables. The results of the fitting procedure were checked as to nonrandomness of deviations. No systematical bias could be detected. (See section D for a detailed discussion relating to important individual gases.) From the smoothing functions, solubility data in terms of mole fraction and Ostwald coefficient at 1 atm partial gas pressure at selected temperatures (with 5 K intervals) have been calculated and compiled in Tables III and IV.

For several gases, the extremely accurate results of Benson et al.[70] have been made available to us prior to publication. Because of their outstanding precision, we believe that these data merit individual treatment. Tables V and VI summarize the pertinent numbers derived from their data. (Also, see section D.)

C. Thermodynamic Functions

One aspect of the thermodynamic description of aqueous solutions of gases should be emphasized at this point. Unfortunately, the low solubility of nonpolar solutes in water renders direct calorimetric studies rather difficult. It is for this reason that thermodynamic quantities have been extracted almost exclusively from solubility data. Whereas free energies can be most readily derived therefrom, evaluation of $\Delta\bar{H}_2°$ involves a differentiation step, and this imposes some demands on the ac-

TABLE I. Coefficients in the Equation $R \ln x_2 = A + B/T + C \ln (T/K) + DT$[a]

Gas no.	Gas	Temp range T/K	A cal K^{-1} mol^{-1}	B cal mol^{-1}	C cal K^{-1} mol^{-1}	D cal K^{-2} mol^{-1}	% σ[b]	Ref (no. data pts used[c])
1	Helium	273–334	−233.163	8737.84	32.2652	−0.0119726	0.67	72(6), 75(3), 76(5), 73(29), 74(3)
2	Neon	273–339	−310.827	12766.8	43.6185	−0.0127534	0.58	72(6), 76(12), 73(28)
3	Argon	274–347	−336.760	16170.1	46.2117	−0.00608793	0.53	*j*(9), 85(6), 77(15), 72(8), *d*(5), 78(8), 71(1)
4	Krypton	274–348	−270.967	15992.9	33.2892	0.0260485	0.47	72(10), 79(19)
5	Xenon	285–345	−360.119	18744.6	49.0332	−0.00311323	0.67	72(8), 80(3)
6	Radon	276–370	−499.309	25864.2	69.3241	0.00101227	1.6	81d(9), 81e(37)
7	Hydrogen	274–339	−357.802	13897.5	52.2871	−0.0298936	0.44	82(9), *e*(2), 83(5), *f*(1), 84(14)
8	Nitrogen	273–346	−327.850	16757.6	42.8400	0.0167645	0.94	85(5), 86(6), 77(32), 82(7), 87(10)
9	Oxygen	274–348	−286.942	15450.6	36.5593	0.0187662	0.31	77(15), 90(16), 82(7), 87(13), 91(22)
10	Ozone[g]	277–293	*−29.7374*	*3905.44*				*h*(2)
11	Carbon monoxide	273–353	−341.325	16487.3	46.3757		0.68	92(8), 93(1)
12	Carbon dioxide[i]	273–353	−317.658	17371.2	43.0607	−0.00219107	0.54	82(8), 95(8), 94(1)
13	Methane	275–353	−365.183	18106.7	49.7554	−0.000285033	1.8	98(6), *k*(3), 82(7), 92(5), 99(4), 251(4), 304(5), 100(5)
14	Ethane	275–353	−533.392	26565.0	74.6240	−0.00457313	1.6	98(4), 82(6), 92(5), 99(4), 101(5), 100(5)
15	Ethylene	287–346	−303.888	15817.6	40.7591		1.4	82(14)
16	Acetylene	274–343	−311.014	16215.8	42.5305		1.3	*l*(3), *m*(4), *n*(1)
17	Propane	273–347	−628.866	31638.4	88.0808		4.6	98(2), 82(5), 394(3), 99(4), 328(11)
18	Propene	294–361	199.656	−3940.90	−35.8336		27.	*o*(5), 389(1), 390(1)
19	Propyne	273–361	−16821.1	45295.1	2933.82	−4.78664	5.4	*p*(5), *q*(4)
20	Cyclopropane	298–361	649.616	−26880.3	−101.150		7.4	*r*(2), *s*(5), 72(1), *t*(6)
21	*n*-Butane	273–349	−639.209	32785.7	89.1483		7.8	98(2), 82(12), 394(2), 99(4), 328(11), 100(5)
22	Isobutane	278–343	190.982	−4912.98	−34.5102		3.1	*u*(14)
23	1-Butene	311–378	*−59.297*	*12730.6*				*v*(3)
24	2-Methylpropene	273–343	−475.781	25385.0	65.3599		7.6	*w*(11)
25	1,3-Butadiene	298–363	−976.088	50382.7	138.778		16.	*x*(1), *y*(6)
26	Ethylacetylene	273–333	171.933	−5084.59	−29.4809		8.2	*q*(4)
27	Vinylacetylene	273–333	−99.0059	6690.87	10.8969		0.24	*q*(4)
28	Neopentane	288–353	−868.764	43323.6	122.986		6.0	394(3), 251(4)
29	CH_3F	273–353	−270.079	15103.1	36.1231		0.87	102(10), 103(2)
30	CH_3Cl	277–353	−342.796	19412.2	46.5481		6.8	104(5), 102(11), 103(3)
31	CH_3Br	278–353	−325.392	19159.9	43.7970		4.7	105(1), 102(12), 103(3)
32	CF_4	276–323	−644.690	30657.7	90.7528		0.52	106(10)
33	CH_2FCl	283–352	−276.044	16178.1	36.8643		0.36	104(4)
34	CHF_2Cl	297–352	−378.939	25999.6	45.2647	0.0642996	4.1	104(4), 107(3)
34a	CHF_3	298–348	*−37.9627*	*6386.96*				107(3)
34b	$CClF_3$	298–348	*−32.5600*	*3204.55*				107(3)
34c	CCl_2F_2	298–348	*−31.8744*	*3480.07*				107(3)
34d	$CClF_2CF_3$	298–348	*−42.5189*	*5568.80*				107(3)
35	Vinyl chloride	273–348	−240.646	15080.2	30.8852		3.4	*z*(4)
36	C_2F_4	273–343	−367.547	21547.6	45.9952	0.0416536	0.77	*aa*(12)
37	C_3F_6	278–343	−132.311	8925.54	13.7311		1.3	*u*(14)
38	COS[bb]	273–303	−439.589	23896.1	60.3429		0.80	*cc*(4), *dd*(7)
39	CH_3NH_2[ee]	298–333	*−18.2657*	*5180.80*				115(1), 116(1)
40	$(CH_3)_2NH$[ee]	298–333	*−28.0155*	*8000.71*				115(1), 116(1)
41	$C_2H_5NH_2$[ee]	298–333	*−25.0844*	*7210.82*				117(1), 115(1)
42	NH_3[ee]	273–373	−162.446	2179.59	32.9085	−0.119722	6.0	113(51)
43	HN_3[ll]	273–323	222.522	−4868.54	−36.7903		0.50	188(4)
44	NF_3	283–323	−503.754	24595.5	70.0480		0.50	106(9), *gg*(4)
45	N_2F_4	288–318	−682.444	33572.0	96.1500		1.3	*gg*(16)
46	N_2O	273–313	−180.950	13205.8	20.0399	0.0238544	1.4	*e*(5), *f*(1), *hh*(10), *ii*(3), 114(1)
47	NO	273–353	−333.515	16358.8	45.3253	−0.0519354	0.66	92(9)
48	H_2S	273–333	−297.158	16347.7	40.2024	0.00257153	0.42	111(9), 112(11)
49	SO_2	283–386	−29.8850	5709.15	0.601884		3.5	108(42), 109(7), 110(4)
50	SF_6	276–323	−877.854	42051.0	125.018		0.53	106(15)
51	Cl_2	283–313	215.390	−4826.15	−38.1252	0.0177270	2.3	*jj*(4), *kk*(4), 61(5)
52	Cl_2O	273–293	*−14.3490*	*3574.66*				*ll*(3)
53	ClO_2	283–333	112.751	284.523	−21.3532		4.0	*mm*(6), *nn*(3)
54	H_2Se	298–343	−147.799	9197.72	18.2608		1.4	*oo*(24)
55	PH_3	298–323	−309.240	16364.9	41.5653		0.95	*pp*(5)

Table I (*Continued*)

Gas no.	Gas	Temp range T/K	A cal K^{-1} mol^{-1}	B cal mol^{-1}	C cal K^{-1} mol^{-1}	D cal K^{-2} mol^{-1}	% σ[b]	Ref (no. data pts used[c])
56	AsH_3	273–299	−286.171	15437.9	38.0934		2.8	*qq*(19)
57	Air[rr]	273–373	−319.323	15492.6	43.0259	0.0196194	0.56	92(101)

[a] Italicized entries are for the equation $RT \ln x_2 = B + AT$. R is the gas constant, T the thermodynamic temperature, and x_2 the mole fraction solubility at 1 atm partial pressure of the gas. [b] Standard deviation of fit in x_2 as a percentage. Not calculated for two constant fits. [c] The number of data points used for each reference. [d] A. Ben-Naim, *J. Phys. Chem.*, **69**, 3245 (1965). [e] C. J. J. Fox, *Z. Phys. Chem*, **41**, 458 (1902). [f] P. Ruetschi and R. F. Amlie, *J. Phys. Chem.*, **70**, 718 (1966). [g] In aqueous solutions, ozone decomposes slowly. It has been suggested that this behavior might be in part responsible for the divergence of reported solubility data. Details may be found in "Gmelin's Handbuch", Vol. 3, Part **4**, pp 1121, 1147, and 1168, Verlag Chemie, Weinheim/Bergstr., 1960. [h] E. Briner and E. Perrottet, *Helv. Chim. Acta*, **22**, 397 (1939). [i] For the reaction $CO_2 + H_2O = HCO_3^- + H^+$, H. S. Harned and R. Davies [*J. Am. Chem. Soc.*, **65**, 2030 (1943)] found $pK_a = 6.352$ on the molality scale at 25 °C. Their results are within 0.002 of the values of R. Näsänen, *Acta Chem. Scand.*, **1**, 204 (1947). For a recent determination of the apparent first ionization constant of carbonic acid in the temperature range 25–350 °C, and for the pressure range 1–2000 bar, see A. J. Read, *J. Solution Chem.*, **4**, 53 (1975). The true ionization constant for carbonic acid, that is, for the reaction $H_2CO_3 = H^+ + HCO_3^-$, was determined via high-field conductance measurements (up to ca. 200 kV/cm) by D. Berg and A. Patterson, *J. Am. Chem. Soc.*, **75**, 5197 (1953). The constant was found to have the value 1.32×10^{-4} at 25 °C. The fraction of CO_2 present as H_2CO_3 is easily obtained from the ratio of the two ionization constants; at this temperature only about 0.35% of the dissolved gas exists in this form. [j] A. Ben-Naim and S. Baer, *Trans. Faraday Soc.*, **59**, 2735 (1963). [k] A. Lannung and J. Chr. Gjaldbaek, *Acta Chem. Scand.*, **14**, 1124 (1960). [l] R. M. Fild and Yu. F. Golynets, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, **2**, 173 (1959); *Chem. Abstr.*, **53**, 19524 (1959). [m] H. Hiraoka, *Rev. Phys. Chem. Jpn.*, **24**, 13 (1954). [n] J. Billitzer, *Z. Phys. Chem.*, **40**, 535 (1902). [o] A. Azarnoosh and J. J. McKetta, *J. Chem. Eng. Data*, **4**, 211 (1959). [p] R. F. Inga and J. J. McKetta, *ibid.*, **6**, 337 (1961). [q] L. B. Simpson and F. P. Lovell, *ibid.*, 7, 498–500 (1962). [r] S. Imai, *Nara Igaku Zasshi*, **12**, 973 (1961); *Chem. Abstr.*, **55**, 26626 (1961). [s] R. F. Inga and J. J. McKetta, *Pet. Refiner*, **40**, 191 (1961). [t] E. S. Thomsen and J. Chr. Gjaldbaek, *Dan. Tidsskr. Farm.*, **37**, 9 (1963). [u] E. F. Nosov and E. V. Barlyaev, *Zh. Obshch. Khim.*, **38**, 211 (1968). [v] W. B. Brooks and J. J. McKetta, *Pet. Refiner*, **34**, 143 (1955). [w] K. S. Kazanskii, S. G. Entelis, and N. M. Chirkov, *Zh. Fiz. Khim.*, **33**, 1409 (1959). [x] S. Ross and J. B. Hudson, *J. Colloid Sci.*, **12**, 523 (1957). [y] S. S. Hotanahalli and S. B. Chandalia, *Pet. Hydrocarbons*, **5**, 81 (1970). [z] W. Hayduk and H. Laudie, *J. Chem. Eng. Data*, **19**, 253 (1974). [aa] I. E. Volokhonovich, E. F. Nosov, and L. B. Zorina, *Russ. J. Phys. Chem.*, **40**, 146 (1966). [bb] Carbonyl sulfide, COS, is known to react slowly with water: $COS + H_2O = H_2S + CO_2$. The kinetics involved have been investigated first by G. Buchböck, *Z. Phys. Chem.*, **23**, 123 (1897), and in more detail by H. W. Thompson, C. F. Kearton, and S. A. Lamb, *J. Chem. Soc.*, 1034 (1934). See also the review article by R. J. Ferm, *Chem. Rev.*, **57**, 621 (1957). [cc] L. W. Winkler, *Z. Phys. Chem.*, **55**, 344 (1906). [dd] L. W. Winkler, *Math. Termesz. Ertesitö (Budapest)*, **25**, 86 (1907); as cited in "International Critical Tables", Vol. 3, McGraw-Hill, New York, N.Y., 1928, p 261. [ee] Ammonia and the amines are weak bases, that is, they react with water according to $R_3N + H_2O = R_3NH^+ + OH^-$, where R may be hydrogen and/or an organic group such as an alkyl group. The basic ionization constant for this reaction, pK_b, is obtained from the commonly tabulated acidic ionization constant, pK_a, which refers to $R_3NH^+ + H_2O = R_3N + H_3O^+$ via the relation $pK_a + pK_b = pK_w$ where pK_w is 13.999 at 25 °C.[419] For ammonia and the amines listed in this table, the following values for pK_b (in parentheses) on the molality scale have been reported (cf. G. Kortüm, "Lehrbuch der Elektrochemie", 5th ed, Verlag Chemie, Weinheim/Bergstr., 1972, p. 378): NH_3 (4.78), CH_3NH_2 (3.37), $(CH_3)_2NH$ (3.22), and $C_2H_5NH_2$ (3.47). For CH_3NH_2 one of the points was at 1 atm; the other was at 0.03 atm and was extrapolated to 1 atm. For $(CH_3)_2NH$ both points were for pressures less than 0.15 atm and were extrapolated to 1 atm. For $C_2H_5NH_2$ one point was at 1 atm and the other at pressures less than 0.02 atm was extrapolated up to 1 atm. These extrapolations are not strictly valid. A comprehensive compilation of dissociation constants of organic bases in aqueous solution has been prepared by D. D. Perrin: Supplement to *Pure and Applied Chem.*, IUPAC, Butterworths, London, 1965, and (updated) Supplement to *Pure and Applied Chem.*, IUPAC, Butterworths, London, 1972. For dissociation constants of organic acids see G. Kortüm, W. Vogel, and K. Andrussow, *Pure Appl. Chem.*, **1**, 187 (1960). [ff] D'Orazio and Wood[188] determined the solubility of HN_3 at four temperatures, and at various rather small partial pressures at each temperature, as indicated in parentheses: 273.15 K (0.0024–0.044 atm), 297.57 K (0.0083–0.133 atm), 309.10 K (0.014–0.201 atm), and 322.61 K (0.023–0.301 atm). Even at these low pressures significant deviations from Henry's law were observed. Thus, $H_{2,1}$ was determined graphically by the usual extrapolation technique (see section II.A, and in particular eq 5 and 11) by plotting the quotient of pressure and mole fraction against pressure. The resulting values for the Henry's law constant were then subjected to a least-squares analysis: $-R \ln (H_{2,1}/\text{atm}) = A + B/T + C \ln (T/\text{K})$. For the constants the following results were obtained: $A = 210.287$ cal K^{-1} mol^{-1}, $B = -4007.21$ cal mol^{-1}, and $C = -35.1601$ cal K^{-1} mol^{-1}. [gg] C. R. S. Dean, A. Finch, and P. J. Gardner, *J. Chem. Soc., Dalton Trans.*, 2722 (1973). Analysis of the results indicated that N_2F_4 reacts slowly with water during measurements. In order to compensate for this reaction, an exponential increase in reaction rate with time was assumed (see G. L Hurst and S. I. Khayat, *Adv. Chem. Ser.*, **No. 54**, 245 (1966)). [hh] W. Knopp, *Z. Phys. Chem.*, **48**, 97 (1904). [ii] W. Kunerth, *Phys. Rev.*, **19**, 512 (1922). [jj] R. P. Whitney and J. E. Vivian, *Ind. Eng. Chem.*, **33**, 741 (1941). [kk] R. P. Whitney and J. E. Vivian, *Pap. Trade J.*, **113**, 31 (1941). [ll] C. H. Secoy and G. H. Cady, *J. Am. Chem. Soc.*, **63**, 2504 (1941). [mm] J. Kepinski and J. Trzeszczynski, *Rocz. Chem.*, **38**, 201 (1964). [nn] J. F. Haller and W. W. Northgraves, *Tappi*, **38**, 199 (1955). [oo] J.-C. Sisi, C. Dubeau, and N. Ozanne, *J. Chem. Eng. Data*, **16**, 78 (1971). [pp] R. E. Weston, *J. Am. Chem. Soc.*, **76**, 1027 (1954). [qq] F. Jung, *Biochem. Z.*, **302**, 294 (1939). [rr] Calculated values of Winkler.[92]

TABLE II. Solubilities of Gases in D_2O[a]

Gas no.	Gas	Temp range T/K	A cal K^{-1} mol^{-1}	B cal mol^{-1}	C cal K^{-1} mol^{-1}	D cal K^{-2} mol^{-1}	% σ[b]	Ref (no. data pts used)
3	Argon	278–298	−313.404	15804.6	42.0368		0.34	327(5)
12	Carbon dioxide	298–353	−300.530	17046.8	40.1326		2.1	*c*(1), *d*(3)
13	Methane	278–298	−342.830	17362.7	46.2764		0.15	100(5)
14	Ethane	278–298	−434.635	22738.7	59.3212		1.1	100(5)
17	Propane	273–323	−653.181	33049.3	91.5327		0.054	328(11)
21	*n*-Butane	273–323	−885.933	43856.5	125.947		5.9	328(11), 100(5)
29	CH_3F	303–313	*−25.3979*	*3517.37*				103(2)
30	CH_3Cl	303–323	*−28.3609*	*4722.23*				103(3)
31	CH_3Br	303–323	*−28.9453*	*5115.95*				103(3)
48a	D_2S	278–323	436.854	−2932.19	88.4166	0.215304	0.23	112(14)

[a] Coefficients in the equation $R \ln x_2 = A + B/T + C \ln (T/\text{K}) + DT$. Italicized entries are for the equation $RT \ln x_2 = B + AT$. R is the gas constant, T the thermodynamic temperature, and x_2 the mole fraction solubility at 1 atm partial pressure of the gas. [b] Standard deviation of fit in x_2 as a percentage. [c] J. Curry and C. L. Hazelton, *J. Am. Chem. Soc.*, **60**, 2771 (1938). [d] J. Kratochvil, J. Sobr, J. Matous, and J. Pick, *Collect. Czech. Chem. Commun.*, **35**, 3761 (1961).

TABLE III. Solubility Data for Selected Gases in Water Using the Constants in Table I
(Upper value, mole fraction × 10^4, lower value, Ostwald coefficient. Partial gas pressure of 1 atm)

T/K	1 (He)	2 (Ne)	3 (Ar)	4 (Kr)	5 (Xe)	6 (Rn)
273.15	0.07553	0.1004	0.4309	0.8834	1.683	4.235
	0.009396	0.01249	0.05360	0.1099	0.2094	0.5271
278.15	0.07367	0.09484	0.3787	0.7526	1.404	3.395
	0.009334	0.01202	0.04798	0.09536	0.1779	0.4302
283.15	0.07221	0.09031	0.3367	0.6498	1.188	2.773
	0.009311	0.01164	0.04341	0.08378	0.1532	0.3576
288.15	0.07111	0.08663	0.3025	0.5680	1.019	2.306
	0.009325	0.01136	0.03967	0.07449	0.1336	0.3025
293.15	0.07033	0.08367	0.2746	0.5025	0.8840	1.950
	0.009374	0.01115	0.03660	0.06698	0.1178	0.2600
298.15	0.06983	0.08133	0.2516	0.4494	0.7761	1.675
	0.009456	0.01101	0.03407	0.06086	0.1051	0.2268
303.15	0.06960	0.07953	0.2326	0.4062	0.6889	1.460
	0.009569	0.01093	0.03197	0.05585	0.09472	0.2008
308.15	0.06961	0.07819	0.2167	0.3708	0.6177	1.291
	0.009712	0.01091	0.03024	0.05174	0.08619	0.1801
313.15	0.06984	0.07729	0.2036	0.3417	0.5592	1.156
	0.009885	0.01094	0.02881	0.04836	0.07915	0.1636
318.15	0.07029	0.07676	0.1926	0.3176	0.5109	1.048
	0.01009	0.01102	0.02764	0.04558	0.07332	0.1504
323.15	0.07094	0.07659	0.1835	0.2978	0.4708	0.9610
	0.01032	0.01114	0.02669	0.04331	0.06844	0.1398
328.15	0.07179	0.07674	0.1760	0.2813	0.4373	0.8911
	0.01058	0.01131	0.02593	0.04145	0.06443	0.1313
333.15	0.07282	0.07720	0.1698	0.2678	0.4093	0.8349
	0.01087	0.01152	0.02533	0.03996	0.06107	0.1246
338.15	0.07404	0.07796	0.1648	0.2568	0.3859	0.7899
	0.01118	0.01177	0.02488	0.03878	0.05829	0.1193
343.15		0.07900	0.1607	0.2479	0.3663	0.7542
		0.01207	0.02457	0.03788	0.05598	0.1153
348.15			0.1576	0.2408	0.3500	0.7264
			0.02437	0.0722	0.05410	0.1123
353.15						0.7054
						0.1103
358.15						0.6904
						0.1091
363.15						0.6807
						0.1087
368.15						0.6759
						0.1090
373.15						0.6754
						0.1100

T/K	7 (H_2)	8 (N_2)	9 (O_2)	11 (CO)	12 (CO_2)
273.15	0.1758	0.1914	0.3941	0.2851	13.78
	0.02187	0.02381	0.04902	0.03546	1.717
278.15	0.1659	0.1695	0.3458	0.2522	11.42
	0.02101	0.02147	0.04381	0.03195	1.449
283.15	0.1577	0.1519	0.3071	0.2257	9.595
	0.02033	0.01959	0.03960	0.02910	1.238
288.15	0.1510	0.1379	0.2759	0.2042	8.161
	0.01981	0.01808	0.03618	0.02678	1.071
293.15	0.1456	0.1265	0.2505	0.1867	7.023
	0.01941	0.01686	0.03339	0.02489	0.9368
298.15	0.1413	0.1173	0.2298	0.1724	6.111
	0.01913	0.01588	0.03111	0.02334	0.8280
303.15	0.1379	0.1098	0.2127	0.1606	5.373
	0.01895	0.01510	0.02925	0.02208	0.7391
308.15	0.1352	0.1038	0.1988	0.1509	4.771
	0.01887	0.01448	0.02773	0.02105	0.6659
313.15	0.1334	0.09894	0.1873	0.1429	4.275
	0.01887	0.01400	0.02650	0.02022	0.6053
318.15	0.1321	0.09510	0.1779	0.1364	3.864
	0.01896	0.01365	0.02552	0.01957	0.5548
323.15	0.1314	0.09213	0.1702	0.1311	3.522
	0.01912	0.01340	0.02475	0.01906	0.5124
328.15	0.1313	0.08991	0.1640	0.1268	3.235
	0.01935	0.01318	0.02417	0.01869	0.4768

TABLE III (*Continued*)

T/K	7 (H_2)	8 (N_2)	9 (O_2)	11 (CO)	12 (CO_2)
333.15	0.1317	0.08835	0.1592	0.1235	2.994
	0.01965	0.01318	0.02375	0.01843	0.4468
338.15	0.1325	0.08739	0.1554	0.1210	2.789
	0.02002	0.01320	0.02357	0.01828	0.4214
343.15	0.1338	0.08697	0.1527	0.1192	2.616
	0.02045	0.01329	0.02333	0.01822	0.3999
348.15		0.08707	0.1508	0.1181	2.469
		0.01346	0.02332	0.01825	0.3818
353.15			0.1499	0.1175	2.344
			0.02343	0.01837	0.3665
358.15				0.1175	
				0.01857	
363.15					
368.15					
373.15					

T/K	13 (CH_4)	14 (C_2H_6)	15 (C_2H_4)	16 (C_2H_2)	17 (*n*-C_3H_8)	18 (propene)
273.15	0.4605	0.8005		14.05	0.7394	
	0.05729	0.09959		1.750	0.09197	
278.15	0.3979	0.6488		12.11	0.5793	
	0.05041	0.08220		1.536	0.07340	
283.15	0.3483	0.5359	1.224	10.56	0.4644	
	0.04491	0.06910	0.1579	1.363	0.05988	
288.15	0.3086	0.4506	1.077	9.316	0.3803	
	0.04047	0.05909	0.1412	1.223	0.04987	
293.15	0.2767	0.3852	0.9564	8.305	0.3177	1.618
	0.03668	0.05135	0.1275	1.108	0.04235	0.2157
298.15	0.2507	0.3345	0.8581	7.479	0.2704	1.336
	0.03395	0.04530	0.1162	1.013	0.03661	0.1809
303.15	0.2295	0.2948	0.7771	6.798	0.2342	1.104
	0.03156	0.04053	0.1068	0.9352	0.03220	0.1518
308.15	0.2121	0.2633	0.7098	6.233	0.2063	0.9144
	0.02960	0.03674	0.09904	0.8702	0.02878	0.1276
313.15	0.1978	0.2384	0.6537	5.764	0.1845	0.7580
	0.02800	0.03373	0.09253	0.8162	0.02611	0.1073
318.15	0.1860	0.2184	0.6068	5.371	0.1675	0.6293
	0.02670	0.03134	0.08707	0.7712	0.02403	0.09031
323.15	0.1764	0.2024	0.5673	5.043	0.1541	0.5232
	0.02565	0.02943	0.08251	0.7337	0.02241	0.07609
328.15	0.1684	0.1896	0.5340	4.767	0.1437	0.4355
	0.02482	0.02793	0.07869	0.7027	0.02117	0.06417
333.15	0.1620	0.1794	0.5060	4.537	0.1356	0.3630
	0.02417	0.02677	0.07550	0.6772	0.02023	0.05417
338.15	0.1569	0.1715	0.4825	4.344	0.1295	0.3030
	0.02370	0.02590	0.07287	0.6564	0.01955	0.04577
343.15	0.1529	0.1654	0.4626	4.185	0.1249	0.2533
	0.02337	0.02527	0.07071	0.6398	0.01910	0.03872
348.15	0.1499	0.1608	0.4461	4.053	0.1218	0.2120
	0.02317	0.02486	0.06896	0.6268	0.01884	0.03278
353.15	0.1479	0.1577				0.1777
	0.02310	0.02465				0.02778
358.15	0.1465	0.1558				0.1492
	0.02314	0.02462				0.02357
363.15						0.1254
						0.02002
368.15						
373.15						

T/K	19 (propyne)	20 (*c*-C_3H_6)	21 (*n*-C_4H_{10})	22 (isobutane)	24 (2-methylpropene)
273.15	30.22		0.6841	0.3135	2.915
	3.770		0.08511	0.03900	0.3628
278.15	23.18		0.5212	0.2692	2.284
	2.943		0.06604	0.03411	0.2894
283.15	18.77		0.4066	0.2312	1.824
	2.424		0.05243	0.02981	0.2352
288.15	15.85		0.3245	0.1985	1.483
	2.082		0.04255	0.02603	0.1944
293.15	13.83	2.262	0.2644	0.1704	1.226
	1.846	0.3016	0.03524	0.02271	0.1634

TABLE III (***Continued***)

T/K	19 (propyne)	20 (c-C_3H_6)	21 (n-C_4H_{10})	22 (isobutane)	24 (2-methylpropene)
298.15	12.33	2.074	0.2197	0.1463	1.029
	1.671	0.2809	0.02975	0.01982	0.1394
303.15	11.17	1.880	0.1860	0.1257	0.8775
	1.537	0.2585	0.02557	0.01728	0.1207
308.15	10.17	1.684	0.1602	0.1080	0.7585
	1.421	0.2353	0.02235	0.01507	0.1058
313.15	9.286	1.498	0.1403	0.09283	0.6644
	1.315	0.2121	0.01985	0.01314	0.09403
318.15	8.436	1.319	0.1247	0.07981	0.5892
	1.212	0.1893	0.01790	0.01145	0.08455
323.15	7.580	1.151	0.1126	0.06866	0.5287
	1.103	0.1675	0.01637	0.009985	0.07689
328.15	6.705	0.9971	0.1030	0.05909	0.4796
	0.9885	0.1469	0.01517	0.008706	0.07067
333.15	5.804	0.8573	0.09541	0.05088	0.4397
	0.8665	0.1279	0.01423	0.007592	0.06561
338.15	4.917	0.7321	0.08950	0.04384	0.4072
	0.7429	0.1106	0.01352	0.006621	0.06150
343.15	4.036	0.6212	0.08492	0.03780	0.3805
	0.6171	0.09494	0.01298	0.005776	0.05815
348.15	3.220	0.5240	0.08146	0.03260	0.3588
	0.4979	0.08100	0.01259	0.005040	0.05546
353.16	2.487	0.4395	0.07896		
	0.3889	0.06871	0.01234		
358.15	1.842	0.3668			
	0.2910	0.05796			
368.15	1.315	0.3047			
	0.2100	0.04865			
373.15					

T/K	25 (1,3-butadiene)	28 (neopentane)	29 (CH_3F)	30 (CH_3Cl)	31 (CH_3Br)
273.15			22.28		
			2.777		
278.15			18.79	38.94	64.84
			2.384	4.953	8.268
283.15		0.2123	16.03	31.79	52.06
		0.02737	2.070	4.112	6.748
288.15	4.594	0.1649	13.83	26.33	42.41
	0.6027	0.02162	1.816	3.461	5.585
293.15	3.406	0.1316	12.06	22.09	35.02
	0.4541	0.01754	1.609	2.951	4.684
298.15	2.601	0.1077	10.62	18.78	29.28
	0.3523	0.01458	1.439	2.547	3.977
303.15	2.044	0.09022	9.433	16.15	24.78
	0.2811	0.01240	1.298	2.224	3.416
308.15	1.649	0.07731	8.455	14.04	21.21
	0.2302	0.01079	1.181	1.962	2.966
313.15	1.364	0.06765	7.642	12.34	18.35
	0.1931	0.009574	1.082	1.749	2.602
318.15	1.156	0.06037	6.960	10.95	16.04
	0.1658	0.008663	0.9994	1.574	2.305
323.15	1.001	0.05489	6.385	9.815	14.15
	0.1455	0.007983	0.9292	1.429	2.061
328.15	0.8845	0.05079	5.899	8.873	12.60
	0.1303	0.007483	0.8696	1.308	1.859
333.15	0.7976	0.04777	5.485	8.089	11.31
	0.1190	0.007127	0.8188	1.208	1.690
338.15	0.7327	0.04564	5.132	7.432	10.24
	0.1107	0.006893	0.7755	1.123	1.548
343.15	0.6848	0.04424	4.830	6.881	9.340
	0.1047	0.006762	0.7385	1.052	1.429
348.15	0.6509	0.04349	4.571	6.416	8.582
	0.1006	0.006724	0.7069	0.9924	1.328
353.16	0.6284	0.04332	4.348	6.022	7.939
	0.09823	0.006771	0.6800	0.9420	1.242
358.15		0.04367			
		0.006901			
368.15					
373.15					

TABLE III (*Continued*)

T/K	32 (CF_4)	34 (CHF_2Cl)	36 (C_2F_4)	37 (C_3F_6)	38 (COS)
273.15	0.07977			0.1149	10.76
	0.009230			0.01429	1.340
278.15	0.06617			0.09687	8.463
	0.008383			0.01227	1.073
283.15	0.05606		0.4331	0.08238	6.775
	0.007228		0.05584	0.01062	0.8741
288.15	0.04844		0.3711	0.07060	5.517
	0.006353		0.04866	0.009258	0.7239
293.15	0.04265	7.629	0.3230	0.06095	4.565
	0.005684	1.018	0.04305	0.008124	0.6088
298.15	0.03819	6.237	0.2853	0.05298	3.835
	0.005172	0.8450	0.03863	0.007174	0.5194
303.15	0.03477	5.193	0.2556	0.04636	3.267
	0.004781	0.7143	0.03514	0.006374	0.4493
308.15	0.03214	4.399	0.2319	0.04082	
	0.004484	0.6141	0.03236	0.005695	
313.15	0.03014	3.788	0.2132	0.03615	
	0.004265	0.5363	0.03017	0.005116	
318.15	0.02864	3.313	0.1982	0.03219	
	0.004110	0.4756	0.02844	0.004619	
323.15	0.02757	2.940	0.1864	0.02882	
	0.004010	0.4278	0.02710	0.004191	
328.15	0.02686	2.646	0.1771	0.02593	
	0.003957	0.3900	0.02609	0.003820	
333.15		2.413	0.1699	0.02344	
		0.3602	0.02536	0.003497	
338.15		2.229	0.1646	0.02128	
		0.3367	0.02487	0.003214	
343.15		2.083	0.1610	0.01941	
		0.3184	0.02460	0.002966	
348.15		1.969	0.1587	0.01777	
		0.3045	0.02453	0.002748	
353.15		1.881			
		0.2942			
358.15					
363.15					
368.15					
373.15					

T/K	42 (NH_3)	44 (NF_3)	45 (N_2F_4)	46 (N_2O)	47 (NO)	48 (H_2S)	49 (SO_2)	50 (SF_6)
273.15	2771			10.32	0.5904	38.07		0.1178
	476.8			1.286	0.07345	4.754		0.01466
278.15	2583	0.2463		8.500	0.5195	32.18	495.2	0.09164
	441.2	0.03120		1.078	0.06581	4.090	66.01	0.01161
283.15	2398	0.2103		7.084	0.4624	27.55	414.9	0.07335
	406.6	0.02712		0.9140	0.05963	3.562	55.81	0.009457
288.15	2217	0.1826	0.2113	5.972	0.4163	23.87	349.8	0.06032
	373.5	0.02394	0.02771	0.7836	0.05459	3.137	47.53	0.007910
293.15	2043	0.1609	0.1787	5.090	0.3786	20.91	296.6	0.05088
	342.2	0.02145	0.02382	0.6788	0.05046	2.792	40.74	0.006782
298.15	1876	0.1439	0.1541	4.383	0.3477	18.51	252.9	0.04394
	312.7	0.01948	0.02086	0.5937	0.04708	2.510	35.14	0.005950
303.15	1718	0.1304	0.1353	3.811	0.3222	16.54	216.9	0.03881
	285.2	0.01793	0.01861	0.5241	0.04430	2.278	30.48	0.005336
308.15	1569	0.1197	0.1209	3.344	0.3012	14.92	186.9	0.03499
	259.7	0.01670	0.01687	0.4667	0.04202	2.085	26.57	0.004882
313.15	1429	0.1111	0.1098	2.960	0.2838	13.58	161.8	0.03218
	236.0	0.01573	0.01553	0.4190	0.04017	1.925	23.28	0.004554
318.15	1299	0.1044	0.1012	2.642	0.2695	12.46	140.8	0.03014
	214.2	0.01498	0.01452	0.3792	0.03867	1.791	20.49	0.004325
323.15	1178	0.09907			0.2577	11.53	123.0	0.02872
	194.2	0.01441			0.03748	1.678	18.11	0.004177
328.15	1066	0.09496			0.2481	10.74	107.9	0.02782
	175.8	0.01399			0.03655	1.584	16.07	0.004099
333.15	963.2				0.2404	10.08	95.06	
	159.0				0.03586	1.505	14.32	
338.15	868.8				0.2343	9.515	84.05	
	143.7				0.03539	1.438	12.80	
343.15	782.5				0.2297		74.60	
	129.7				0.03510		11.49	

TABLE III (*Continued*)

T/K	42 (NH_3)	44 (NF_3)	45 (N_2F_4)	46 (N_2O)	47 (NO)	48 (H_2S)	49 (SO_2)	50 (SF_6)
348.15	703.8				0.2263		66.44	
	117.0				0.03499		10.34	
353.15	632.2				0.2242		59.37	
	105.5				0.03505		9.336	
358.15	567.2				0.2231		53.22	
	95.02				0.03526		8.454	
363.15	508.4						47.85	
	85.53						7.678	
368.15	455.3						43.16	
	76.94						6.991	
373.15	407.4						39.03	
	69.17						6.383	

T/K	51 (Cl_2)	53 (ClO_2)	54 (H_2Se)	56 (AsH_3)	57 (air)
273.15				3.270	0.2294
				0.4069	0.02853
278.15	29.09			2.777	0.2034
	3.696			0.3519	0.02576
283.15	25.21	325.9		2.386	0.1823
	3.259	43.43		0.3077	0.02351
288.15	21.87	267.6		2.073	0.1652
	2.874	36.06		0.2719	0.02166
293.15	18.98	220.6	16.85	1.820	0.1511
	2.534	30.06	2.250	0.2427	0.02014
298.15	16.48	182.4	15.11	1.614	0.1395
	2.236	25.16	2.049	0.2186	0.01889
303.15	14.33	151.4	13.63	1.445	0.1299
	1.973	21.13	1.876	0.1986	0.01786
308.15	12.47	126.0	12.36		0.1220
	1.741	17.80	1.727		0.01702
313.15	10.86	105.2	11.28		0.1154
	1.538	15.05	1.598		0.01633
318.15	9.461	88.10	10.34		0.1100
	1.359	12.75	1.485		0.01578
323.15		73.99	9.526		0.1055
		10.84	1.387		0.01534
328.15		62.32	8.819		0.1018
		9.239	1.300		0.01501
333.15		52.62	8.200		0.09892
		7.893	1.225		0.01476
338.15			7.657		0.09663
			1.157		0.01459
343.15			7.179		0.09489
			1.098		0.01450
348.15			6.755		0.09366
			1.045		0.01448
353.15					0.09288
					0.01452
358.15					0.09253
					0.01462
363.15					0.09257
					0.01478
368.15					0.09299
					0.01500
373.15					0.09377
					0.01527

curacy of the experimental technique. The situation is even more aggravated in case of the partial molar heat capacity change on solution and higher derivatives. As a consequence, care must be exercised in selecting and weighing data, and subjecting them to rigorous statistical analysis.[67]

To the extent that the approximations discussed in preceding sections are applicable, that is, in particular eq 29, the associated standard changes of thermodynamic functions[10] (cf. sections II.A and II.D) at 1 atm partial gas pressure as derived from eq 35, are given by

$$\Delta\bar{H}_2° = -B + CT + DT^2 \tag{37a}$$

$$\Delta\bar{S}_2° = A + C + C\ln(T/\mathrm{K}) + 2DT \tag{37b}$$

$$\Delta\bar{C}_{P2}° = C + 2DT \tag{37c}$$

$$\left(\frac{\partial\Delta\bar{C}_{P2}°}{\partial T}\right)_P = 2D \tag{37d}$$

Since the quantity $\Delta\bar{C}_{P2}°$ represents the difference in the partial molar heat capacity of the solute in aqueous solution at infinite dilution to that in the ideal gas phase, the partial molar heat capacity of dissolved gas at infinite dilution may be obtained by adding the corresponding ideal gas heat capacity, i.e.

$$\bar{C}_{P2}^{\circ\mathrm{L}} = \Delta\bar{C}_{P2}° + C_{P2}^{*\mathrm{V}} \tag{38}$$

We note that the nature of eq 35 implies that $\Delta\bar{C}_{P2}°$ is a linear function of temperature.

TABLE IV. Solubility Data for Gases in D_2O Using the Constants in Table II
(Upper value, mole fraction × 10^4; lower value, Ostwald coefficient. Partial gas pressure of 1 atm)

T/K	3 (Ar)	12 (CO_2)	13 (CH_4)	14 (C_2H_6)	17 (C_3H_8)
273.15					0.8239 0.1025
278.15	0.4270 0.05409		0.4349 0.05510	0.6983 0.08848	0.6359 0.08057
283.15	0.3756 0.04844		0.3782 0.04876	0.5748 0.07412	0.5026 0.06481
288.15	0.3341 0.04382		0.3328 0.04364	0.4808 0.06305	0.4062 0.05327
293.15	0.3003 0.04002		0.2962 0.03948	0.4082 0.05441	0.3353 0.04469
298.15	0.2724 0.03689	6.142 0.8322	0.2664 0.03607	0.3514 0.04758	0.2822 0.03821
303.15		5.347 0.7355			0.2419 0.03326
308.15		4.701 0.6562			0.2110 0.02944
313.15		4.172 0.5907			0.1871 0.02648
318.15		3.735 0.5362			0.1684 0.02417
323.15		3.372 0.4905			0.1538 0.02237
328.15		3.068 0.4522			
333.15		2.813 0.4198			
338.15		2.597 0.3923			
343.15		2.413 0.3689			
348.15		2.257 0.3490			
353.15		2.124 0.3321			

T/K	21 (n-C_4H_{10})	29 (CH_3F)	30 (CH_3Cl)	31 (CH_3Br)	48a (D_2S)
273.15	0.7749 0.09640				
278.15	0.5725 0.07253				31.87 4.050
283.15	0.4361 0.05624				27.23 3.520
288.15	0.3421 0.04486				23.52 3.091
293.15	0.2756 0.03674				20.52 2.740
298.15	0.2278 0.03084				18.08 2.453
303.15	0.1928 0.02651	9.662 1.330	16.07 2.213	23.03 3.173	16.09 2.216
308.15	0.1668 0.02328	8.789 1.227	14.15 1.978	20.06 2.805	14.46 2.020
313.15	0.1475 0.02087	8.019 1.136	12.51 1.773	17.56 2.489	13.11 1.858
318.15	0.1330 0.01908		11.11 1.596	15.43 2.218	11.99 1.723
323.15	0.1221 0.01776		9.895 1.441	13.61 1.983	11.07 1.611

TABLE V. Coefficients in the Equation $\ln x_2 = a_0 + a_a1/T + a_2/T^2$ for Benson and Krause's Data[a]

Gas	T/K	No. pts	a_0	$a_1 \times 10^{-3}$/K	$a_2 \times 10^{-5}/K^2$	%σ[b]
Helium	274–323	13	−5.0746	−4.1278	6.2725	0.12
Neon	274–323	15	−4.2988	−4.8711	7.9358	0.24
Krypton	275–318	8	−3.6326	−5.6640	11.224	0.11
Xenon	274–318	13	−2.0917	−6.6935	13.417	0.20
Oxygen	274–308	21	−4.0605	−5.4167	10.261	0.024

[a] Reference 70. Coefficients are those calculated by Benson and Krause. T is the thermodynamic temperature and x_2 is the mole fraction solubility at 1 atm partial pressure of thegas. [b] Standard deviation of fit in x_2 as a percentage.

TABLE VI. Gas Solubilities for Benson and Krause's Data Using the Constants in Table V
(Upper value, mole fraction × 10^4; lower value, Ostwald coefficient. Partial gas pressure of 1 atm)

T/K	He	Ne	Kr	Xe	O_2
273.15	0.07660	0.1017	0.8916	1.816	0.3954
	0.009529	0.01266	0.1109	0.2259	0.04918
278.15	0.07449	0.09598	0.7573	1.486	0.3459
	0.009438	0.01216	0.09595	0.1883	0.04383
283.15	0.07289	0.09131	0.6530	1.239	0.3067
	0.009398	0.01177	0.08420	0.1597	0.03955
288.15	0.07172	0.08755	0.5708	1.050	0.2752
	0.009405	0.01148	0.07485	0.1377	0.03609
293.15	0.07092	0.08455	0.5053	0.9032	0.2497
	0.009453	0.01127	0.06735	0.1204	0.03328
298.15	0.07046	0.08218	0.4525	0.7881	0.2288
	0.009540	0.01113	0.06127	0.1067	0.03098
303.15	0.07028	0.08034	0.4095	0.6966	0.2117
	0.009662	0.01105	0.05630	0.09577	0.02910
308.15	0.07038	0.07897	0.3743	0.6230	0.1974
	0.009818	0.01102	0.05222	0.08692	0.02755
313.15	0.07069	0.07800	0.3452	0.5632	
	0.01001	0.01104	0.04885	0.07972	
318.15	0.07124	0.07738	0.3210	0.5144	
	0.01022	0.01110	0.04606	0.07381	
323.15	0.07199	0.07709			
	0.01047	0.01121			

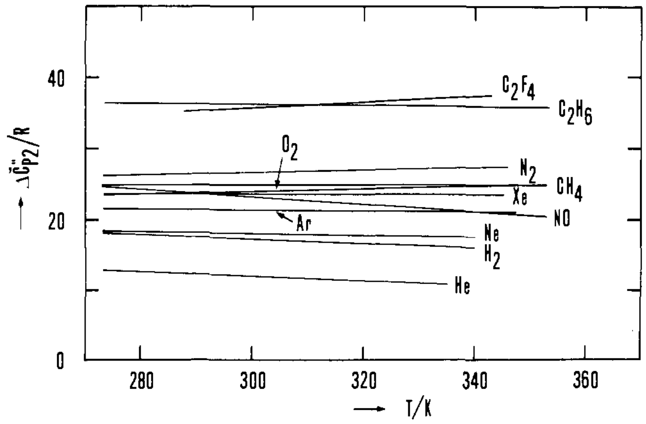

Figure 1. Temperature dependence of the partial molar heat capacity change upon solution, $\Delta C_{P2}°/R$, of several gases in water at constant partial pressure of gas, P_2 = 1 atm. Apparently, for the majority of gases this quantity does not change significantly over the indicated temperature range. (The line for NO should be deleted as the data show no temperature dependence for this gas.)

The standard changes of partial molar enthalpy and entropy, respectively, as derived from eq 36 are

$$\Delta\bar{H}_2° = -B \tag{39a}$$

$$\Delta\bar{S}_2° = A \tag{39b}$$

For gases dissolved in water, Table VII presents the thermodynamic quantities referring to the solution process as calculated from eq 37 and 39. Table VIII is for Benson and Krause's data. Similarly, Table IX contains all results for D_2O. A graphical representation of the change of the partial molar heat capacity at infinite dilution as a function of temperature for some selected gases is shown in Figure 1.

D. Discussion for Individual Systems

Individual comments follow for classes of gases and individual gases. Benson and Krause's results[70] will be discussed at the end of this section.

1. The Rare Gases—He, Ne, Ar, Kr, Xe, Rn

Morrison and Johnstone[72] measured the solubility of He, Ne, Ar, Kr, and Xe in water over about a 70 °C range. Their data on these gases are the most extensive, but, unfortunately, it is not the most accurate when compared with recent highly reliable work. Most other workers measured only one gas, and many workers measured only at one temperature. Comments on individual gases follow.

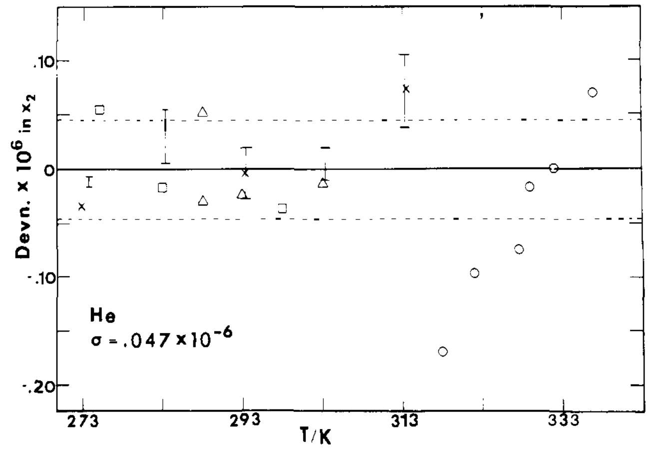

Figure 2. Deviation plot in x_2 for helium. Dashed line indicates one standard deviation from zero: ○, ref 72; □, ref 75; △, ref 76; I-error bars indicate range of closely spaced points from ref 73; X, ref 74.

a. *Helium.* The most precise data are those of Weiss,[73,74] but they only cover the temperature range from 0 to 40 °C. Cady[75] and Lannung's[76] data are close to Weiss' within this temperature range. To extend the temperature range covered, Morrison and Johnstone's[72] high-temperature data were spliced onto the other data used. Figure 2 is a deviation plot for the best fit for helium.

b. *Neon.* For neon, we again spliced the high-temperature Morrison and Johnstone[72] data on to that of Weiss[73] and Lannung.[76]

c. *Argon.* Argon was the most intensively studied of the rare gases, probably because it is relatively inexpensive and also a major constituent of air (about 1% by volume). Some 25 papers were examined for this gas. Morrison and Johnstone[72] had the only reliable high-temperature data. Klots and Benson[77] (2–27 °C) and Murray and Riley[78] (1–35 °C) had the best lower temperature data. These judgments were made on the basis of the reliability of the experimental methods used, the reproducibility

TABLE VII. Gas Solubilities in Water. Partial Molar Gibbs Energy ($\Delta\mu_2^\circ$), Enthalpy ($\Delta\overline{H}_2^\circ$), Entropy ($\Delta\overline{S}_2^\circ$), and Heat Capacity ($\Delta\overline{C}_{P2}^\circ$) of Solution at 283.15, 298.15, 313.13, and 328.15 K, and 1 Atm Partial Pressure of Gas for Selected Gases

	1 (He)	2 (Ne)	3 (Ar)	4 (Kr)	5 (Xe)	6 (Rn)
283.15 K						
$\Delta\mu_2^\circ$/cal mol^{-1}	6661	6535	5795	5425	5085	4608
$\Delta\overline{H}_2^\circ$/cal mol^{-1}	−562	−1438	−3573	−4479	−5110	−6154
$\Delta\overline{S}_2^\circ$/cal K^{-1} mol^{-1}	−25.51	−28.16	−33.09	−34.98	−36.01	−38.01
$\Delta\overline{C}_{P2}^\circ$/cal K^{-1} mol^{-1}	25.49	36.40	42.76	48.04	47.27	69.90
298.15 K						
$\Delta\mu_2^\circ$/cal mol^{-1}	7034	6944	6274	5931	5607	5151
$\Delta\overline{H}_2^\circ$/cal mol^{-1}	−182	−896	−2933	−3752	−4402	−5105
$\Delta\overline{S}_2^\circ$/cal K^{-1} mol^{-1}	−24.20	−26.29	−30.88	−32.48	−33.57	−34.40
$\Delta\overline{C}_{P2}^\circ$/cal K^{-1} mol^{-1}	25.13	36.01	42.58	48.82	47.18	69.93
313.15 K						
$\Delta\mu_2^\circ$/cal mol^{-1}	7388	7325	6722	6400	6093	5641
$\Delta\overline{H}_2^\circ$/cal mol^{-1}	192	−358	−2296	−3014	−3695	−4056
$\Delta\overline{S}_2^\circ$/cal K^{-1} mol^{-1}	−22.98	−24.53	−28.80	−30.06	−31.26	−30.97
$\Delta\overline{C}_{P2}^\circ$/cal K^{-1} mol^{-1}	24.77	35.63	42.34	49.60	47.08	69.96
328.15 K						
$\Delta\mu_2^\circ$/cal mol^{-1}	7724	7680	7139	6833	6545	6081
$\Delta\overline{H}_2^\circ$/cal mol^{-1}	561	173	−1661	−2264	−2990	−3006
$\Delta\overline{S}_2^\circ$/cal K^{-1} mol^{-1}	−21.83	−22.88	−26.82	−27.72	−29.06	−27.70
$\Delta\overline{C}_{P2}^\circ$/cal K^{-1} mol^{-1}	24.41	35.25	42.22	50.38	47.00	69.99

	7 (H_2)	8 (N_2)	9 (O_2)	11 (CO)	13 (CH_4)
283.15 K					
$\Delta\mu_2^\circ$/cal mol^{-1}	6222	6243	5847	6020	5776
$\Delta\overline{H}_2^\circ$/cal mol^{-1}	−1489	−3283	−3594	−3356	−4041
$\Delta\overline{S}_2^\circ$/cal K^{-1} mol^{-1}	−27.23	−33.64	−33.34	−33.11	−34.67
$\Delta\overline{C}_{P2}^\circ$/cal K^{-1} mol^{-1}	35.36	52.33	47.19	46.38	49.59
298.15 K					
$\Delta\mu_2^\circ$/cal mol^{-1}	6616	6727	6328	6499	6276
$\Delta\overline{H}_2^\circ$/cal mol^{-1}	−965	−2495	−2882	−2660	−3297
$\Delta\overline{S}_2^\circ$/cal K^{-1} mol^{-1}	−25.43	−30.93	−30.89	−30.72	−32.11
$\Delta\overline{C}_{P2}^\circ$/cal K^{-1} mol^{-1}	34.46	52.84	47.75	46.38	49.59
313.15 K					
$\Delta\mu_2^\circ$/cal mol^{-1}	6985	7171	6774	6942	6740
$\Delta\overline{H}_2^\circ$/cal mol^{-1}	−455	−1698	−2162	−1965	−2554
$\Delta\overline{S}_2^\circ$/cal k^{-1} mol^{-1}	−23.76	−28.32	−28.53	−28.44	−29.68
$\Delta\overline{C}_{P2}^\circ$/cal K^{-1} mol^{-1}	33.56	53.34	48.31	46.38	49.58
328.15 K					
$\Delta\mu_2^\circ$/cal mol^{-1}	7330	7576	7184	7352	7167
$\Delta\overline{H}_2^\circ$/cal mol^{-1}	42	−894	−1433	−1269	−1810
$\Delta\overline{S}_2^\circ$/cal K^{-1} mol^{-1}	−22.21	−25.82	−26.26	−26.27	−27.36
$\Delta\overline{C}_{P2}^\circ$/cal K^{-1} mol^{-1}	32.66	53.84	48.88	46.38	49.57

	14 (C_2H_6)	15 (C_2H_4)	16 (C_2H_2)	17 (C_3H_8)	18 (propene)
283.15 K					
$\Delta\mu_2^\circ$/cal mol^{-1}	5533	5068	3856	5614	
$\Delta\overline{H}_2^\circ$/cal mol^{-1}	−5802	−4277	−4173	−6698	
$\Delta\overline{S}_2^\circ$/cal K^{-1} mol^{-1}	−40.03	−33.00	−28.36	−43.48	
$\Delta\overline{C}_{P2}^\circ$/cal K^{-1} mol^{-1}	72.03	40.76	42.53	88.08	
298.15 K					
$\Delta\mu_2^\circ$/cal mol^{-1}	6106	5548	4265	6232	5285
$\Delta\overline{H}_2^\circ$/cal mol^{-1}	−4722	−3665	−3535	−5377	−6743
$\Delta\overline{S}_2^\circ$/cal K^{-1} mol^{-1}	−36.32	−30.90	−26.16	−38.94	−40.34
$\Delta\overline{C}_{P2}^\circ$/cal K^{-1} mol^{-1}	71.90	40.76	42.53	88.08	−35.83
313.15 K					
$\Delta\mu_2^\circ$/cal mol^{-1}	6624	5996	4641	6783	5904
$\Delta\overline{H}_2^\circ$/cal mol^{-1}	−3645	−3054	−2897	−4056	−7280
$\Delta\overline{S}_2^\circ$/cal K^{-1} mol^{-1}	−32.79	−28.90	−24.07	−34.61	−42.10
$\Delta\overline{C}_{P2}^\circ$/cal K^{-1} mol^{-1}	71.76	40.76	42.53	88.08	−35.83
328.15 K					
$\Delta\mu_2^\circ$/cal mol^{-1}	7090	6415	4988	7271	6548
$\Delta\overline{H}_2^\circ$/cal mol^{-1}	−2570	−2443	−2259	−2734	−7818
$\Delta\overline{S}_2^\circ$/cal K^{-1} mol^{-1}	−29.44	−26.99	−22.08	−30.49	−43.78
$\Delta\overline{C}_{P2}^\circ$/cal K^{-1} mol^{-1}	71.62	40.76	42.53	88.08	−35.83

TABLE VII (*Continued*)

	19 (propyne)	20 (c-C_3H_6)	21 (n-C_4H_{10})	22 (isobutane)	23 (1-butene)
283.15 K					
$\Delta\mu_2^\circ$/cal mol^{-1}	3533		5688	6006	
$\Delta\underline{H}_2^\circ$/cal mol^{-1}	−6004		−7543	−4859	
$\Delta\underline{S}_2^\circ$/cal K^{-1} mol^{-1}	−33.68		−46.73	−38.37	
$\Delta\underline{C}_{P2}^\circ$/cal K^{-1} mol^{-1}	223.15		89.15	−34.51	
298.15 K					
$\Delta\mu_2^\circ$/cal mol^{-1}	3969	5025	6354	6595	
$\Delta\underline{H}_2^\circ$/cal mol^{-1}	−3733	−3278	−6206	−5376	
$\Delta\underline{S}_2^\circ$/cal K^{-1} mol^{-1}	−25.83	−27.85	−42.13	−40.15	
$\Delta\underline{C}_{P2}^\circ$/cal K^{-1} mol^{-1}	79.55	−101.15	89.15	−34.51	
313.15 K					
$\Delta\mu_2^\circ$/cal mol^{-1}	4344	5480	6954	7211	5838
$\Delta\underline{H}_2^\circ$/cal mol^{-1}	−3617	−4795	−4869	−5894	−12731
$\Delta\underline{S}_2^\circ$/cal K^{-1} mol^{-1}	−25.42	−32.81	−37.75	−41.85	−59.30
$\Delta\underline{C}_{P2}^\circ$/cal K^{-1} mol^{-1}	−64.05	−101.15	89.15	−34.51	0.0
328.15 K					
$\Delta\mu_2^\circ$/cal mol^{-1}	4766	6008	7488	7851	6728
$\Delta\underline{H}_2^\circ$/cal mol^{-1}	−5655	−6312	−3532	−6412	−12731
$\Delta\underline{S}_2^\circ$/cal K^{-1} mol^{-1}	−31.75	−37.54	−33.58	−43.46	−59.30
$\Delta\underline{C}_{P2}^\circ$/cal K^{-1} mol^{-1}	−207.65	−101.15	89.15	−34.51	0.0

	24 (2-methyl-propene)	25 (1,3-butadiene)	26 (ethyl-acetylene)	27 (vinyl-acetylene)	28 (neopentane)
283.15 K					
$\Delta\mu_2^\circ$/cal mol^{-1}	4844		3532	3922	6054
$\Delta\underline{H}_2^\circ$/cal mol^{-1}	−6878		−3263	−3605	−8500
$\Delta\underline{S}_2^\circ$/cal K^{-1} mol^{-1}	−41.40		−24.00	−26.59	−51.40
$\Delta\underline{C}_{P2}^\circ$/cal K^{-1} mol^{-1}	65.36		−29.48	10.90	122.99
298.15 K					
$\Delta\mu_2^\circ$/cal mol^{-1}	5440	4891	3903	4317	6777
$\Delta\underline{H}_2^\circ$/cal *mol*$^{-1}$	−5898	−9006	−3705	−3442	−6655
$\Delta\underline{S}_2^\circ$/cal K^{-1} mol^{-1}	−38.03	−46.61	−25.52	−26.02	−45.05
$\Delta\underline{C}_{P2}^\circ$/cal K^{-1} mol^{-1}	65.36	138.78	−29.48	10.90	122.99
313.15 K					
$\Delta\mu_2^\circ$/cal mol^{-1}	5986	5538	4297	4703	7408
$\Delta\underline{H}_2^\circ$/cal mol^{-1}	−4918	−6924	−4147	−3279	−4811
$\Delta\underline{S}_2^\circ$/cal K^{-1} mol^{-1}	−34.82	−39.80	−26.97	−25.49	−39.02
$\Delta\underline{C}_{P2}^\circ$/cal K^{-1} mol^{-1}	65.36	138.78	−29.48	10.90	122.99
328.15 K					
$\Delta\mu_2^\circ$/cal mol^{-1}	6485	6086	4712	5082	7949
$\Delta\underline{H}_2^\circ$/cal mol^{-1}	−3937	−4843	−4590	−3115	−2966
$\Delta\underline{S}_2^\circ$/cal K^{-1} mol^{-1}	−31.76	−33.30	−28.34	−24.98	−33.26
$\Delta\underline{C}_{P2}^\circ$/cal K^{-1} mol^{-1}	65.36	138.78	−29.48	10.90	122.99

	29 (CH_3F)	30 (CH_3Cl)	31 (CH_3Br)	32 (CF_4)	33 (CH_2FCl)
283.15 K					
$\Delta\mu_2^\circ$/cal mol^{-1}	3621	3236	2958	6804	3050
$\Delta\underline{H}_2^\circ$/cal mol^{-1}	−4875	−6232	−6759	−4961	−5740
$\Delta\underline{S}_2^\circ$/cal K^{-1} mol^{-1}	−30.01	−33.44	−34.32	−41.55	−31.04
$\Delta\underline{C}_{P2}^\circ$/cal K^{-1} mol^{-1}	36.12	46.55	43.80	90.75	36.86
298.15 K					
$\Delta\mu_2^\circ$/cal mol^{-1}	4057	3719	3456	7391	3502
$\Delta\underline{H}_2^\circ$/cal mol^{-1}	−4333	−5534	−6101	−3600	−5187
$\Delta\underline{S}_2^\circ$/cal K^{-1} mol^{-1}	−28.14	−31.04	−32.06	−36.86	−29.14
$\Delta\underline{C}_{P2}^\circ$/cal K^{-1} mol^{-1}	36.12	46.55	43.80	90.75	36.86
313.15 K					
$\Delta\mu_2^\circ$/cal mol^{-1}	4466	4168	3921	7911	3925
$\Delta\underline{H}_2^\circ$/cal mol^{-}	−3791	−4836	−5445	−2238	−4634
$\Delta\underline{S}_2^\circ$/cal K^{-1} mol^{-1}	−26.37	−28.75	−29.91	−32.41	−27.33
$\Delta\underline{C}_{P2}^\circ$/cal K^{-1} mol^{-1}	36.12	46.55	43.80	90.75	36.86
328.15 K					
$\Delta\mu_2^\circ$/cal mol^{-1}	4849	4582	4354	8365	4322
$\Delta\underline{H}_2^\circ$/cal mol^{-1}	−3249	−4137	−4788	−877	−4081
$\Delta\underline{S}_2^\circ$/cal K^{-1} mol^{-1}	−24.68	−26.57	−27.86	−28.16	−25.61
$\Delta\underline{C}_{P2}^\circ$/cal K^{-1} mol^{-1}	36.12	46.55	43.80	90.75	36.86

TABLE VII (*Continued*)

	34 (CHF_2Cl)	35 (vinyl chloride)	36 (C_2F_4)	37 (C_3F_6)	44 (NF_3)
283.15 K					
$\Delta\bar{\mu}_2^\circ$/cal mol^{-1}	3779	3684	5653	6587	6060
$\Delta\bar{H}_2^\circ$/cal mol^{-1}	−8028	−6335	−5185	−5038	−4761
$\Delta\bar{S}_2^\circ$/cal K^{-1} mol^{-1}	−41.70	−35.38	−38.28	−41.05	−38.22
$\Delta\bar{C}_{P2}^\circ$/cal K^{-1} mol^{-1}	81.68	30.89	69.58	13.73	70.05
298.15 K					
$\Delta\bar{\mu}_2^\circ$/cal mol^{-1}	4372	4203	6200	7197	6606
$\Delta\bar{H}_2^\circ$/cal mol^{-1}	−6788	−5872	−4131	−4832	−3711
$\Delta\bar{S}_2^\circ$/cal K^{-1} mol^{-1}	−37.43	−33.79	−34.65	−40.35	−34.60
$\Delta\bar{C}_{P2}^\circ$/cal K^{-1} mol^{-1}	83.61	30.89	70.83	13.73	70.05
313.15 K					
$\Delta\bar{\mu}_2^\circ$/cal mol^{-1}	4903	4698	6693	7798	7099
$\Delta\bar{H}_2^\circ$/cal mol^{-1}	−5520	−5409	−3060	−4626	−2660
$\Delta\bar{S}_2^\circ$/cal K^{-1} mol^{-1}	−33.28	−32.27	−31.14	−39.67	−31.16
$\Delta\bar{C}_{P2}^\circ$/cal K^{-1} mol^{-1}	85.54	30.89	72.08	13.73	70.05
328.15 K					
$\Delta\bar{\mu}_2^\circ$/cal mol^{-1}	5371	5171	7135	8388	7541
$\Delta\bar{H}_2^\circ$/cal mol^{-1}	−4222	−4945	−1969	−4420	−1609
$\Delta\bar{S}_2^\circ$/cal K^{-1} mol^{-1}	−29.23	−30.83	−27.74	−39.03	−27.88
$\Delta\bar{C}_{P2}^\circ$/cal K^{-1} mol^{-1}	87.46	30.89	73.33	13.73	70.05

	46 (N_2O)	47 (NO)	50 (SF_6)	53 (ClO_2)
283.15 K				
$\Delta\bar{\mu}_2^\circ$/cal mol^{-1}	4081	5616	6652	1927
$\Delta\bar{H}_2^\circ$/cal mol^{-1}	−5619	−3525	−6652	−6331
$\Delta\bar{S}_2^\circ$/cal K^{-1} mol^{-1}	−34.26	−32.28	−46.99	−29.16
$\Delta\bar{C}_{P2}^\circ$/cal K^{-1} mol^{-1}	33.55	45.33	125.02	−21.35
298.15 K				
$\Delta\bar{\mu}_2^\circ$/cal mol^{-1}	4581	6083	7308	2372
$\Delta\bar{H}_2^\circ$/cal mol^{-1}	−5110	−2845	−4777	−6651
$\Delta\bar{S}_2^\circ$/cal K^{-1} mol^{-1}	−32.51	−29.94	−40.53	−30.26
$\Delta\bar{C}_{P2}^\circ$/cal K^{-1} mol^{-1}	34.26	45.33	125.02	−21.35
313.15 K				
$\Delta\bar{\mu}_2^\circ$/cal mol^{-1}	5056	6515	7870	2834
$\Delta\bar{H}_2^\circ$/cal mol^{-1}	−4591	−2165	−2902	−6971
$\Delta\bar{S}_2^\circ$/cal K^{-1} mol^{-1}	−30.81	−27.72	−34.40	−31.31
$\Delta\bar{C}_{P2}^\circ$/cal K^{-1} mol^{-1}	34.98	45.33	125.02	−21.35
328.15 K				
$\Delta\bar{\mu}_2^\circ$/cal mol^{-1}		6915	8342	3311
$\Delta\bar{H}_2^\circ$/cal mol^{-1}		−1485	−1026	−7292
$\Delta\bar{S}_2^\circ$/cal K^{-1} mol^{-1}		−25.60	−28.55	−32.31
$\Delta\bar{C}_{P2}^\circ$/cal K^{-1} mol^{-1}		45.33	125.02	−21.35

	55 (PH_3)	56 (AsH_3)	57 (air)
283.15 K			
$\Delta\bar{\mu}_2^\circ$/cal mol^{-1}		4693	6140
$\Delta\bar{H}_2^\circ$/cal mol^{-1}		−4652	−3310
$\Delta\bar{S}_2^\circ$/cal K^{-1} mol^{-1}		−33.00	−33.37
$\Delta\bar{C}_{P2}^\circ$/cal K^{-1} mol^{-1}		38.09	43.03
298.15 K			
$\Delta\bar{\mu}_2^\circ$/cal mol^{-1}	5226	5173	6624
$\Delta\bar{H}_2^\circ$/cal mol^{-1}	−3972	−4080	−2664
$\Delta\bar{S}_2^\circ$/cal K^{-1} mol^{-1}	−30.85	−31.04	−31.15
$\Delta\bar{C}_{P2}^\circ$/cal K^{-1} mol^{-1}	41.57	38.09	43.03
313.15 K			
$\Delta\bar{\mu}_2^\circ$/cal mol^{-1}	5674	5625	7075
$\Delta\bar{H}_2^\circ$/cal mol^{-1}	−3349	−3509	−2019
$\Delta\bar{S}_2^\circ$/cal K^{-1} mol^{-1}	−28.81	−29.17	−29.04
$\Delta\bar{C}_{P2}^\circ$/cal K^{-1} mol^{-1}	41.57	38.09	43.03
328.15 K			
$\Delta\bar{\mu}_2^\circ$/cal mol^{-1}	6091	6049	7496
$\Delta\bar{H}_2^\circ$/cal mol^{-1}	−2725	−2938	−1374
$\Delta\bar{S}_2^\circ$/cal K^{-1} mol^{-1}	−26.87	−27.38	−27.03
$\Delta\bar{C}_{P2}^\circ$/cal K^{-1} mol^{-1}	41.57	38.09	43.03

TABLE VIII. Gas Solubilities in Water Using Benson and Krause's Data. Partial Molar Gibbs Energy ($\Delta\mu_2^\circ$), Enthalpy ($\Delta\bar{H}_2^\circ$), Entropy ($\Delta\bar{S}_2^\circ$), and Heat Capacity ($\Delta\bar{C}_{P2}^\circ$) of Solution at 283.15, 298.15, 313.15, and 328.15 K, and 1 Atm Partial Pressure of Gas

	He	Ne	Kr	Xe	O_2
283.15 K					
$\Delta\mu_2^\circ$/cal mol^{-1}	6656	6529	5422	5062	5847
$\Delta\bar{H}_2^\circ$/cal mol^{-1}	−602	−1459	−4499	−5531	−3639
$\Delta\bar{S}_2^\circ$/cal K^{-1} mol^{-1}	−25.63	−28.21	−35.04	−37.41	−33.50
$\Delta\bar{C}_{P2}^\circ$/cal K^{-1} mol^{-1}	31.09	39.34	55.64	66.51	50.87
298.15 K					
$\Delta\mu_2^\circ$/cal mol^{-1}	7029	6937	5927	5598	6331
$\Delta\bar{H}_2^\circ$/cal mol^{-1}	−159	−899	−3706	−4584	−2914
$\Delta\bar{S}_2^\circ$/cal K^{-1} mol^{-1}	−24.11	−26.28	−32.31	−34.15	−31.01
$\Delta\bar{C}_{P2}^\circ$/cal K^{-1} mol^{-1}	28.04	35.48	50.18	59.99	45.88
313.15 K					
$\Delta\mu_2^\circ$/cal mol^{-1}	7380	7319	6393	6089	6779
$\Delta\bar{H}_2^\circ$/cal mol^{-1}	242	−392	−2990	−3727	−2259
$\Delta\bar{S}_2^\circ$/cal K^{-1} mol^{-1}	−22.79	−24.62	−29.96	−31.35	−28.86
$\Delta\bar{C}_{P2}^\circ$/cal K^{-1} mol^{-1}	25.42	32.16	45.49	54.38	41.59
328.15 K					
$\Delta\mu_2^\circ$/cal mol^{-1}	7713	7677	6827	6540	7198
$\Delta\bar{H}_2^\circ$/cal mol^{-1}	606	68	−2338	−2949	−1664
$\Delta\bar{S}_2^\circ$/cal K^{-1} mol^{-1}	−21.66	−23.19	−27.93	−28.92	−27.00
$\Delta\bar{C}_{P2}^\circ$/cal K^{-1} mol^{-1}	23.15	29.29	41.43	49.52	37.87

TABLE IX. Gas Solubilities in D_2O. Partial Molar Gibbs Energy ($\Delta\mu_2^\circ$), Enthalpy ($\Delta\bar{H}_2^\circ$), Entropy ($\Delta\bar{S}_2^\circ$), and Heat Capacity of Solution ($\Delta\bar{C}_{P2}^\circ$) at 283.15, 298.15, 313.15, and 328.15 K, and 1 Atm Partial Pressure of Gas for Selected Gases

	3 (Ar)	13 (CH_4)	14 (C_2H_6)	17 (C_3H_8)	21 (n-C_4H_{10})	29 (CH_3F)	30 (CH_3Cl)	31 (CH_3Br)
283.15 K								
$\Delta\mu_2^\circ$/cal mol^{-1}	5733	5729	5494	5569	5649			
$\Delta\bar{H}_2^\circ$/cal mol^{-1}	−3902	−4260	−5942	−7132	−8195			
$\Delta\bar{S}_2^\circ$/cal K^{-1} mol^{-1}	−34.03	−35.28	−40.39	−44.86	−48.89			
$\Delta\bar{C}_{P2}^\circ$/cal K^{-1} mol^{-1}	42.04	46.28	59.32	91.53	125.9			
298.15 K								
$\Delta\mu_2^\circ$/cal mol^{-1}	6227	6241	6077	6207	6333	4055	3734	3514
$\Delta\bar{H}_2^\circ$/cal mol^{-1}	−3271	−3565	−5052	−5759	−6305	−3517	−4722	−5116
$\Delta\bar{S}_2^\circ$/cal K^{-1} mol^{-1}	−31.86	−32.89	−37.33	−40.13	−42.39	−25.40	−28.36	−28.95
$\Delta\bar{C}_{P2}^\circ$/cal K^{-1} mol^{-1}	42.04	46.28	59.32	91.53	125.9	0.0	0.0	0.0
313.15 K								
$\Delta\mu_2^\circ$/cal mol^{-1}				6775	6923			
$\Delta\bar{H}_2^\circ$/cal mol^{-1}				−4386	−4416			
$\Delta\bar{S}_2^\circ$/cal K^{-1} mol^{-1}				−35.64	−36.21			
$\Delta\bar{C}_{P2}^\circ$/cal K^{-1} mol^{-1}				91.53	125.9			
328.15 K								
$\Delta\mu_2^\circ$/cal mol^{-1}				7277	7421			
$\Delta\bar{H}_2^\circ$/cal mol^{-1}				−3013	−2527			
$\Delta\bar{S}_2^\circ$/cal K^{-1} mol^{-1}				−31.36	−30.32			
$\Delta\bar{C}_{P2}^\circ$/cal K^{-1} mol^{-1}				91.53	125.9			

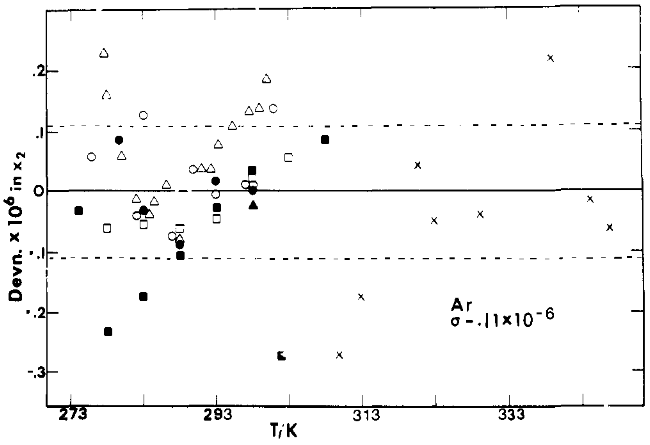

Figure 3. Deviation plot for argon. ○, A. Ben-Naim and S. Baer, *Trans. Faraday Soc.*, **59**, 2735 (1963); □, ref 85; △, ref 77; X, ref 72; ●, A. Ben-Naim, *J. Phys. Chem.*, **69**, 3245 (1965); ■, ref 78; ▲, ref 71.

of each worker's own work, and the reproducibility between workers. Six of the papers rejected had measurements at only one temperature, and two were at two temperatures. However, all eight of these papers had data which differed from the smoothing equation of the seven papers used by more than 2%. One standard deviation for all of the data used for the smoothing equation corresponded to 0.53% fit in the mole fraction solubility. A deviation plot for argon is shown in Figure 3 where the dashed lines mark the boundary of ±1 standard deviation. The data from other papers were rejected because of 2% or more deviation from the smoothing equation, overall poor precision in the original measurements, or highly erratic fitting of the points to the smoothing equation, i.e., too much scatter in the data. The analysis for other gases was similar to this treatment for the data for argon.

d. *Krypton.* The data of Weiss[79] and Morrison and Johnstone[72] were combined to give the best fit here.

e. *Xenon.* The data of Morrison and Johnstone[72] and Yeh and Peterson[80] were combined for xenon.

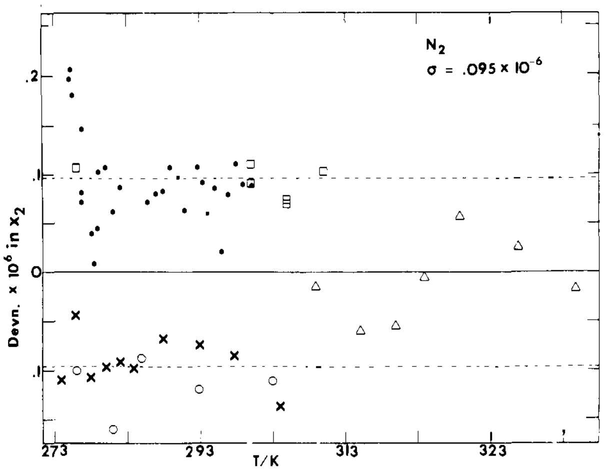

Figure 4. Deviation plot in x_2 for nitrogen: ○, ref 85; □, ref 86; △, ref 82; X, ref 87; ●, ref 77.

f. *Radon.* Most people cite Valentiner[81] as the source of data on radon solubilities, although Valentiner (and Antropoff[81a] and Schulze[81b]) used the smoothed results of earlier workers reported by Meyer[81c] in a review article. We smoothed the data of Kofler[81d] and Szeparowicz.[81e] Earlier, preliminary results of Kofler are reported in ref 81f. Other sources of data on radon solubilities which we did *not* use in our smoothing are from Hofmann,[81g] Boyle,[81h] and Ramstedt.[81i]

2. The Permanent Gases—H_2, N_2, O_2, CO, CO_2

a. *Hydrogen.* Both Morrison and Billett[82] (12–72 °C) and Winkler[83] (1–50 °C) measured hydrogen solubilities over wide temperature ranges. The best recent measurements are those of Crozier[84] (1-29 °C). (We could not find any data for D_2 solubilities in water.)

b. *Nitrogen.* Morrison and Billett's[82] high-temperature (5-73 °C total range, 36–73 °C used for fitting) data were added to those of Douglas,[85] Farhi et al.,[86] Klots and Benson,[77] and Murray et al.[87] The latter values were tripled to give them equal weight with those of Klots and Benson. A deviation plot for nitrogen is given in Figure 4.

c. *Oxygen.* Oxygen is one of the two gases whose solubilities in water have been determined by both chemical and physical methods. Including Winkler[88,89] (whose data we did *not* use), the chemical approach was restricted to the range 0 to 37 °C. The chemical data used were those of Montgomery et al.,[90] Murray et al. (values doubled),[87] and Carpenter.[91] There were many more determinations made via physical approaches. The best data were those of Klots and Benson,[77] Morrison and Billett[82] (only used above 30 °C), and Murray et al.[87] The last set of values were tripled to give equal weight with those of Klots and Benson. Figure 5 shows the deviation plot with the chemically arrived at data indicated by the filled-in symbols and the physical by open symbols. There appeared to be no systematic deviations between physical and chemical methods. Also, the oxygen data were fit to a standard deviation of about 0.3% in the mole fraction for all of the data used. Of the common gases, the solubility of oxygen in water is the most reliably known. *We recommend that our critically selected data (and the fitting function) be used as standards for comparison and for checking gas solubility apparatuses.*

d. *Carbon Monoxide.* There appear to be no modern measurements of this gas in water. So we used the data generated around the turn of the century by Winkler[89,92] and Christoff.[93] The solubility of carbon monoxide in water needs to be remeasured using modern techniques.

e. *Carbon Dioxide.* The solubility of carbon dioxide was determined by a great many workers, most frequently at the single temperature of 25 °C. We chose to use Morrison and Billett's[82] high-temperature values and the Weiss recalculated[94] values of the original measurements of Murray and Riley.[95] Weiss took into account corrections for nonideal behavior in the gas phase and for dissociation in distilled water in his recalculation. (Weiss' paper[94] also deals with the solubility of carbon dioxide in seawater.) A deviation plot for this system is Figure 6. As a parting observation to this section, we note that although Bunsen[59–62] made many measurements on a wide variety of gases, we did not use any of his data for this review.

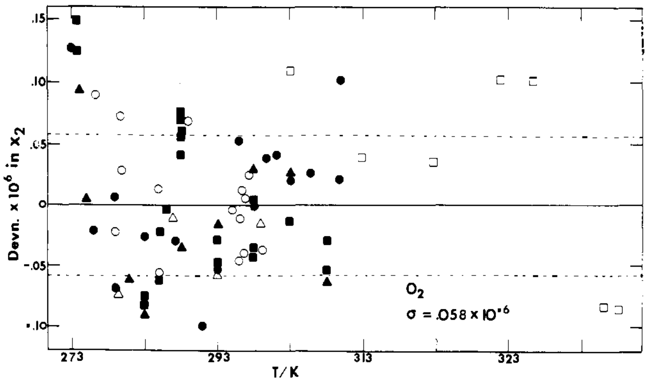

Figure 5. Deviation plot in x_2 for oxygen. Filled in symbols are for chemical methods, and open symbols are for physical methods: ○, ref 77; □, ref 82; △, ref 87; ●, ref 90; ▲, ref 87; ■, ref 91.

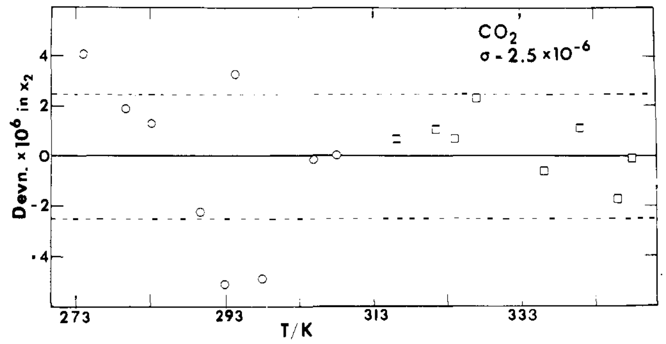

Figure 6. Deviation plot in x_2 for carbon dioxide: ○, ref 94; □, ref 82.

3. Hydrocarbon Gases

McAuliffe[96,97] measured the solubilities of many hydrocarbon gases in water via a gas chromatographic technique but, unfortunately, most of his data are only qualitative in nature. Bunsen's[59–62] measurements were all also rejected.

a. *Methane.* We used Morrison and Billett's[82] and Winkler's[92] data above 35 °C to extend the temperature range. Other contributors are noted in Table I.

b. *Ethane.* Reliable data were obtained from Claussen and Polglase,[98] Wen and Hung,[99] Ben-Naim and coworkers,[100,101] and Morrison and Billett.[82]

c. *Propane.* Morrison and Billett[82] supplied the high-temperature data for fitting.

d. *Butane.* All sources except McAuliffe[96,97] were used here since the agreement was good.

e. *Cyclopropane.* There were relatively few measurements for this gas, and we used almost all of them. The agreement was poor, but there were no decent criteria for improving the choice.

f. *Other Hydrocarbons.* No special comments; see Table I for citations.

4. Halogen-Containing Gases

a. *Methyl Halides.* The data of Glew and Moelwyn-Hughes[102] were used for CH_3F, CH_3Cl, and CH_3Br and covered the widest range of temperature (ca. 0 to 80 °C). In addition, Swain and

Thorton's data[103] were used for these gases, Boggs and Buck[104] for CH_3Cl alone, and Haight[105] for CH_3Br.

b. *NF_3, CF_4, and SF_6.* We considered the work of Ashton et al.,[106] to be the only reliable data for these gases.

c. *Freons.* Parmelee[107] is the main source for solubilities of the "freons" ($CHClF_2$, CCl_2F_2, $CClF_2CF_3$, $CClF_3$, CHF_3) in water. His measurements are of poor precision.

5. Sulfur-Containing Gases

a. *Sulfur Dioxide.* There were many measurements, but the most reliable were those of Beuschlein and Simenson,[108] Hudson,[109] and the recent measurements of Tokunaga.[110]

b. *Hydrogen Sulfide.* We judged the data of Wright and Maass[111] and Clarke and Glew[112] to be the most reliable.

6. Nitrogen-Containing Gases

a. *Ammonia.* We felt the early extensive data of Sims[113] to be the most reliable.

b. *Nitrous Oxide* (*N_2O*). The data of several early workers and one recent single temperature measurement[114] were used here.

c. *Nitric Oxide* (*NO*). The best data here were those of Winkler.[89,92]

d. *Amines.* For the methyl- and ethylamines we used the data of Doyer,[115] Felsing and Phillips,[116] and Dailey and Felsing.[117]

7. Air

There appear to be no modern wide temperature range experimental determinations of the solubility of air in water. Thus, we present only the values *calculated* by Winkler[92] from his experimental N_2 and O_2 solubilities, which, however, should be a fair approximation to directly measured solubilities (see section IV.E.1).

8. Benson and Krause's[70] Data on He, Ne, Kr, Xe, and O_2

Benson and Krause use an apparatus in which they determine the amount of gas in a dry state which was dissolved in a saturated aqueous solution. Corrections for gas imperfections are readily made. They estimate the overall precision of their data to be of the order of 0.02%. This is borne out in Table V where their fit of their data is of the same order. However, the constants reported in Table V, the solubilities in Table VI, and the thermodynamic functions in Table VIII are to be considered *tentative* since they are continuing to improve their measurements. For these gases Benson and Krause's data are probably the best available. We have treated their data separately because of its tentative nature, but felt it was important to report them in this review.

IV. Discussion

A. Introductory Remarks

If chemically reacting gases are put aside, water appears, in comparison with the majority of organic liquids, to be a rather poor solvent for gases. Partial molar enthalpy, entropy, and heat capacity changes upon solution show exceptional values, a circumstance which has been amply discussed in the literature (cf. Introduction, and in particular references 7–9, and the valuable articles by Klapper[118] and Franks and Reid[119]). A further important difference is that the partial molar volume of most solutes in water does *not* differ significantly from the molar volume at the respective normal boiling point,[120–123] as compared to the substantial increases observed with nonpolar liquids.[124–127] Measurement of partial molar volumes of gases dissolved in liquids is quite difficult, a fact which is reflected by the scarcity of experimental results. A survey by Lyckman et al.[128] resulted in a rough linear correlation between the reduced quantities $\bar{V}_2^{\circ L}P_{c2}/(RT_{c2})$ vs. $TP_{c2}/(c_1T_{c2})$. Here P_{c2} and T_{c2} are the critical pressure and temperature, respectively, of the gas, and c_1 denotes the cohesive energy density of the solvent, which quantity may often be approximated by the ratio of the energy of vaporization over molar volume, i.e., $c_1 = \Delta U_1^{vap}/V_1^{\circ L}$. However, for expanded solvents, that is, for solvents at temperatures not far removed from T_{c1}, the partial molar volume of the gas tends to be much larger than that derived by the correlation.[17] As to the chemical nature of the solvents, they ranged from nonpolar *n*-heptane to perfluoro-*n*-heptane and highly polar water. A quite general correlation for partial molar volumes of gases at infinite dilution on the basis of a corresponding states formulation was given by Brelvi and O'Connell.[129] For nonpolar liquids, Schumm and Brown[130] have suggested a correlation between $\bar{V}_2^{\circ L}/V_1^{\circ L}$ and the Hildebrand solubility parameter $\delta_1 = c_1^{1/2}$ of the solvent. It is against this background that the discussion will be carried out.

TABLE X. Comparison of Calorimetric Enthalpies of Solution with Those Derived from Solubility Measurements[a]

	$-\Delta \bar{H}_2^\circ$/kcal mol^{-1}				
		Gas solubility			
Solute	Calorimetry[132]	V[81]	L[76]	B[b]	W[c]
Neon	1.4	1.83	0.81	0.94	0.90
Argon	2.88	2.74	2.59		2.93
Krypton	3.78	3.69		3.77	3.75
Xenon	4.12	4.29		4.65	4.40

[a] All values for 298.15 K. [b] Table VIII, from ref 70. [c] This work, Table VII.

Results on the Henry's law constant contain less information referring to a binary system than a full excess Gibbs energy curve, G^E, over the whole concentration range. But in some sense they offer more information than the usual excess Gibbs energy data which are generally determined at much higher solute concentration. This is so since essentially a single solute molecule is introduced into the solvent and no direct interactions between solute molecules are possible. Thus, the Henry's law constant provides direct information on the unlike interactions solute–solvent. Although interactions between like solvent molecules also enter, it has been assumed in many cases that their contribution to $H_{2,1}$ is insignificant. However, quite recently, Neff and McQuarrie[131] have shown that the effect on solvent–solvent interaction while adding one solute molecule to the liquid cannot be neglected (see section IV.C).

As already indicated, a general disadvantage of deriving $\Delta \bar{C}_{P2}^\circ$, and to a lesser extent $\Delta \bar{H}_2^\circ$, from solubilities is that values obtained by this method can be greatly in error. Thus, it would be eminently useful to be able to compare such derived quantities with corresponding results obtained calorimetrically. In spite of the experimentally quite formidable task, two such studies have been reported: 56 nonaqueous gas–solvent systems have been investigated by Jadot,[131a] whereas Alexander[132] has determined the partial molar enthalpy of solution $\Delta \bar{H}_2^\circ$ for Ne, Ar, Kr, and Xe, respectively, in water at 25 °C. Table X compares his results with those obtained from solubility measurements. With the exception of Ne, agreement is satisfactory. However, in view of the very low solubility of this rare gas and the associated experimental difficulties, this is not too surprising. Apparently no other measurements of this sort have been made with any gases apart from those of very high solubility, such as ammonia.[132a–c] However, in these cases the usual treatment of data is inapplicable anyway (see section II.E).

Since water is such a unique and important solvent, a few words concerning our knowledge of the structure of the pure liquid seem to be in order. An excellent and timely introduction to a molecular theory of both water and aqueous solutions has recently been presented by Ben-Naim.[133] Although water is the most common liquid on earth, no theory developed so far explains all its properties quantitatively. Roughly, one may divide current model theories into two categories. The first group comprises the "continuum" models,[134-136] whereas the second group regards water from the point of view of "mixture" models.[137-139] A particularly valuable statistical-mechanical contribution to the mixture-model approach in terms of quasi-component distribution functions was given by Ben-Naim.[140-142] For a recent interstitial model of fluid water, see Bell and Sallouta.[143] Before leaving this subject, we note some recent theoretical developments exploiting the possibilities of computer experiments. The most important contributions to clarify at least some issues of the water problem resulted from work of Rahman and Stillinger[144] utilizing a model for the water molecule described by Ben-Naim and Stillinger[145] (based on the Bjerrum four-point-charge model for a water molecule[146]), and from the efforts of Barker and Watts[147] whose calculations were based on the Rowlinson model.[148] Any pair potential for liquid water should be constructed in such a way as to favor configurations consistent with tetrahedral geometry. In the Ben-Naim–Stillinger model the four point charges are located at the vertices of a regular tetrahedron, with its center coincident with the center of the molecule. By combining coulombic with dispersion interaction of the Lennard-Jones type, an effective pair potential[148a] displaying some characteristics of a hydrogen bond potential is obtained. It induces preferential bonding along directions pointing from the center toward the four vertices of the tetrahedron. For numerical results, see also Ben-Naim.[149] Models of liquid water in the tradition of the cell theory of fluids have been presented by Weissman and Blum[149a] and more recently by Weres and Rice,[149b] whose detailed investigation includes treatment of the structural (orientational) entropy contribution. These latter authors also discuss rather extensively the deficiencies of several other approaches such as those of Bell,[143a] Angell,[149c] and Ben-Naim and Stillinger.[145]

There exist a number of excellent review articles on the theory of liquid water of which we will cite a few recent ones (in chronological order): Ben-Naim,[150] Frank,[151] Gibbs et al.,[152] Perram and Levine,[153] Nemethy,[154] Ben-Naim,[155] and Rice.[155a] A very useful critical survey on restrictions for an acceptable model for water has been given by Frank.[156] Within the framework of a general review on recent developments in liquid-state physics, various aspects of the state of the art with respect to water have been discussed in some detail by Kohler, Wilhelm, and Posch[157] (see also the chapter on liquid water in Kohler's monograph on liquids[158]).

Various experimental techniques have been used to obtain information on the structure of water. Particularly valuable have been the Raman and infrared spectral investigations, x-ray and neutron scattering methods, and NMR studies. An excellent collection of pertinent contributions in all these areas of research can be found in Franks,[159] Luck,[160] and Walrafen.[161] An ambitious effort to comprehensively survey the theory of, as well as experimental techniques dealing with, the hydrogen bond in general and with water in particular is the three-volume work edited by Schuster, Zundel, and Sandorfy.[161a]

In the next section we discuss several semiempirical methods for correlating solubility and derived thermodynamic quantities with various macroscopic properties[10,14] which generally refer to the dissolved gas. This will be followed by an appraisal of more rigorous approaches and a few consequences resulting therefrom. A discussion of various aspects of solution thermodynamics in deuterium oxide will be deferred to section IV.D.

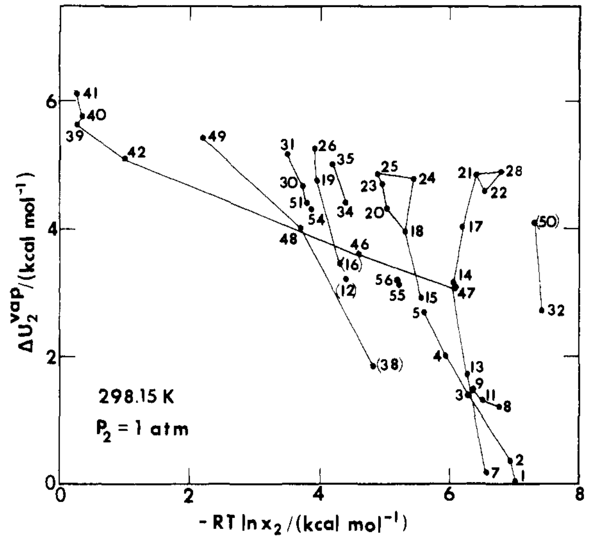

Figure 7. Plot of the energy of vaporization, ΔU_2^{vap}, of gases at the normal boiling point against their solubility in water, $-RT \ln x_2$, at 298.15 K and 1 atm partial gas pressure. The significance of the numbers is: 1, He; 2, Ne; 3, Ar; 4, Kr; 5, Xe; 6, Rn; 7, H_2; 8, N_2; 9, O_2; 10, O_3; 11, CO; 12, CO_2; 13, CH_4; 14, C_2H_6; 15, C_2H_4; 16, C_2H_2; 17, C_3H_8; 18, C_3H_6; 19, C_3H_4; 20, c-C_3H_6; 21, n-C_4H_{10}; 22, isobutane; 23, 1-butene; 24, 2-methylpropene; 25, 1,3-butadiene; 26, ethylacetylene; 27, vinylacetylene; 28, neopentane; 29, CH_3F; 30, CH_3Cl; 31, CH_3Br; 32, CF_4; 33, CH_2FCl; 34, CHF_2Cl; 34a, CHF_3; 34b, $CClF_3$; 34c, CCl_2F_2; 34d, $CClF_2CF_3$; 35, vinyl chloride; 36, C_2F_4; 37, C_3F_6; 38, COS; 39, CH_3NH_2; 40, $(CH_3)_2NH$; 41, $C_2H_5NH_2$; 42, NH_3, 43, HN_3; 44, NF_3; 45, N_2F_4; 46, N_2O; 47, NO; 48, H_2S; 49, SO_2; 50, SF_6; 51, Cl_2; 52, Cl_2O; 53, ClO_2; 54, H_2Se; 55, PH_3; 56, AsH_3; 57, air.

B. Semiempirical Correlations

From a practical viewpoint, semiempirical correlations have an advantage over more fundamental methods in that they yield reasonable answers with a minimum of information and effort. For example, one may correlate the solubility in a particular solvent with the energy of vaporization at the normal boiling point of the gas, i.e., $RT \ln x_2$ vs. ΔU_2^{vap}. This plot was introduced by Hildebrand[162-164] to replace the "force constants" derived from gas imperfections or transport properties on the basis of an assumed pair potential. As can be seen from Figure 7, the resulting correlation for water is much less satisfactory compared to any case involving a nonpolar solvent,[10,12,14] since a priori it is not always clear in what position relative to the others a particular gas, whose solubility is to be estimated, should be placed.

Essentially similar behavior is found with plots of $\ln x_2$ vs. α_2 (polarizability), $\ln x_2$ vs. σ_2 (hard-sphere diameter), and $\ln x_2$ vs. T_{b2} (normal boiling temperature), or T_{c2} (critical temperature), respectively. The graphs show considerable scatter as evidenced by the representative Figures 8 (α_2) and 9 (T_{c2}).

An interesting extension of earlier work[165,166] to include highly polar and hydrogen bonded solvents was reported by Hayduk and Laudie.[167] Based on the empirical concept of hydrogen-bonding factors expressed as (for a specific gas dissolved in a particular solvent)

$$\chi_{\text{solvent}} = x_2/x_2^{\text{ideal}} \tag{40}$$

where x_2^{ideal} denotes the ideal mole fraction solubility, simple, nearly linear relations between the logarithms of χ_{solvent} and log χ_{ref} of a suitable reference substance, such as water or acetone, were obtained. Since the ideal gas solubility is known and χ_{solvent} may be extracted from the correlation for any desired gas, solubilities can be estimated, apparently with a fair degree of agreement. (Here an ideal gas solubility is based on the assumption of an ideal gas phase, an ideal solution, and no Poynting correction required (that is essentially Raoult's law is assumed): $x_2^{\text{ideal}} = P_2/P_2^\circ$ where P_2° is the vapor pressure of pure liquified

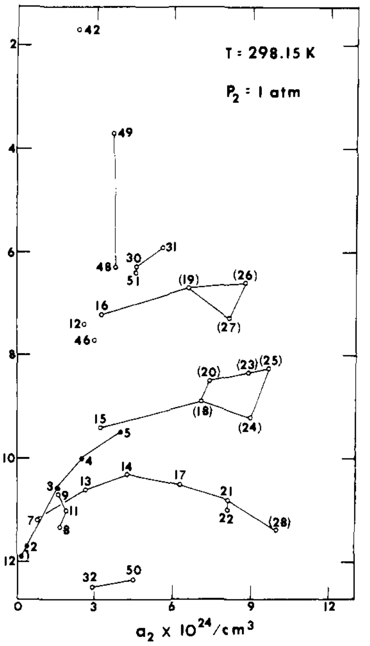

Figure 8. Graph of solubility in water as $-\ln x_2$ against the average polarizability α_2, of the gas. Partial gas pressure of 1 atm at 298.15 K. (See Figure 7 caption for key to numbers.)

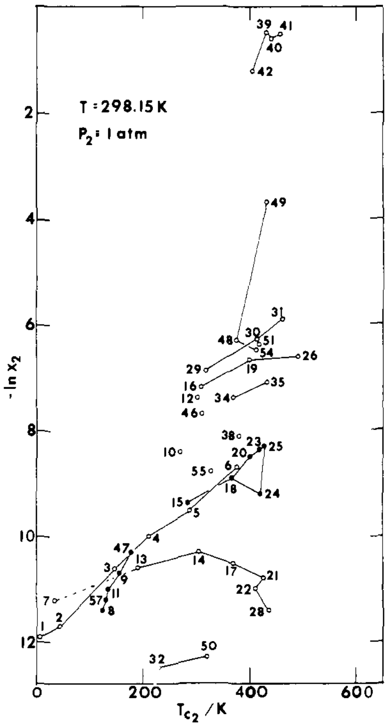

Figure 9. Solubility of gases at 1 atm partial pressure and 298.15 K as $-\ln x_2$ against T_{c2}, the critical temperature of the gas. (See Figure 7 caption for key to numbers.)

gas.) Extrapolation of solubilities in associated solvents to other temperatures is suggested via plots of log x_2 vs. log (T/K). From the evidence presented, it appears that at the solvent critical temperature the solubilities for all gases tend to a common value which is characteristic for a given solvent.

However, to date a really successful general and simple correlation for the solubility of gases in water is still lacking. This is clearly in contrast to the situation with nonpolar liquids.[162-165,168-170] (For a detailed discussion see ref 10 and 14.)

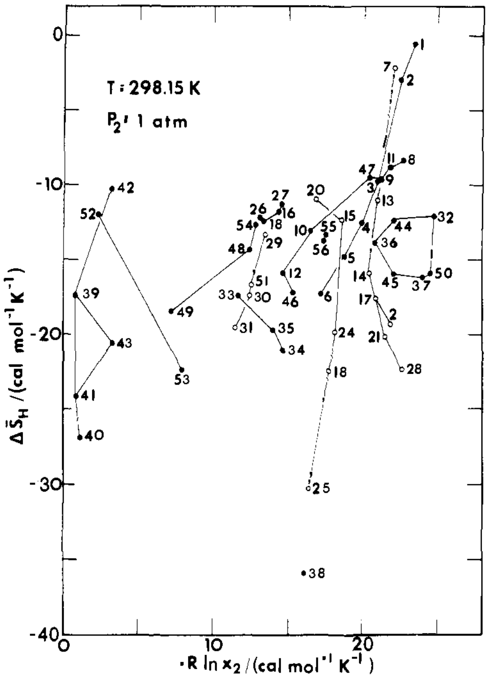

Figure 10. Difference between the partial molar entropy of dissolved gas (equilibrium mole fraction x_2) and the molar entropy of gas in its standard state, i.e., $\Delta\bar{S}_H = \bar{S}_2^L - S_2^{*V}$, plotted against the solubility expressed as $-R \ln x_2$ at 298.15 K and 1 atm partial gas pressure. (See Figure 7 caption for key to numbers.)

To some extent the above statements are also valid for the standard entropy change upon solution. In water, this quantity does not follow the general pattern usually observed in nonpolar (or slightly polar) solvents.[58,125,171-177] This is clearly depicted in Figure 10, where we plotted the difference between the partial molar entropy of dissolved gas (equilibrium mole fraction x_2) and the molar entropy of gas in its gaseous standard state, i.e., $\bar{S}_2^L - S_2^{*V}$, against the solubility expressed as $-R \ln x_2$ at 298.15 K and 1 atm partial gas pressure. For nonpolar or slightly polar liquids this plot gives a reasonably straight line whose intercept at $-R \ln x_2 = 0$ is remarkably close to -21.0 cal K^{-1} mol^{-1} (at 298.15 K). The slope varies somewhat with the nature of the solvent, but is generally of the order 1.5 to 1.8. As to the significance of these figures we refer to references 58, 164, 176, and 177. In the last of these references (177) it was shown that such a linear relationship follows from scaled particle theory (see next section), although slope and intercept differ appreciably from experimental values.] As already indicated, the close parallel observed in nonpolar solvents between the relative excess of partial molar volume of dissolved gas over its molar volume at its normal boiling point, and the part of the entropy change attributable to expansion[12,58,125] is not preserved when water is the solvent. Arguments based on loss of entropy resulting from destruction (deactivation) of hydrogen bonds[135] upon contact with "inert" surfaces (dissolved gas) suggest a relation between the standard entropy change on solution and a quantity representative for the surface area per mole of solute.[12] Whereas the original suggestion was based on a correlation with the molar volume at the boiling point, an inherently more suitable corresponding states quantity is V_{c2}, the critical volume of the gas. Figure 11 apparently provides some evidence for this hypothesis. (See also the empirical linear correlation between $\Delta\bar{S}_2°$ and the molar volume at the normal boiling point as suggested by Powell and Latimer.[178]) However, this explanation for the behavior of nonpolar solutes in water has been challenged by several authors, notably by Franks and Reid,[119] and most recently by Ben-Naim[179] (see also Rowlinson[180]). In particular, the former authors rightly point out that the Miller–Hildebrand model is unable to account for the observed large values of $\Delta\bar{C}_{P2}°$. More general arguments of Ben-Naim, which are based on the Kirkwook–Buff theory of solution,[181] also favor the contention that in liquid water a simple nonpolar solute may in fact

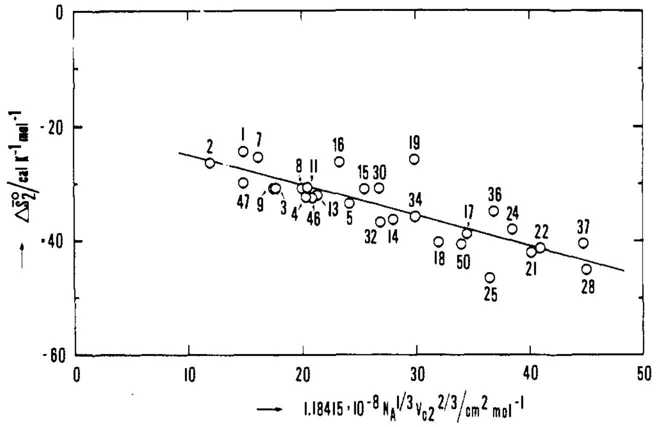

Figure 11. Relation between the partial molar entropy of solution of gases in water, $\Delta\bar{S}_2^\circ$, at 298.15 K and 1 atm partial gas pressure, and a quantity proportional to the surface area per mole of dissolved gas, that is, $N_A^{1/3}V_c^{2/3}$. N_A is Avogadro's constant. The numerical factor is $(6.02252 \times 10^{23})^{-1/3}$ or 1.18415×10^{-8}. (See Figure 7 caption for key to numbers.)

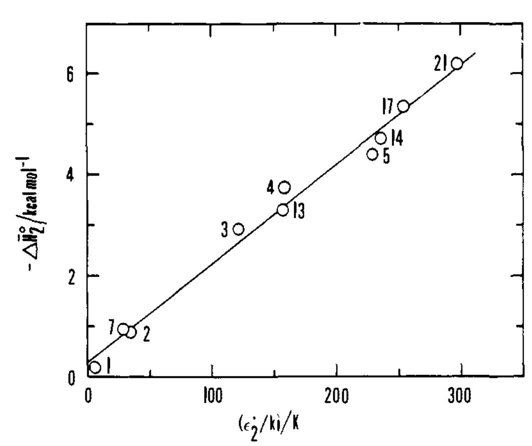

Figure 12. Correlation of the partial molar enthalpy of solution of gases in water, $\Delta\bar{H}_2^\circ$, with the force constant ϵ_2^*/k of selected gases (the rare gases He through Xe, normal alkanes up to n-C_4H_{10}, and H_2) at 298.15 K and a partial gas pressure of 1 atm. k is Boltzmann's constant. (See Figure 7 caption for key to numbers.)

increase the average number of hydrogen bonds (see also ref 182).

Among the common methods used to correlate partial molar enthalpies of solution with physical properties of the gas are partial molar volume, force constants, and polarizability.[11] Figure 12 shows the relation between $\Delta\bar{H}_2^\circ$ and the respective force constant ϵ^*_2/k for selected gases; Figure 13 indicates the influence of polarizability on this quantity.

The empirical Barclay-Butler rule[2,183-184a] relates enthalpy and entropy changes accompanying the solution process in a simple, linear manner. It appears indeed that this rule is satisfied by a substantial number of nonpolar solutes (cf. also Frank and Evans[2] and Klapper[118]), as can be seen from Figure 14, which also includes results for more complex solutes.

The exceptionally large values of $\Delta\bar{C}_{P2}^\circ$ in water have generally been connected with changes in the structure (ref 2, 3, 11, 98, 102, 185–194) of water. [For example, the heat capacity change on solution of CH_4 in water at 25 °C is 49.6 cal K^{-1} mol^{-1} compared to 6.2 cal K^{-1} mol^{-1} in benzene as derived from Horiuti's work.[10,124] The corresponding figures for hydrogen are 34.5 and 2.7 cal K^{-1} mol^{-1} (Cook et al.[195]). Even in two-dimensionally hydrogen-bonded liquids such as ethanol[190] $\Delta\bar{C}_{P2}^\circ$ is very small.] Its conventional interpretation rests on two contentions: (1) dissolution of inert solutes increases the "structure" in water, that is, some kind of "microscopic iceberg" formation takes place; and (2) as the temperature is raised, these icebergs "melt", thus giving rise to the observed large values of the partial molar heat capacity. Although the essential idea of this explanation is intuitively appealing, Ben-Naim[194,196] has recently shown, with the aid of a formally exact two structure model,[7] that on the basis of our present knowledge of the structure of water no prediction of the partial molar heat capacity of a solute seems feasible. Exactly these (and related) ambiguities arising from various concepts of water structure were dealt with in an article by Holtzer and Emerson.[197] For a discussion of aqueous solubility with specific reference to gas hydrates,[198] see Glew.[5,102]

Although the numerical values may be subject to appreciable uncertainity, it appears that qualitatively $\Delta\bar{C}_{P2}^\circ$ increases with increasing size of the solute molecule.

The more of less pronounced failure of simple methods of correlating gas solubilities in water with some gas property

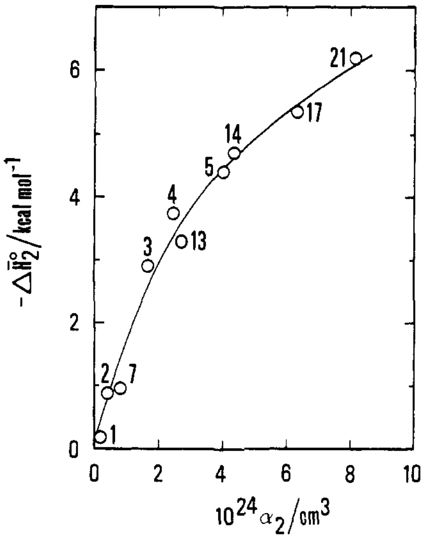

Figure 13. Correlation of the partial molar enthalpy of solution of gases in water, $\Delta\bar{H}_2^\circ$, with the average polarizability of the dissolved gas, α_2, for several gases (the rare gases He through Xe, normal alkanes up to n-C_4H_{10}, and H_2) at 298.15 K and a partial gas pressure of 1 atm. (See Figure 7 caption for key to numbers.)

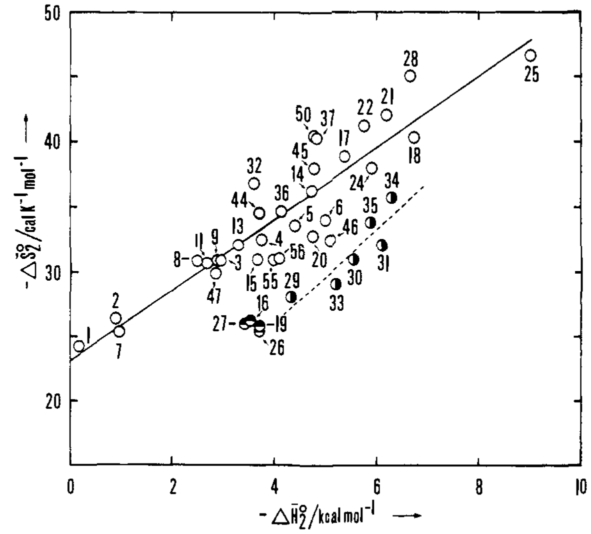

Figure 14. A Barclay-Butler plot or the partial molar entropy of solution of the gas, $\Delta\bar{S}_2^\circ$, against the partial molar enthalpy of solution, $\Delta\bar{H}_2^\circ$, at 298.15 K and 1 atm partial gas pressure. (See Figure 7 caption for key to numbers.) It appears that there is one rather good straight line which represents nonpolar or slightly polar gases with a permanent dipole moment less that ca. 0.5 D (solid line, open circles ○); and another which represents the strongly polar solutes (broken line, ◑). Interestingly, the acetylene derivatives (⊖) form a group very near the broken ("polar") line.

supports the contention that, in general, it is rather unlikely for a single parameter to produce a useful correlation (Prausnitz and Shair[199]). Hence, these authors suggest a correlation of the activity coefficient of the gas (referred to the hypothetical pure liquid solute) with its "liquid" molar volume $V_2{}^L$ (a quantity closely related to the partial molar volume), and the solubility parameter δ_2 according to

$$\ln \gamma_2 / V_2{}^L = f(T, \delta_2, \text{properties of the solvent}) \quad (41)$$

Indeed, isotherms of this quantity plotted against δ_2 result in rather smooth curves for strongly polar solvents including water.[199]

C. More Rigorous Approaches. The Hydrophobic Effect

One of the first rigorous approaches to the problem of gas solubility in water was that of Eley[1,1a] in his now classical papers of 1939. The idea of decomposing the solution process into two consecutive processes, that is, one associated with cavity formation,[200,200a] and the other with interaction between solute and solvent, has indeed been extremely stimulating to theory. The approach adopted by Eley for water led to an invariably negative enthalpy of solution, a substantial negative entropy of solution which is largely responsible for the poor solvent properties of this liquid, and to large partial molar heat capacities of the solute. The model also indicated that $\partial \Delta \bar{C}_{P2}{}^\circ / \partial T$ should be negative for all weakly interacting solutes. Whereas Eley proposed that a nonpolar molecule dissolved in water would preferentially occupy the interstitial cavities of the low-density hydrogen-bonded network, Frank et al.[2,137] suggested that the position of equilibrium between water aggregates of an ice-like nature and nonstructured water (without a hydrogen-bonded network) is shifted toward the structured form by nonpolar solutes. However, as already pointed out by Klapper,[118] the theories of Eley and Frank et al. are not mutually exclusive.[184,201] The statement that the solute promotes water structure[201a,b] necessitates that the solute is located within the structured part, that is, interstitially.

With the advent of scaled-particle theory[202-213] (abbreviated SPT) of simple classical fluids and mixtures therefrom, an accurate expression for the Gibbs energy of cavity formation became available. (For pure liquids see also the detailed survey on recent developments in liquid state physics by Kohler, Wilhelm, and Posch.[157]) For mixtures of hard convex particles of arbitrary shape, Gibbons[213] derived an equation of state in terms of average radius, surface area, and volume of molecules of various species. In the special case of mixtures of hard spheres it was found that the SPT equation of state of Lebowitz et al.[212] was recovered. Incidentally this equation is identical with the Percus-Yevick[214] compressibility equation for mixtures (Lebowitz[215,216] and Baxter[217]). Although the theory was originally devised to deal with rigid sphere assemblies only, its scope has since been increased to include a wide class of real fluids (see, for example, the excellent review by Reiss[206]). Specifically, Pierotti[218] applied SPT to solutions of gases in liquids and in particular to aqueous solutions.[189,219,220,220a] The highly successful evaluation of the standard changes of thermodynamic functions referring to the solution process stimulated further work in this and related areas. In particular, Wilhelm and Battino applied SPT to the solubility of gases in a variety of liquids ranging from nonpolar hydrocarbons[53,176,177,221-223] to perfluorinated compounds,[224] hydrogen-bonded solvents,[225,226] and octamethylcyclotetrasiloxane[227] (as an example of a very large, approximately globular molecule). From the limiting behavior of Henry's law constant, that is, from the intercept of the plot ln $H_{2,1}$ vs. α_2 (the polarizability of the solute gas), it was possible to extract effective hard-sphere diameters σ_1 for water[189] and a large number of other liquids.[228] This semiempirical approach eventually led also to an estimate of the temperature dependence of effective σ_1 for a variety of solvents (Wilhelm[229]).

Quite recently, Neff and McQuarrie[131] applied perturbation theory for mixtures[230-233] to solutions of gases in nonpolar, simple fluids. They were able to show that Pierotti's relations may be obtained as special cases of the more rigorous perturbation treatment; that is, their expression for the chemical potential included an extra term which considers the change in the hard-sphere radial distribution function of the solvent upon adding a solute molecule. The resulting decrease in solvent–solvent interaction apparently represents a significant effect in the solvation process, even in dilute solutions. They also pointed out correctly that the Pierotti approach, that is, using experimental real fluid pressure in the reference term, is inconsistent with perturbation theory.

In complete analogy to the Eley model the solution process Pierotti[218] used was considered to consist of two steps. For dilute solutions, this led to

$$\Delta\mu_2{}^\circ/RT = \ln (H_{2,1}/\text{atm}) = \mu_c/RT + \mu_{in}/RT + \ln (RT/V_1{}^{\circ L}\ \text{atm}) \quad (42)$$

where μ_c and μ_{in} denote the partial molar Gibbs energies corresponding to cavity formation and interaction, respectively. The Gibbs energy of cavity formation is related to size parameters of the solvent (1) and solute (2) via

$$\mu_c/RT = 6\left(\frac{y}{1-y}\right)\left[2\left(\frac{\sigma_{12}}{\sigma_1}\right)^2 - \frac{\sigma_{12}}{\sigma_1}\right] + 18\left(\frac{y}{1-y}\right)^2\left[\left(\frac{\sigma_{12}}{\sigma_1}\right)^2 - \frac{\sigma_{12}}{\sigma_1} + \frac{1}{4}\right] - \ln(1-y) \quad (43)$$

with $\sigma_{12} = (\sigma_1 + \sigma_2)/2$, $y = \pi\sigma_1{}^3 N_A/(6V_1{}^{\circ L})$, and σ_1 and σ_2 being effective hard-sphere diameters (Wilhelm and Battino[228]). By assuming a Lennard-Jones (6,12) pairwise additive potential plus an inductive term, the Gibbs energy of interaction is approximated by (polar solvent with dipole moment $\bar{\mu}_1$ and nonpolar solute with polarizability α_2)

$$\mu_{in} = \mu_{in,disp} + \mu_{in,ind} = -3.555R\pi \frac{N_A}{V_1{}^{\circ L}} \sigma_{12}{}^3 \frac{\epsilon^*{}_{12}}{k} - 1.333N_A{}^2\pi \frac{\bar{\mu}_1{}^2\alpha_2}{V_1{}^{\circ L}\sigma_{12}{}^3} \quad (44)$$

The energy parameter characteristics of 1–2 interaction is denoted by ϵ_{12}^*/k. Appropriate differentiation of eq 42 then yields all the other thermodynamic functions pertaining to the solution process. For simple dense fluids, the Lennard-Jones (6,12) pair potential

$$U(r) = 4\epsilon^*[(\sigma/r)^{12} - (\sigma/r)^6]$$

is generally regarded as a satisfactory "effective" pair potential; that is, corrections due to three-body (and higher order) interactions are incorporated. Here, ϵ^* denotes the depth of the potential well, σ is defined by $U(\sigma) = 0$, and $r^* = 2^{1/6}\sigma$ is the distance of the minimum.

The relation of this approach to a generalized van der Waals treatment of fluids[17c,d,157,234-241] was exploited by Klapper[118] who derived expressions for $\bar{V}_2{}^\circ$, the partial molar volume at infinite dilution,[242] and for $\Delta\bar{S}_2{}^\circ$ and $\Delta\bar{H}_2{}^\circ$, the latter being based on the entropy cycle of Yosim and Owens,[243-245] and on a procedure proposed by Boublik and Benson,[246] respectively.

In view of the highly directional interactions (hydrogen bonds) operating in liquid water, the successful prediction of partial molar enthalpies, entropies, and heat capacities of solution of gases in water, and their partial molar volumes at infinite dilution (see Table XI) was quite surprising and stimulated further work in this field.[219,220] Thus in order to restore chemical detail, Stillinger[247] recently reexamined scaled particle theory as applied to aqueous solutions of spherical, nonpolar solutes. The

TABLE XI. Partial Molar Quantities Referring to the Solution Process in Water at 298.15 K[a]

	$\Delta\mu_2°/RT$		$-\Delta\overline{H}_2°/RT$		$-\Delta\overline{S}_2°/R$		$\Delta\overline{C}_{P2}°/R$		$\overline{V}_2{}^{\circ L}$/cm^3 mol^{-1}	
Solute	Calcd	Expt	Calcd	Expt	Calcd	Expt	Calcd	Expt	Calcd	Expt
Helium	11.53	11.87	0.84	0.31	12.4	12.2	10.3	12.6	17.9	29.7[b]
Argon	10.28	10.59	4.12	4.95	14.4	15.5	15.8	21.4	30.5	32[b]
Xenon	9.20	9.46	7.42	7.43	16.6	16.9	21.8	23.7	46.2	
Nitrogen	11.12	11.35	3.97	4.21	15.1	15.6	18.2	26.6	36.5	33[b]
Oxygen	10.58	10.68	4.09	4.86	14.3	15.5	16.2	24.0	31.5	32[b]
Methane	10.55	10.59	5.22	5.56	15.8	16.2	19.2	25.0	39.3	37.3[c]
CF_4	12.00	12.47	6.83	6.08	18.8	18.5	27.6	45.7	63.5	
SF_6	11.58	12.33	10.46	8.06	22.0	20.4	34.9[d]	62.9	92.1[d]	

[a] Calculated values obtained through application of the scaled particle theory.[9,189] Partial gas pressure of 1 atm. [b] Experimental partial molar volumes at infinite dilution taken from Enns et al.,[122] with the exception of methane. See also Tiepel and Gubbins[249] for additional data. [c] Reference 121. [d] E. Wilhelm, unpublished results.

resulting more detailed version of SPT for water as a solvent incorporates experimental surface tensions as well as radial distribution functions for pure water. For the central quantity, the contact correlation function, the following is observed:

(a) The more accurate Stillinger procedure yields substantially larger maxima, though roughly at the same position as Pierotti's hard-sphere approximation.

(b) The Pierotti approximation is distinctly less sensitive to temperature; that is, it depends essentially on the number density.

An interesting conjecture concerning the influence of the strong directional hydrogen-bonding forces (as evidenced by the larger maximum in the contact correlation function) upon local solvent structure induced by a spherical solute, suggested the existence of convex water-molecule cages (Figure 15), at least for smaller solutes. Although the bonding situation shown in Figure 15 is clearly unrealistic, its basic idea, that is, the orientational bias of the first-layer water molecules, might indeed be a relevant feature in a detailed description of aqueous solutions. However, as yet, no detailed calculations of thermodynamic quantities referring to the solution process have been reported.[247a]

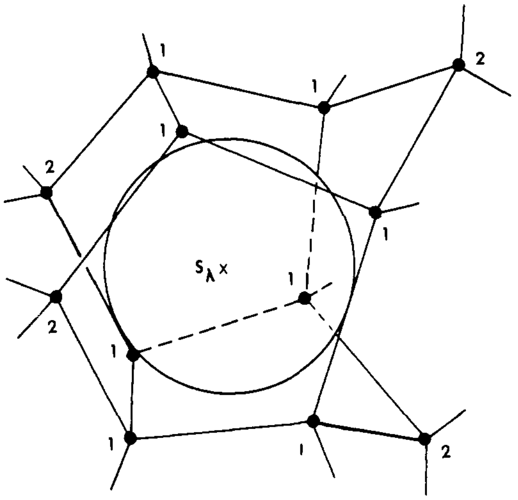

Figure 15. "Random" water molecule cage enclosing the rigid-sphere solute, whose exclusion sphere is denoted by S_λ. The oxygen nuclei are shown as dark circles, and hydrogen bonds as dark lines. Protons can be distributed asymmetrically along the bonds in a variety of ways. Oxygen nuclei "1" are closer to the solute than those of type "2". Note that the eight water molecules nearest to the center of S_λ are all oriented so that one of the four tetrahedral bond directions points radially outward. For each of these eight, then, the remaining three bond directions straddle S_λ. As a result, the dipole moment direction for these solvent molecules cannot point either toward, or directly away from the hard-sphere solute. The four more remote solvent molecules may point their dipole moment vectors either inward or outward along the radial direction (from Stillinger[247]).

Aqueous solubility of methane and the methyl halides has been discussed with special reference to gas hydrates by Glew,[5,102] who compares the thermodynamic properties of aqueous solutions with those of the solid clathrates.[198] Water shell stabilization by dissolved nonelectrolytes such as ethylene oxide, dioxane, and *tert*-butyl alcohol has been investigated by Glew, Mak, and Rath.[248] Dilute solutions of these substances (94–97 mol % water) exhibit anomalous properties. The water activity coefficients pass through minima, indicating maximum water structure stabilization. For all solutes the composition dependence of the proton magnetic resonance chemical shift of water is moved toward lower magnetic field. This is indicative of stronger water–water hydrogen bonding. Additional evidence of stabilization of adjacent water into more ordered, hydrogen-bonded cages was found in the increase in partial molar volume of water to a maximum at 3–4 mol % solute. These results have been exploited to obtain estimates as to the average coordination number in these shells (see also Namiot[248a]).

Perturbation theory has also been applied in predicting thermodynamic properties of gases dissolved in pure water and in aqueous, electrolyte solutions[249,250] (for further information on this latter topic see ref 251–256). Tiepel and Gubbins'[250] method is based on the perturbation theories of Leonard, Henderson, and Barker[230,257] with the following modifications: (a) They chose the Weeks–Chandler–Anderson reference system.[258] (b) The second-order term in λ (a perturbation parameter measuring the strength of attractive potential) is included. Terms in $\alpha\lambda$ or α^2 (where α denotes the perturbation parameter measuring inverse steepness of the repulsive potential) are not taken into account. For the effective temperature dependent hard sphere diameter they use the familiar Barker–Henderson expression[259]

$$\sigma_{\text{eff}}(T) = \int_0^R \{1 - \exp[-U_{\text{ref}}(r)/kT]\}\, dr \tag{45a}$$

where R denotes the range of the potential $U_{\text{ref}}(r)$. Various methods of evaluating the temperature dependence of effective hard-sphere diameters of dense fluids[260,261] have been compared by Wilhelm[229] (see also Bienkowski and Chao[262]). In the case of the Weeks–Chandler–Anderson decomposition $R = r^*$ is the distance of the potential minimum $-\epsilon^*$. (This topic was treated in detail in ref 232; its relation to the van der Waals model of fluids is discussed in ref 157.) Thus the reference and perturbation potentials are given by

$$\begin{aligned} U_{\text{ref}}(r) &= U(r) + \epsilon^* && \text{for } r < r^* \\ &= 0 && r > r^* \\ U_{\text{pert}}(r) &= -\epsilon^* && r < r^* \\ &= U(r) && r > r^* \end{aligned} \tag{45b}$$

with $U(r)$ being a suitably chosen (total) pair potential. By invoking the rather stringent uniform distribution approximation, that is, for the reference mixture distribution function

$$\begin{aligned} g_{ij}{}^{\text{ref}}(r) &= 1 && \text{for } r > \sigma_{ij} \\ &= 0 && r < \sigma_{ij} \end{aligned} \tag{45c}$$

Tiepel and Gubbins arrive at fairly simple final equations. The appropriate hard-sphere reference quantities are calculated with the aid of the equation of state of Carnahan and Starling[283] as extended to mixtures by Boublik.[264] However, the same criticism as in the case of Pierotti's[189] original application of SPT to aqueous solutions applies (Stillinger[247]), since the highly structured nature of the solvent is not taken into account explicitly. Basically, this is true for all van der Waals type approaches which are designed to apply to nonpolar solvents only.[265,266] Whereas Pierotti, Neff and McQuarrie, and Tiepel and Gubbins actually start from a molecular picture and use (effective) Lennard-Jones parameters, Snider and Herrington[265] use experimental Henry's law constants to determine the solute–solvent van der Waals constant. The originally rather poor agreement of predicted enthalpies of solution and partial molar volumes could later be shown to be due to mistaken value of Henry's law constant.[267] For a review of perturbation methods for calculating properties of liquid mixtures including gas–liquid systems, see Gubbins.[268]

Starting with Frank and Evans'[2] influential classic paper dealing with dilute solutions, the statistical mechanical treatment of aqueous solutions of gases is intimately connected with efforts to quantify the broad concept of "structure" of water in solution and in the pure liquid (see also section IV.A). The actual meaning of the term "structure" as applied to liquid water may vary to some extent with different authors. A particularly appealing and simple definition was provided by Franks[269] in terms of molecular dynamics: In liquid water, the molecular reorientation time, resulting from either rotational or translational diffusion, is of the order of 10^{-11} s, and if a dissolved solute can substantially lengthen this period, say by an order of magnitude to 10^{-10} s, the effect may adequately be referred to as structure promotion. Conversely, if the solute initiates a shortening of the reorientation time, then this solute is termed a structure breaker. NMR relaxation studies, that is, the experimentally accessible intramolecular proton relaxation rate, provide a basis for obtaining information on the central quantity, the rotational correlation time τ_c of water. A quantitative discussion of the influence of inorganic ions as well as of nonelectrolytes on τ_c has recently been presented by Hertz and Zeidler.[269a] Specifically, for nonpolar solutes (where τ_c increases), the discussion has been conducted, respectively, in terms of effective radii of hydrogen bonded aggregates, a^*, which quantity may in turn be influenced either (a) by changes in the effective water–water pair potential upon addition of solute, or (b) by a change of the water–water first coordination number in the hydration sphere as compared to pure water, and in terms of the influence of increased microviscosity η^* (i.e., increased background effect):

$$\tau_c = 4\pi(a^*)^3\eta^*/(3kT) \qquad (46)$$

The latter possibility would certainly not be called a "structure increase" effect. Apparently, no decision as to predominance of any one of these three effects can be made yet. However, the effect of structure reinforcement is used almost exclusively when discussing phenomena associated with aqueous solutions of nonpolar solutes (see below).

In order to simulate some of the outstanding properties of aqueous solutions and thereby gain new insight into their molecular origin, models have been designed which, though occasionally very artificial, still retain essential features of the real system but are simple enough so that an accurate statistical-mechanical analysis is feasible. A prominent example is the theoretical study of Nemethy and Scheraga[3,138,270] on aqueous solutions of hydrocarbons. Their model is based on their proposed structure of pure water which is considered to consist of hydrogen-bonded clusters embedded in and in equilibrium with monomeric non-hydrogen-bonded water molecules which, however, can still interact via dipole and London forces. The clusters are regarded as being compact; that is, they contain as many tetracoordinated molecules as possible. In dilute solutions, the main difference with respect to water is that the distribution of the water molecules in the layer next to the solute is shifted in favor of more "ice-like" structures, or, in other words, the net number of water molecules in clusters (four-bonded water network) near the solute particle is increased. The calculated Gibbs energies, enthalpies, and entropies of solution for the first four *n*-alkanes agree reasonably well with experimental data. To a lesser extent this is also the case with partial molar heat capacities, whereas agreement between predicted and observed volume changes for the transfer of a hydrocarbon from a nonpolar medium into aqueous solutions is rather poor. For criticism of various aspects of this theory see Klapper[118] and Franks.[271] Nemethy and Scheraga's model which is based on the concept of increased ordering of water around nonpolar solutes is similar to the concept of Frank and Evans.[2] Occasionally this solution effect is called "hydrophobic hydration" (see, for example, the excellent article by Franks[271]). The limiting variation with solute concentration of some partial molar thermodynamic quantities of a hard-sphere solute in relation to hydrophobic hydration has been calculated on the basis of scaled particle theory by Lucas.[272]

Further efforts to elucidate the origin of the large negative solution entropies on the basis of a mixture model of liquid water have been reported by Frank and Quist,[201] Frank and Franks,[184] and Mikhailov.[185] A more general mixture model approach to obtain exact expressions for the "stabilization effect" induced by the solute, and to discuss concepts such as "structural changes", is due to Ben-Naim.[142]

Aqueous solutions of aliphatic hydrocarbons have also been examined in terms of the significant structure theory[273] (see also ref 139 and 274). Although some inference as to "iceberg formation" adjacent to a hydrocarbon molecule might be drawn, it is questionable whether these results have anything more than qualitative significance. (Here, the degree of "iceberg formation" is identified with the per cent decrease in molar volume of the water layer, V_L, next to the solute molecule from the bulk value at 298.15 K ($V_w° = 18.009$ cm^3 mol^{-1}) in the direction to the calculated cluster volume at the same temperature [i.e., to the volume of hypothetical solid water of dense ice-III structure, V_S (298.15 K) = 17.656 cm^3 mol^{-1})]. Agreement between theoretically and experimentally determined partial molar Gibbs energy changes, entropy changes, and enthalpy changes for methane through butane dissolved in water is not entirely satisfactory. No sensible results for $\Delta \bar{C}_{P2}°$ could be obtained.

For a survey of independent evidence for "hydrophobic hydration" in terms of distribution functions, see Franks,[271] where he emphasized the work of Hertz et al.[275-277] and Hertz and Zeidler[269a] (see also Krishnan and Friedman[278]). In the first of these studies, Hertz[275] investigates a multitude of physicochemical properties of aqueous solutions of compounds with alkyl groups. In order to make the concept of structure increase or decrease conceptually more precise, the degree of structure is characterized by the sharpness of the maxima of the orientation dependent molecular distribution functions $g_{H_2O-H_2O}$ and $g_{H_2O\text{-solute}}$. Combination with thermodynamic results, dielectric and nuclear magnetic relaxation data, viscosity, etc., led him to conclude that the structure of the solution is increased, however, with a concomitant decrease in the average strength of hydrogen bonds due to deformation of bonds. This somewhat surprising conclusion is in striking variance with that reached by Glew et al.[248]

Reorientation correlation times derived from nuclear magnetic relaxation and self-diffusion coefficients form the basis of an investigation on mixtures of water with pyridine, methanol, ethanol, tetrahydrofuran, etc. (Goldammer and Hertz[276]). The most important results were that: (1) generally there is structural reinforcement at low solute concentrations; (2) long-lived rigid hydration cages surrounding the solute are absent at low concentrations; and (3) there is some evidence for solute-solute association, that is, for microheterogeneity (see below).

Orientation of the water molecule in the hydrophobic hydration sphere of aqueous solutions of HCOOD, CHD_2CD_2COOD, and CHD_2OD was investigated by Hertz and Rädle.[279] The dipole moment of the water molecule points away from the methyl group of the solute. Their results for the angle relative to a radial reference axis are 96° for formic acid, 107.5° for propionic acid, and 102.5° for methanol (compare this to the schematic picture of Stillinger, Figure 15). Surprisingly, hydration of the carboxylic proton in formic acid does not differ significantly from that of the inert methyl group.[279a]

Recently, hydrophobic interaction was examined via ^{13}C NMR spin-lattice relaxation time measurements by Howarth.[279b] This technique is particularly useful for investigating molecular motion because for most molecules the ^{13}C relaxation is dominated by dipolar coupling with directly bonded protons.[279c] The results on aqueous solutions of propyl alcohol and *tert*-butyl alcohol represent evidence that water is rather unusual in the extent to which it restricts the motion of hydrophobic solute moieties. In conjunction with the concomitant reduction in the motion of neighboring solvent molecules,[276,279d] the large negative partial molar entropies of solution apparently can be quantitatively accounted for. In addition, Howarth suggested that a simple van der Waals approach (assuming an approximately zero enthalpy of cavity formation in water) should lead to a linear correlation, through the origin, between the square root of the enthalpy of vaporization at the normal boiling point of the solute, $(\Delta H_2^{\text{vap}})^{1/2}$, and its enthalpy of solution, $\Delta \bar{H}_2°$. Such a linear relation is indeed observed for $\Delta \bar{H}_2° \lesssim 5$ kcal mol^{-1}, the deviations at higher values being tentatively attributed to the formation of dimers, trimers, etc., of solute molecules, in other words, the formation of "hydrophobic bonds" as discussed below.

A great number of other studies applying various spectroscopic methods, x-ray and neutron scattering, nuclear magnetic resonance techniques, dielectric and ultrasonic methods, etc.,[160,279e] to elucidate the structure of liquid water and aqueous solutions have been reported. Unfortunately, most of these investigations are limited to ionic solutions and rarely to systems treated in this paper, that is, gas-liquid systems. Although some implications derived from the results obtained by these methods may be extrapolated to dilute solutions of gases, more research in this direction would be highly desirable.[280]

Optical studies on molecular oxygen dissolved in water have been carried out by Heidt and Johnson,[280a] and more recently by Jortner and Sokolov.[280b] The latter authors assigned the observed diffusive absorption spectra without fine structure in the range $\lambda = 200$ to 220 nm to charge-transfer spectra of oxygen, with this molecule acting as electron acceptor. In addition to water several other solvents were studied,[280b,c] the results being in complete agreement with the conclusions reached by Tsubomura and Mulliken.[280d] The most conspicuous result was the linear dependence of the equivalent energy of the charge-transfer band onset on the ionization energy of the solvent molecule as evidenced by Figure 16. For extremely weak interactions of this kind,[280e] theory predicts the following relation between ν and I_P:

$$h\nu = I_P - E - W + 2\beta^2/(I_P - E - W) \approx I_P - E - W \qquad (47)$$

since $\beta^2 \ll (I_P - E - W)$. Here h is Planck's constant, ν the transition frequency, I_P the (vertical) lowest ionization potential of the donor,[280f] E the (vertical) electron affinity of the acceptor (oxygen), W the electrostatic and other interaction energy between the molecules in the charge-transfer state, and β the resonance integral. If W is assumed to be relatively constant for various donors, a linear relation between ν and I_P is expected (as shown in eq 47). The deviation of the slope obtained from Figure 16 (slope = 0.65) from unity was tentatively explained to be due to the dependence of W on I_P.[280b,g]

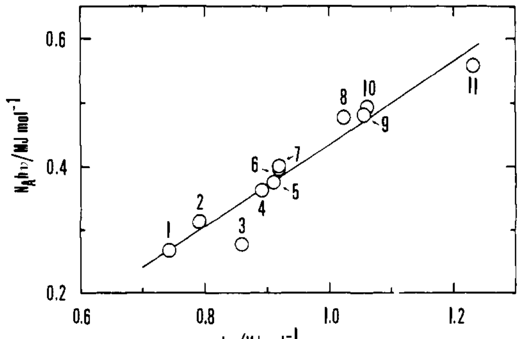

Figure 16. Dependence of the equivalent energy $N_A h\nu$ of the charge-transfer band onset for oxygen in various solvents on the ionization energy, I_p, of the solvent: (1) aniline, (2) anisole, (3) pyrrole, (4) toluene, (5) chlorobenzene, (6) benzene, (7) dioxane, (8) ethanol, (9) methanol, (10) cyclohexane, and (11) water.

An interesting technique designed to allow differentiation between various models of pure liquid water (and dilute solutions) was reported by O'Neil and Adami:[281] by measuring the oxygen isotope fractionation (O^{18}/O^{16}) between CO_2 and H_2O,[282] the temperature dependence and absolute value of the oxygen isotope partition function ratio $Q_{O^{18}}/Q_{O^{16}}$ of liquid water was determined from −2 to 85 °C (at ~1-2 °C intervals). A linear relationship between ln $(Q_{O^{18}}/Q_{O^{16}})_{H_2O}$ and T^{-1} was obtained and discussed in terms of the Bigeleisen-Mayer[283] theory of isotopic fractionation. The results are compatible with either a continuum model for liquid water, or with mixture models possessing certain specified characteristics.

Isotopic fractionation of the common isotopic species of nitrogen and oxygen in water during the solution process has been measured in the range 2-27 °C[283a] and was reported in the form of equilibrium constants for reactions of the following type: $^{34}O_2(g) + {}^{32}O_2(aq) = {}^{34}O_2(aq) + {}^{32}O_2(g)$. Obviously, the equilibrium constant may be expressed as $K = H'_{2,1}/H_{2,1}$ where the prime denotes the lighter isotopic species. At 0 °C, the (extrapolated) values were $K_{O_2} = 1.00080$ and $K_{N_2} = 1.00085$; i.e., the *heavier* species is *more* soluble. In both cases *K decreases* with increasing temperature. Aside from relevance to a better understanding of the geochemical cycles of these gases,[283b] the results were also exploited to yield estimates for the size of the cavities occupied by the gases.

Mathematical models of particular convenience were the one-dimensional model for aqueous solutions of inert gases by Lovett and Ben-Naim,[284] and later the two-dimensional system of water-like particles[285-288] which was investigated by means of the Percus-Yevick integral equations. Before that investigation, systematic studies on two-component systems using a set of four Percus-Yevick equations were carried out only in the case of spherical particles (Throop and Bearman[289,290]). From the fragmentary results reported in ref 287 it appears that some qualitative conclusions as to "hydrophobic interaction" (abbreviated HI) can be drawn.[187,271] In particular, the high peak in the calculated pair distribution function $g_{ss}(r)$ for two solute particles in "water" was interpreted as a simulation of the excess tendency of simple solutes to "adhere" to each other (see below). Furthermore the maximal enhancement of the first peak for a specific solute diameter seems to indicate a close relationship between hydrophobic interaction and structure of the solvent. In this context, Ben-Naim means structure as the capability of the water-like particles to participate locally in a mode of packing which has a geometrical structure similar to the corresponding solid phase.

The term "hydrophobic interaction" or occasionally "hydrophobic bond", has actually been applied to several phe-

TABLE XII. Comparison of Gibbs Energies of Cavity Formation, μ_c, and of Interaction (Solute-Solvent), μ_{in}, as Calculated by Herman,[307] with Experimental Results for Some Hydrocarbon Gases Dissolved in Water at 298.15 K[a]

Solute	10^{20} A/m^2	$(\mu_c + \mu_{in})/RT$ Calcd	$(\mu_c + \mu_{in})/RT$ Expt
Methane	122.7	2.721	3.382
Ethane	153.1	2.986	3.095
Propane	180.0	3.306	3.308
Isobutane	203.7	3.646	3.920
n-Butane	207.0[b]	3.796	3.514
	202.9[c]	3.404	
Neopentane	224.3	3.946	4.228

[a] According to eq 42 the relation of these quantites to Henry's law constant is given by $(\mu_c + \mu_{in})/RT = \ln(H_{2,1}/\mathrm{atm}) - \ln(RT/V_1{}^{\circ L}\ \mathrm{atm})$. A is the cavity surface area. Partial gas pressure of 1 atm. [b] Cavity surface area for the trans conformation. [c] Cavity surface area for the somewhat contracted gauche conformation.

nomena closely related to the peculiar features exhibited by aqueous solutions.[291] It includes, for example, the folding of a polymer chain in such a way as to remove the nonpolar groups from the aqueous medium, the reversible aggregation of molecules (or ions) with long nonpolar chains as in the case of phospholipids, stabilization of ordered macromolecular structures such as helices, and, on a more elementary level, dimerization of two simple solute particles as represented by the rare gases, methane, etc., in water. [The isothermal unfolding of the globular proteins was treated in considerable detail by Tanford[292,293] (see also ref 294–296).] However, we stress the following: the "hydrophobic bond" is not a bond in the usual sense of the word; the molecular interactions termed "hydrophobic" are rather a consequence of the strong van der Waals forces[297,298] and highly directional hydrogen bond forces between two water molecules which exceed the attractive interaction between a water molecule and a nonpolar molecule (see also the discussion in ref 298a).

Classical statistical mechanical treatment of the hydrophobic effect started with the ambitious attempt by Nemethy and Scheraga,[299] followed more recently by Ben-Naim[300-303] and Yaacobi and Ben-Naim[304] (a discussion of the latter work is deferred to section IV.E.2). Since the objective of Scheraga and Nemethy was to elucidate protein stability on the basis of amino acid model compounds, no discussion of their results will be presented. Ben-Naim considers a system composed of water molecules and two single spherical nonpolar solutes. After breaking the Helmholtz energy of the system into three contributions, (a) a free energy term depending solely on properties of the solvent, (b) a contribution of the isolated solute pair interaction (which is independent of the solvent), and (c) the hydrophobic contribution A^{HI} (which depends on both solvent properties and separation of solutes), he establishes two approximate links between hydrophobic interaction and experimental results. In particular, for two specific examples the quantity

$$\delta A^{\mathrm{HI}}(R_{12}) = A^{\mathrm{HI}}(R_{12}) - A^{\mathrm{HI}}(R_{12} = \infty) \qquad (48)$$

is discussed. It represents the indirect part (i.e., the part that originates from the presence of the solvent) of free energy change for the process of bringing the two solute particles from infinity to some distance R_{12} in water: (1) As an approximation to the hydrophobic interaction between two methane molecules, he obtains the relation ($\tilde{\sigma} = 0.1533$ nm, i.e., the carbon–carbon distance in ethane; it is assumed that the force field produced by the two methane molecules will be about the same as that produced by a single ethane molecule):

$$\delta A^{\mathrm{HI}}(R_{12} = \tilde{\sigma}) = \Delta\mu^{\circ}{}_{C_2H_6} - 2\Delta\mu^{\circ}{}_{CH_4} \qquad (49)$$

(2) It is possible to inquire about $\delta A^{\mathrm{HI}}(R_{12} = 0)$, for which case as a second specific example, a crude approximation yields:

$$\delta A^{\mathrm{HI}}(R_{12} = 0) = \Delta\mu^{\circ}{}_{\mathrm{Xe}} - 2\Delta\mu^{\circ}{}_{CH_4} \qquad (50)$$

However, in one important case an exact expression for $\delta A^{\mathrm{HI}}(R_{12} = 0)$ can be given: For hard-sphere solutes

$$\delta A_{\mathrm{HS}}{}^{\mathrm{HI}}(R_{12} = 0) = -\Delta\mu^{\circ}{}_{\mathrm{HS}} \qquad (51)$$

That is, the free energy of solution of a single hard sphere offers information on HI of a pair of hard-sphere solutes. In fact, Ben-Naim considers $\delta A_{\mathrm{HS}}{}^{\mathrm{HI}}(R_{12} = 0)$ as the most fundamental quantity in discussing HI (for an investigation of some consequences in connection with more general "solvophobic interactions", see Wilhelm and Battino[9] and Yaacobi and Ben-Naim[304a]).

An estimate of the strength of the hydrophobic interaction at distances other than 0 or $\tilde{\sigma}$, in particular at σ, the molecular diameter (hard-sphere diameter) of the solute, was obtained via the function

$$y(R_{12}) = \exp[-\delta A^{\mathrm{HI}}(R_{12})/kT] \qquad (52)$$

As expected, for the absolute values $\delta A^{\mathrm{HI}}(0) > \delta A^{\mathrm{HI}}(\tilde{\sigma}) > \delta A^{\mathrm{HI}}(\sigma)$. Furthermore, it was shown that the strength of HI *increases* with increasing temperature, a behavior which is different from the solvophobic interaction in alcohols. The above treatment has been generalized to include interactions between a set of $M > 2$ hydrophobic particles.[306]

The solubilities of hydrocarbons together with estimates of free energies of hydrophobic interaction between two such molecules (say ethane in a specific relative orientation) as a function of separation were calculated by Hermann[307] on the basis of perturbation theory similar to the approach of Neff and McQuarrie.[131] In order to obtain actual numerical results, several rather stringent simplifying assumptions were introduced: (a) Although water is not a simple liquid, an effective Lennard-Jones pair potential was assumed. Parameters were determined from experimental surface tension data, the result being $\epsilon^*{}_{H_2O}/k = 302$ K and $\sigma_{H_2O} = 0.267$ nm. (b) Since perturbation theory in the form used is only applicable to spherical solutes, and since hydrocarbon molecules are often far from spherical, he assumed that solvent cavities of equal areas have equal Gibbs energies of cavity formation μ_c, which in turn may be exploited to define effective average solute diameters. The quite elaborate method of determining cavity surface areas A propounded in this paper resulted in substantial differences compared with those obtained earlier,[308] even for simple solutes such as methane: 10^{20} $A/\mathrm{m}^2 = 122.7$ (ref 307) vs. 152.4 (ref 308). Agreement between theoretically and experimentally determined partial molar Gibbs energies (cf. eq 42) and hence solubilities for methane through neopentane dissolved in water is not entirely satisfactory, as can be seen from Table XII (the quantity μ_{in} denotes the contribution due to solvent-solute interaction; for details see ref 307). Particularly surprising are the large deviations for the pseudosphericals methane and neopentane in *opposite* directions.

This method was also applied in calculations of free energies of hydrophobic interaction between hydrocarbon pairs[307,309] and between higher aggregates,[309] respectively. The HI free energy between species A and B is defined as the difference in the sum $\mu_c + \mu_{in}$ for the pair of solute particles at some specified distance such as the contact distance and at infinite separation:

$$\begin{aligned}\mu^{\mathrm{HI}} = \mu_c(\mathrm{A+B}) + \mu_{in}(\mathrm{A+B}) - [\mu_c(\mathrm{A}) + \mu_{in}(\mathrm{A})]_\infty \\ - [\mu_c(\mathrm{B}) + \mu_{in}(\mathrm{B})]_\infty \qquad (53)\end{aligned}$$

This is purely a solvent effect and does not include the hydrocarbon–hydrocarbon interaction energy. Figure 17 shows μ^{HI} between two ethane molecules in a particular relative orientation as a function of mutual distance. Other orientations were in-

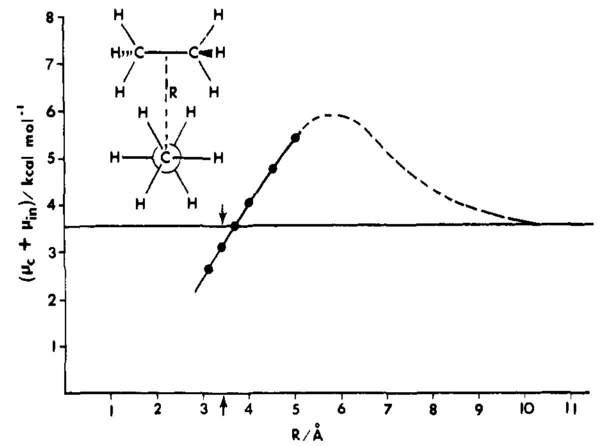

Figure 17. Hydrophobic interaction between two ethane molecules in the indicated relative orientation. The function ($\mu_c + \mu_{in}$) is plotted against the separation R. The horizontal line represents the total solvation free energy at infinite separation (not including the free energy of mixing). The Gibbs energy of hydrophobic interaction μ^{HI} of eq 53 is obtained for any desired distance by subtracting from the value of ($\mu_c + \mu_{in}$) the value of this function at infinite separation, that is, 3538 cal mol^{-1}. In this orientation the distance of closest approach is about 3.4 Å (indicated by arrows in the figure) between carbon-carbon bond centers; the nearest hydrogen-hydrogen intermolecular distance is then 2.39 Å. This separation corresponds to $\mu^{HI} = -450$ cal mol^{-1} (from Hermann[307]).

vestigated in ref 309. For a methane pair,[309] μ^{HI} for a center-to-center distance of 1.54 Å is -2.5 kcal/mol (unfortunately, temperature was not specified in ref 309), similar to the result of Ben-Naim,[300] i.e., -2.15 kcal/mol at 298.15 K.

Finally, a few words should be said about application of the Monte Carlo method in evaluating configuration integrals and thermodynamic functions of solvation and hydrophobic interaction of nonpolar molecules in water.[310] The treatment is based on Dashevsky and Sarkisov's earlier paper on liquid water,[311] where they made use of the atom-atom potentials H···H and O···O obtained by Kitaygorodsky et al.[312,313] and of an adjusted hydrogen bond potential of the Morse type.

$$U(r)_{O\cdots H} = D\{1 - \exp[-n(r - r_0)]\}^2 \qquad (54)$$

Here r_0 is the equilibrium O···H distance, D the depth of the potential, and n an empirical parameter. Calculations were performed for ensembles consisting of 63 water molecules plus 1 methane molecule, or plus 1 hard sphere, respectively (solvation); or for 62 water molecules plus 2 methane molecules, or plus 2 hard spheres, respectively (hydrophobic interaction). Interestingly, the calculated thermodynamic functions of hard-sphere solvation are qualitatively similar to those obtained by Pierotti,[189] with the exception of the enthalpic contribution. Quantitative agreement between calculated and experimental results for the solubility of methane were not satisfactory: at 300 K theory predicts $x_{CH_4} = 1 \times 10^{-5}$ vs. a measured value of 2.4×10^{-5}. In addition the calculated solubility shows a rather different temperature behavior from the experimental solubility. From calculations performed on the 62 + 2 ensembles, the free energy and entropy of HI of two methane molecules and two hard spheres, respectively, as well as the dependence of these quantities on mutual separation have been obtained and the predominantly entropic nature of HI confirmed. However, in view of the limited size of the ensembles, the quantitative significance of the numerical results should not be overestimated.

D. Heavy Water

Up to this point theoretical considerations were limited to the thermodynamic properties of solutions in H_2O. Because of the differences in masses and of the resulting isotope effect on the vibrational frequencies of deuterium oxide ("heavy water"), D_2O, there are significant differences in the magnitude of most physical properties.[314-320] These solvent isotopic effects are well suited for comparative studies carried out to elucidate the role of hydrogen bonds in solution thermodynamics.

Pure liquid D_2O is believed to possess a higher degree of hydrogen bonding than H_2O, that is, to be more "structured".[321-324a] (See also the critical discussion, particularly with respect to the dielectric constant, by Holtzer and Emerson.[197]) A very detailed comparison of the properties of light and heavy water on the basis of the Nemethy-Scheraga[138] model was presented by these authors,[321] together with evidence supporting the above contention. Additional evidence comes from the measured isotope fractionation factor ($^{18}O/^{16}O$) between CO_2 and D_2O,[325] which at 25 °C is 1.0256, as opposed to 1.0407 for CO_2-H_2O. This large difference was again taken to imply a more ordered structure for D_2O.[281]

Against this background, solubility experiments were carried out, with particular emphasis on obtaining information about the strength of the solute-solute interaction between two simple solutes, that is, on hydrophobic interaction.

From the solubility of methyl halides in H_2O and D_2O which showed only a rather small isotope effect, Swain and Thornton[103] inferred that these molecules occupy preferentially preexisting cavities (see also ref 102).

An attempt to interpret differences in the thermodynamic functions of solution in D_2O and H_2O in terms of the two-structure model[7,326] for liquid water is due to Ben-Naim.[327] In the special case of argon he considers the negative sign of the entropy contribution resulting from the displacement of the equilibrium concentrations of monomeric water and fully hydrogen bonded water (i.e., the relaxation term), and concludes that the "stabilization of the structure of the solvent" is greater in D_2O than in H_2O.

With reference to the problem of the hydrophobic effect, thermodynamic parameters for the transfer of model compounds from water to heavy water should help to throw some light on the nature of solute-solvent interaction. Table XIII contains the standard Gibbs energy, enthalpy, and entropy of transfer of several solutes (argon[327] and several hydrocarbons[100,328]) from H_2O to D_2O at 298.15 K, i.e.,

$$\Delta\mu_2{}^{\circ}{}_{tr} = (\Delta\mu_2{}^{\circ})_{D_2O} - (\Delta\mu_2{}^{\circ})_{H_2O} \qquad (55)$$

TABLE XIII. Standard Thermodynamic Functions Referring to the Transfer of Argon and Some Hydrocarbons from H_2O to D_2O at 298.15 K and a Partial Gas Pressure of 1 Atm[a]

Solute	$\Delta\mu_2{}^{\circ}{}_{tr}$/cal mol^{-1}	$\Delta\bar{H}_2{}^{\circ}{}_{tr}$/cal mol^{-1}	$\Delta\bar{S}_2{}^{\circ}{}_{tr}$/cal K^{-1} mol^{-1}
Argon	−47	−338	−0.98
Methane	−36	−268	−0.78
Ethane	−29	−330	−1.01
Propane	−25	−382	−1.20
n-Butane	−21	−99	−0.26

[a] Results obtained using the data in Tables VII and IX.

and the corresponding derivatives with respect to temperature. The negative free energy of transfer has been interpreted as an indication of stronger hydrophobic interaction of these molecules in H_2O than in D_2O,[329] and both negative $\Delta\bar{H}_2{}^{\circ}{}_{tr}$ and $\Delta\bar{S}_2{}^{\circ}{}_{tr}$ have been taken as suggesting that "structure promotion" by nonpolar solutes is greater in D_2O than in H_2O.[328] However, one has to keep in mind that, in particular, these latter two functions may vary considerably with temperature as can be seen from Figure 18 for propane and *n*-butane: for butane at 0 °C $\Delta\mu_2{}^{\circ}{}_{tr} = -67$ cal mol^{-1}, $\Delta\bar{H}_2{}^{\circ}{}_{tr} = -1019$ cal mol^{-1}, and $\Delta\bar{S}_2{}^{\circ}{}_{tr} = -3.48$ cal K^{-1} mol^{-1}, whereas at 30 °C both transfer enthalpy and entropy have already changed sign! We note that $\Delta\mu_2{}^{\circ}{}_{tr}$ of butane shows a trend inversion around 25 °C, whereas for propane this quantity becomes just positive at about 50 °C. The temperature range

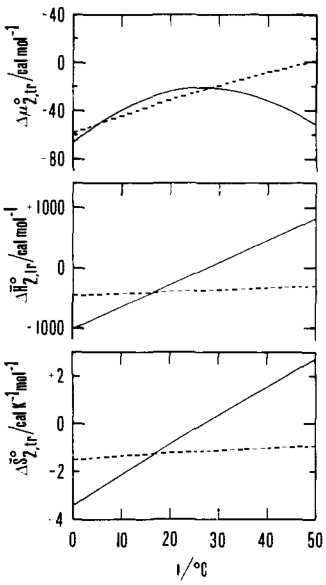

Figure 18. Standard Gibbs energy, $\Delta\mu_2{}^\circ{}_{tr}$, enthalpy, $\Delta \bar{H}_2{}^\circ{}_{tr}$, and entropy of transfer, $\Delta \bar{S}_2{}^\circ{}_{tr}$, from H_2O to D_2O of *n*-butane (solid line) and propane (broken line) as a function of temperature. Partial gas pressure is 1 atm.

TABLE XIV. Standard Thermodynamic Functions Referring to the Transfer of Several Halomethanes from H_2O to D_2O at 298.15 K and a Partial Gas Pressure of 1 Atm[a]

Solute	$\Delta\mu_2{}^\circ{}_{tr}$/cal mol^{-1}	$\Delta \bar{H}_2{}^\circ{}_{tr}$/cal mol^{-1}	$\Delta \bar{S}_2{}^\circ{}_{tr}$/cal K^{-1} mol^{-1}
CH_3F	−2	816	2.74
CH_3Cl	14	812	2.68
CH_3Br	58	986	3.11

[a] Results obtained using the data in Tables VII and IX.

covered by the methane and ethane systems is too small to allow any definite conclusion to be drawn. However, it seems that $\Delta\mu_2{}^\circ{}_{tr}$ becomes more positive with increasing temperature. Even relatively minor inaccuracies in the experimental results may lead to appreciable errors in the transfer functions. Thus with due caution, from the result of Kresheck et al.,[328] and Ben-Naim et al.,[100] on hydrocarbons it appears that (a) the transfer process becomes less favorable as the temperature is raised (with the possibility of a trend inversion at elevated temperatures as is apparently the case with *n*-butane), and (b) the structural order of the solvent in the hydrocarbon solutions increases with decreasing temperature faster in D_2O than in H_2O (see also ref 321).

The situation is somewhat different for the halomethanes (see Table XIV and Figure 19), where $\Delta\mu_2{}^\circ{}_{tr}$ apparently *decreases* first (becomes more negative) with increasing temperature, thus making the transfer process more favorable as the temperature is raised. At more elevated temperatures a trend inversion seems to be operative. No firm conclusions as to transfer enthalpy and entropy can be drawn because of the scarcity of solubility data for D_2O.

Scaled particle theory has also been applied by Philip and Jolicoeur[334a] to the calculation of the changes in thermodynamic functions associated with the formation of a cavity in several isotopic varieties of liquid water and methanol. Transfer functions for a hard-sphere solute have been computed for the following solvent pairs: $H_2O \rightarrow D_2O$, $H_2O \rightarrow H_2{}^{18}O$, $H_2{}^{18}O \rightarrow D_2{}^{18}O$, and $CH_3OH \rightarrow CH_3OD$. See also Lucas.[247a]

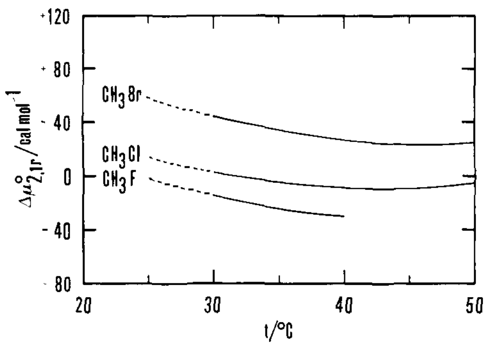

Figure 19. Standard Gibbs energy of transfer, $\Delta\mu_2{}^\circ{}_{tr}$, from H_2O to D_2O of the halomethanes CH_3X (X = F, Cl, Br) as a function of temperature (partial gas pressure of 1 atm). The dotted portions of the curves represent extrapolation to 298.15 K, the results being listed in Table XIV.

Recently, a comparative study on hydrophobic interaction in heavy and light water was carried out by Ben-Naim, Wilf, and Yaacobi.[100] They computed the strength of HI for the pairs methane–methane, ethane–ethane, etc., using the formalism of Ben-Naim.[300,301] $\delta G^{HI}(\sigma)$ was calculated for the hypothetical "reactions"

$$2(\text{methane}) \rightarrow \text{ethane}$$

$$2(\text{ethane}) \rightarrow n\text{-butane}$$

$$4(\text{methane}) \rightarrow n\text{-butane}$$

Hydrophobic interaction was thus estimated in this paper by

$$\delta G^{HI}(\sigma) = \Delta\mu^\circ{}_{C_2H_6} - 2\Delta\mu^\circ{}_{CH_4} \tag{56}$$

etc., although the original statistical mechanical treatment[300,301] was carried out in terms of the Helmholtz energy. However, the Gibbs energy is much more directly related to experimental quantities which usually are reported at constant pressure. The most conspicuous result is that HI for these reactions is stronger in H_2O than in D_2O, thus corroborating the conclusion arrived at in ref 328. The authors also discuss the general difficulties in accounting for quantum corrections[335] to the free energy of cavity formation and hence HI at zero separation (see eq 51).

Recently, Ben-Naim[336] devised a new measure to estimate structural changes in water induced by the dissolution of solute molecules (S). This measure relates the isotope effect on the Gibbs energy of solution in light and heavy water with the change in the average number of hydrogen bonds that occurs in the solution. A model for the solvent–solvent pair potential is presumed to be of the form[133,150]

$$U(\mathbf{X}_i,\mathbf{X}_j) = U(R_{ij}) + U_{el}(\mathbf{X}_i,\mathbf{X}_j) + \epsilon_{HB}G(\mathbf{X}_i,\mathbf{X}_j) \tag{57}$$

where $\mathbf{X}_i$, $\mathbf{X}_j$ denote both the positional and orientational coordinates of the two water molecules *i* and *j*, and R_{ij} is the distance. The first term on the right-hand side is a spherically symmetrical contribution to the total pair potential, whereas the second term includes interaction via electric multipoles. The third term refers to the hydrogen bond (HB) potential: It consists of an energy parameter ϵ_{HB} (HB energy) and a geometrical factor $G(\mathbf{X}_i,\mathbf{X}_j)$ which assumes a maximum value of unity whenever the two water molecules are perfectly hydrogen bonded. After introducing several simplifying assumptions, the following approximate relation is obtained:

$$\Delta\mu^\circ{}_S(\text{in } D_2O) - \Delta\mu^\circ{}_S(\text{in } H_2O) = (\epsilon_{D_2O} - \epsilon_{D_2O})\Delta\langle G\rangle_S \tag{58}$$

The quantity

$$\Delta\langle G\rangle_S = \langle G\rangle_S - \langle G\rangle_0 \tag{59}$$

may be interpreted as reflecting the structural change in the solvent induced by the dissolution of solute S. Here, $\langle\,\rangle$ with index S or 0 denotes the ensemble average of $G_N = \Sigma_{i<j}G(\mathbf{X}_i,\mathbf{X}_j)$ in the solution and in the pure liquid, respectively. Using as an estimate[3,138,321] $\epsilon_{D_2O} - \epsilon_{H_2O} = -0.23$ kcal/(mol of bonds), information as to the magnitude and direction of the structural

changes in water upon dissolution may be obtained from experimental free energies $\Delta\mu^\circ_S$. In accord with many previous conclusions, it appears that argon, methane, ethane, and propane, respectively, indeed stabilize the structure of water, in the sense that the average number of hydrogen bonds becomes larger in the presence of the solute. This effect diminishes with increasing temperature. For butane $\Delta\langle G\rangle_S$ becomes negative at 25 °C. This is an indication that the stabilization effect depends decisively on the size and shape of the solute molecule. A possible generalization of this scheme to include more complicated processes, such as hydrophobic interaction, has been indicated.

A recent extensive bibliography on deuterium and heavy water was prepared by Vasaru et al.[336a]

E. Miscellaneous

1. Solubility of Gas Mixtures in Water

Considerably less work has been done on the saturation solubility properties of gas mixtures in water,[92,337–342] probably the most precise and extensive being that by Benson and Parker,[343] who also critically review the older literature. Generally, it is believed that mixtures of atmospheric gases behave more or less independently when dissolved in liquid water (see also Gurikov[344]). For example, Glasstone,[345] using Winkler's data,[92] has demonstrated that the solubilities of oxygen, nitrogen, and argon each multiplied by their atmospheric pressure may be used to calculate the solubility of air in H_2O to within 1%. However, recently, Maharajh and Walkley[346,347] have reported that mixtures of gases containing oxygen do not behave independently with consequent substantial individual deviations from Henry's law values. Since these results are in variance with other findings (see ref 348–351), it has been suggested on the basis of recent experimental results[352] that these deviations are largely due to inherent difficulties in the adopted gas chromatographic technique.[353–357] However, there is clearly need for more extensive data on solubility of binary and multicomponent gas mixtures in liquids in general and in water in particular.

2. Solubility of Gases in Liquid Mixtures Containing Water

Although in principle this topic is outside the scope of this article, a few papers of immediate pertinence to one or several of the problems considered in the preceding sections will be discussed.

A fair estimate of the solubility of a gas (subscript 1) in a simple binary solvent mixture (subscripts 2 and 3) may be obtained, provided its solubility is known (that is, Henry's law constants $H_{1,2}$ and $H_{1,3}$, respectively) in each of the pure solvents forming the mixture. Such a procedure may be based, for example, on the Wohl expansion,[358] which yields (in its simplest two-suffix version[17]) for the ternary excess Gibbs energy at constant temperature

$$G^E/RT = a_{12}x_1x_2 + a_{13}x_1x_3 + a_{23}x_2x_3 \tag{60}$$

where the a_{ij} are constants characteristic of the ij binary pair. O'Connell and Prausnitz[359] have shown that, for this simple model, the parameters a_{13} and a_{12} are related to the two binary Henry's law constants via

$$a_{13} = a_{12} + \ln (H_{1,3}/H_{1,2}) \tag{61}$$

For Henry's law constant in a binary solvent mixture the desired final result is

$$H_{1,\text{mixt}} = x_2 \ln H_{1,2} + x_3 \ln H_{1,3} - a_{23}x_2x_3 \tag{62}$$

Equation 62 has been extended to multicomponent solvents, and the same equation was shown by Kehiaian to result when Kohler's equation describes the solvent-solvent binaries.[360,361] If the binary solvent system exhibits positive deviations from Raoult's law, that is, $a_{23} > 0$, $H_{1,\text{mixt}}$ will be smaller than that in a corresponding perfect mixture, whereas the opposite is true for $a_{23} < 0$. The parameter a_{23} may be estimated from regular solution theory

$$a_{23} \approx (\delta_2 - \delta_3)^2(V_2^{\circ L} + V_3^{\circ L})/2RT \tag{63}$$

where δ is the solubility parameter, or from vapor-liquid equilibrium data on the solvent mixture.

A correlation based on corresponding states theory has been proposed by Gunn et al.[362] This too is only applicable to nonpolar mixtures.

Using the Kirkwood–Buff solution theory[181] based on pair distribution functions, O'Connell[363] developed expressions to predict Henry's law constants for gases in mixed solvents, including systems with highly polar components and water. However, some of the terms containing pair distribution functions explicitly cannot be evaluated, and consequently they were substituted for by a simple empirical form. Satisfactory agreement with experiment was found. The expression has been generalized to multicomponent solvents.

An evaluation of several additive excess free energy models[359,363–368] for predicting gas solubilities in mixed solvents was carried out by Puri and Ruether.[369] The errors for most models were greatest for systems having water as a component. Most surprisingly, none of the models was as accurate as the assumption of ideality (Krichevsky equation;[364] m denotes the number of solvent components)

$$\ln H_{1,\text{mixt}} = \sum_{i=2}^{m} x_i \ln H_{1,i} \tag{64}$$

which results from eq 62 by setting a_{23} equal to zero. However, much more data must be available before any firm conclusions as to the choice of models can be drawn.

Scaled particle theory, too, has been used to predict the solubility of gases, and associated thermodynamic quantities, in binary mixtures containing water. In particular, Lucas and Feillolay[369a] utilized the Lebowitz-Rowlinson formalism[216] to calculate the free energy of cavity formation in water–methanol mixtures. Interestingly, the calculated enthalpies of solution for argon as a function of concentration and temperature agreed rather well with experiment, whereas the calculated solubilities were not in accord with measured values. A systematic experimental investigation on the solubility of some tetraalkylcarbon, -silicon, -germanium, and -tin compounds in binary mixtures of water with methanol, ethanol, dioxane, acetone, and acetic acid at 25 °C was reported by de Ligny and van der Veen.[369b] Applying scaled particle theory in the manner suggested in ref 369a, they were able to predict correctly the solubility of these rather large molecules in the mixed solvent water-methanol from the results on the pure solvents.

A simplified form of perturbation theory for mixtures has been utilized to predict gas solubilities in mixed aqueous solvent systems by Tiepel and Gubbins[250a] (see also ref 250). For the determination of the molecular Lennard-Jones (6,12) potential parameters σ and ϵ/k for nonpolar as well as for polar components, they use the correlation schemes of Tee, Gotoh, and Stewart,[369c] and that of Bae and Reed,[369d] respectively. However, since the calculations are rather sensitive to errors in σ (see also ref 9), solvent σ values were obtained by fitting gas solubility data for single solvents to the theoretical expression. Henry's law constant (at 298.15 K) was predicted well for the solubility of argon in four binary mixtures at a solvent composition of 50% by mass (H_2O + CH_3OH, + C_2H_5OH, + ethylene glycol, and + *p*-dioxane).

In connection with the interpretation of the anomalous values of the thermodynamic functions of solution of gases in water, Ben-Naim has carried out several studies to elucidate the change of these quantities, when changing continuously from pure water to pure organic solvent.[7,190,191,304,370] Water-alcohol mixtures have been of particular interest.[371] In ref 370, the discussion was based on the two-structure model of liquid water.[326,372] From an analysis of the experimental solubility data in terms of relaxation contributions and contributions from the hypothetical "frozen-in" system, and thermodynamic arguments, Ben-Naim concludes that for H_2O–CH_3OH and H_2O–C_2H_5OH the composition range may be divided into three parts according to the different effect on the structure of water: (a) $x_{ROH} \leqslant 0.03$, both gases and alcohol stabilize the structure; (b) $0.03 \leqslant x_{ROH} \leqslant 0.2$, the gas molecules still stabilize the structure whereas the alcohol destabilizes it; (c) $x_{ROH} \geqslant 0.2$, both solutes destabilize the structure. The more recent paper of Yaacobi and Ben-Naim[304] is concerned with one aspect of the general problem of HI, that is, dependence of its strength upon variation of solvent composition from pure water to pure ethanol. From measured solubilities of methane and ethane, these authors eventually extract numerical results for the free energy referring to HI, and corresponding entropy and enthalpy values which indicate that, as far as structural changes of the solvent are concerned, mixtures with $0.2 \leqslant x_{C_2H_5OH} \leqslant 1$ behave as a "normal" solvent; that is, changes induced by HI in this region are negligible.

Further work on hydrophobic interaction in mixtures containing water was reported by Ben-Naim and Yaacobi,[373] who determined the solubility, and hence standard Gibbs energy, enthalpy, and entropy of solution of methane and ethane in water–1,4-dioxane solutions. The strength of HI measured by $G^{HI}(\tilde{\sigma})$ as well as its temperature dependence was estimated from experimental data according to eq 56. It was found that HI first increases upon addition of dioxane (mole fraction x) to pure water in the region $0 \leqslant x \leqslant 0.15$. At higher concentrations of dioxane the hydrophobic interaction gradually weakens until the low value for pure dioxane is reached. The corresponding entropy and enthalpy changes exhibit a more abrupt behavior as a function of concentration of dioxane. In particular, the very large positive value of the entropy change decreases steeply within the range $0 \leqslant x \leqslant 0.25$. Perhaps the most conspicuous difference to the water-ethanol system[304] is the behavior in very dilute solutions: addition of small quantities of ethanol ($x \leqslant 0.05$) to water weakens the HI, whereas in the same region dioxane strengthens the HI. Its significance with respect to structure stabilization was discussed.

Additional data on methane and ethane solubility in aqueous solutions of electrolytes and nonelectrolytes (1-propanol, dimethyl sulfoxide, and 1,4-dioxane, all at low concentration $x = 0.03$, and sucrose) may be found in ref 101.

Further work along these lines was reported in ref 373a (solubility of argon in mixtures of water and ethylene glycol, 5-25 °C), and 373b (solubility of oxygen in mixtures of ethyl alcohol with water, 4-50 °C).

For a recent spectroscopic investigation of the structure of various alcohol–water solutions, see Bonner and Choi.[373c] The data indicate that in water-rich solutions the fraction of both nonbonded alcohol and water OH groups would be very small, a result which is incompatible with the large fraction of broken hydrogen bonds calculated by Laiken and Nemethy.[373d] by statistical mechanical methods.

A correlation of gas solubilities with the kinetics of hydrolysis in binary aqueous mixtures was presented by Blandamer et al.[373e]

The NMR chemical shift of the water proton in aqueous solutions of alcohols was measured and critically discussed by Marciacq-Rousselot and Lucas.[373f] A NMR study (spin-echo method) on the stabilization of water structure by addition of methyl or ethyl alcohol was also reported by Matyash and Yashkichev.[373g]

3. *Some Ecologically and Biologically Important Systems*

The role of gas dissolution in the ecological balance of fresh-water and sea-water systems[71,340,374-374e] has attracted great interest. Notable are the results of Benson and Parker[343] on solubility of air in sea water[374f] and the data of Enns et al.[122] which have contributed to an increased knowledge of gas equilibria in the deep sea. Several extensive tables presenting the solubility of oxygen[71,87,91,374i] and other gases[71,87,374j] as a function of temperature and salinity[374k] have been prepared, the latter often being accounted for[71,374l,m] by the empirical Setschenow relation[374n]

$$\ln \gamma = k_s S \tag{65}$$

Here, γ denotes the ratio of solubility of a particular gas in pure water to that in sea water, k_s is the salting coefficient, and S is the salinity (usually in parts per thousand). For gases in an aqueous solution of a single electrolyte, scaled particle theory has been applied by Shoor and Gubbins,[252] Lucas,[253] and Masterton[254] to predict k_s. Recently, Masterton[254a] extended this theory to treat seawater. See also Krishnan and Friedman,[254b] and Gerecke and Bittrich.[18a]

The existence of crystalline clathrate hydrate of oxygen in the swimbladder of some deep-sea fish was discussed in detail by Hemmingsen[374o] (see also Enns et al.[374p]).

In situ rates of oxygen utilization and CO_2 production in the equatorial Pacific were calculated (vertical diffusion–advection model[374q]) by Kroopnick[374d] (see also Ben-Yaakov[374r] and Wong[374s]). The process of gas exchange (O_2, CO_2, and water vapor) across an air–water interface has been investigated by Liss.[374t]

Gas dissolution in rain water has recently been used to identify the origins of atmospheric pollutants and natural gases.[375] In particular, the concentration of carbon monoxide in rainwater shows up to a 200-fold supersaturation relative to the partial pressure of the gas in the atmosphere. These results indicate the existence of an additional natural source of CO not heretofore considered. Methane concentrations measured in the same samples show that the partitioning of this gas, unlike that of CO, is very close to the equilibrium value. Although it is generally agreed upon that the residence time of CO in the atmosphere is short, it is not yet possible to specify completely the sources and sinks playing important roles in its geochemical cycle. Production of CO in clouds has been tentatively attributed to the photochemical oxidation of organic matter or the slight dissociation of CO_2 induced by electrical discharges, or both. Measurements have shown that the ocean[376-378] is an important natural source of this gas. Because of its environmental implications, analysis of atmospheric trace gases which might reach surface water via rain has become increasingly important. See, for example, Wilkniss et al.[379] (CO_2, CCl_4, CH_4, Rn, Freon-11).

Data on solubility properties of gases in water have been used in the study of anesthetic action.[380-380c] Featherstone et al.,[381,382] determined the solubility of anesthetic gases in aqueous bovine serum albumin, hemoglobin, and γ-globulin (N_2O, Xe, and cyclopropane), and in blood and protein solutions (Xe and cyclopropane).[382a] X-ray diffraction analysis was used by Schoenborn to study the binding of Xe to horse hemoglobin,[382b] and of Xe and cyclopropane to myoglobin and hemoglobin.[382c] A survey of weak molecular binding forces (van der Waals and hydrogen bonds) with emphasis on binding studies of inert gaseous anesthetic agents by x-ray diffraction analysis was prepared by Schoenborn and Featherstone[382d] (see also ref 382e). The influence of Xe on protein hydration as measured by microwave absorption technique was investigated in ref 382f: a definite increase in irrotationally bound water due to the presence of Xe was observed. Clathrate models for the thermodynamics of interaction between metmyoglobin and an anesthetic gas were discussed by Rothstein and Featherstone.[382g] For a comprehensive general review on partition coefficients, see Leo, Hansch, and Elkins.[383] Based on the experimental determination of partition coefficients of 32 gaseous anesthetics in the system octanol-water, Hansch et al.[383a] formulated a quantitative relation between anesthetic potency, as measured by the effective anesthetic pressure, and the partition coefficient. Their results suggested that the phase in which anesthetic action occurs is lipophilic in character, in agreement with the conclusions of Miller et al.[383b] However, concomitantly they established the major role of polar interaction in disrupting nerve functions. Exploiting the Miller-Pauling theory,[380a,b] which places the site of action of narcotic agents in the aqueous phase of the central nervous system, Haberfield and Kivuls[383c] correlated successfully the entropy of solution in water, $\Delta\bar{S}^\circ{}_2$, of 15 anesthetic gases with the equilibrium solubility x_A in water at the anesthetic pressure P_A of each gas ($x_A = P_A/H_{2,H_2O}$):

$$-\Delta\bar{S}^\circ{}_2/R = -3.56 \log x_A + 3.17 \qquad (66)$$

The effect of inert gas pressure on protein structure and function was investigated by Featherstone et al.[383d] Pressure reversal of anesthesia is an example of the effect of pressure on the central nervous system and has led to the formulation of the critical volume hypothesis.[383e] Miller[383f] proposed to extend this hypothesis to include the high-pressure neurological syndrome; that is, general anesthesia or pressure-induced convulsions occur when a hydrophobic region is expanded or compressed beyond a certain critical amount, respectively. In his opinion, the most probable site of action is situated in the lipid bilayer of some membranes,[383g,h] whose perturbations in turn influence the function of membrane proteins in the neurological apparatus. For additional recent contributions to the highly active field of anesthesia research, see ref 383i–n, and in particular the article by Featherstone and Settle on the pharmacology of the noble gases He, Ne, Ar, Kr, and Xe.[383n]

Enhancement of solubility of hydrocarbons in water by micelles has been well established,[384,385] but only quite recently was a quantitative study of the effect of dissolved paraffinic gases (ethane and propane) on surface tension and critical micelle concentration (CMC) of aqueous solutions of dodecylamine hydrochloride presented (Metzer and Lin[386]). The gases lowered the CMC in a manner equivalent to the effect of increasing the hydrocarbon chain length of the hydrochloride (0.35 unit of $-CH_2-$ for ethane and 0.80 for propane). Size and chemical nature determine the magnitude of the CMC. The variation of the CMC with chain length for a specific homologous series can be represented by[387]

$$\log(\mathrm{CMC/mol\ l^{-1}}) = A - Bn_C \qquad (67)$$

where A and B are constants, and n_C is the number of carbon atoms in the nonpolar side chain. Whereas A varies in a somewhat irregular manner with different head groups, the constant B has been connected with the contribution of hydrophobic bonding to micelle formation.[388]

Wishnia's[384] investigation of the solubility of ethane, propane, butane, and pentane in water and aqueous sodium dodecyl sulfate solutions suggested partial penetration, if not complete solution, of the low molecular weight hydrocarbon in the detergent micelle. Similar conclusions were reached by McBain who reported propylene solubilities in various detergents.[389-391]

Studies on solubility of simple hydrocarbons in protein, detergent and denaturating solutions of urea and guanidinium chloride by Wishnia[384,392,393] and Wetlaufer et al.[394,395] are interesting with respect to hydrophobic interaction in complex systems. Solutions of hydrocarbons in protein solutions should exhibit all the characteristics of HI. Wishnia[396] calculated from solubility studies the thermodynamic functions for the transfer of butane, pentane, and neopentane to water from ideal solutions, dodecyl sulfate micelles, ferrimyoglobin, deoxyhemoglobin, etc. The data, particularly the exceedingly large $\Delta\bar{C}^\circ{}_{P\mathrm{tr}}$, have been interpreted in terms of strong HI. The available evidence eventually led this author to distinguish between three kinds of hydrophobic regions in the protein molecule (see also ref 397).

Extensive surveys of systems of biological and ecological importance and their interrelation with solubility in the most general sense (of which gas solubility is, of course, only a small, but albeit important segment) have been prepared by Hauser[398] (lipids), Eagland[399] (nucleic acids, peptides and proteins), Suggett[400] (polysaccharides), and Molyneux[401] (synthetic polymers). See also ref 401a and 401b.

V. Appendix

A. The Second Virial Coefficient of Water

The compressibility factor of a real gas may be expanded either in a series in inverse powers of volume

$$PV/RT = 1 + B/V + C/V^2 + \ldots \qquad (68a)$$

or in a power series in the pressure

$$PV = RT + B'P + C'P^2 + \ldots \qquad (68b)$$

where all the virial coefficients are independent of pressure or density. The advantage of the former expansion over the latter has been discussed by Rowlinson.[402] It can be shown that $B = B'$ and $C = C'RT + (B')^2$, with more complicated equations between the higher coefficients. A detailed discussion of difficulties encountered when fitting experimental data to either one of the virial equations has been given by Prausnitz.[17]

Data on the second virial coefficient of water vapor for temperatures below 100 °C are scarce. This is due to experimental difficulties. Some of the earliest accurate measurements are those of Keyes et al.[403,404] (see also Stockmayer[405]). Within the range 311 to 733 K the second virial coefficient is adequately presented by

$$B/\mathrm{cm^3\ g^{-1}} = 1.89 - (2641.6K/T)\exp\{1.858 \times 10^5(K/T)^2\} \qquad (69a)$$

In 1947 Keyes[406] published virial coefficients (up to the fourth) for water vapor from 0 to 150 °C according to the pressure equation. A revised version of the Keyes equation, eq 69a, was given by this author[406a] in 1958 (for the inverse volume expansion eq 68a):

$$B/\mathrm{cm^3\ g^{-1}} = 2.062 - (2901.7K/T) \times \exp\{1.7095 \times 10^5(K/T)^2\} \qquad (69b)$$

This expression covers a somewhat larger temperature range than previously. For a detailed discussion of the second virial coefficient at relatively low temperatures (312–398 K), in particular with respect to adsorption of water vapor on the container surface, see Keyes.[406b] Another set of low-temperature virial coefficients (second and third for the pressure equation) was obtained from the experimental heat capacity data of McCullough et al.[407]

More recent measurements at more elevated temperatures (Kell et al.[408]) indicate that the Keyes equation (eq 69a) may be substantially in error for $T < 400$ K. These authors report values for B and C (inverse volume series) and compare them with second virial coefficients obtained from the vapor pressure and the enthalpy of vaporization ΔH_{vap}:[409]

$$\left(\frac{PV}{RT}\right)_\sigma = \frac{\Delta H_{\mathrm{vap}}}{RT^2(1 - V_\sigma{}^{\mathrm{L}}/V_\sigma)(\partial \ln P/\partial T)_\sigma} = 1 + B/V_\sigma \qquad (70)$$

provided that coefficients higher than the second make negligible contributions under these conditions. Here, the index σ denotes

TABLE XV. Experimental Second Virial Coefficients of Pure Water Vapor

	$-B$/cm^3 mol^{-1}				
t/°C	O'C[410]	KI[403]	KII[a]	C-H[409]	K-McL-W[b]
0		2068	1854		
25	1165	1256	1162		
50	803	839	794		
75	590	594	578		
100	454	450	441	460	469

[a] Reference 406. The tabulated values are practically identical with the virial coefficients calculated from eq 69b. [b] Reference 408. These authors use essentially the same methods as Curtiss and Hirschfelder.[409] Enthalpies of vaporization were taken from N. S. Osborne, H. F. Stimson, and D. C. Ginnings [*J. Res. Natl. Bur. Stand.*, **23**, 261 (1939)], as did Curtiss and Hirschfelder. The vapor pressure along the orthobaric curve and its derivative, however, were taken from O. C. Bridgeman and E. W. Aldrich, *J. Heat Transfer*, **86C**, 279 (1964).

properties along the orthobaric curve, V_σ and V_σ^L being the molar volume of coexisting water vapor and liquid water, respectively.

For applications of vapor phase corrections (see section II), second virial coefficients as determined by O'Connell[31,410] (25-100 °C) are recommended. In Table XV they are compared with various other experimental values.

Second and third virial coefficients of D_2O in the range 150-500 °C have been reported by Kell, McLaurin, and Whalley.[410e] Their experimental data show that the difference between the second virial cefficients of H_2O and D_2O is rather small and positive, that is, B_{D_2O} is more negative than B_{H_2O}. At 150 °C this difference amounts to $(B_{H_2O} - B_{D_2O})/\text{cm}^3\ \text{mol}^{-1} \approx 3.7$.

B. The Critical Properties of Water

Critical properties have been extensively reviewed by Kobe and Lynn,[411] and more recently by Kudchadker, Alani, and Zwolinski.[412] The recommended values for water are: T_c = 647.30 K, P_c = 221.2 bars, V_c = 57.1 cm^3 mol^{-1}, and $(PV/RT)_c$ = 0.2347.

The situation is less satisfactory in the case of D_2O. Kell[315] has collected critical parameters of this liquid. All the D_2O data were obtained by classical analysis; it seems that no values from scaling-law analysis[413,414] are available. The most recent results of Blank,[415] albeit for T_c and P_c only, are: T_c = 643.81 K, P_c = 216.59 bars. Elliott[416] suggests T_c = 644.25 K, P_c = 221.36 bars, V_c = 59.2 cm^3 mol^{-1}, and $(PV/RT)_c$ = 0.2446, which are slightly different from results quoted by other authors.[417,418]

C. Thermodynamics of the Ionization of Water

Recently, Olofson and Hepler[419] have summarized results of numerous experimental investigations on the thermodynamics of ionization of liquid water from 0 to 300 °C, and from 1 to nearly 8000 atm. As a result of their careful numerical analysis, the authors give a set of consistent "best" values for the thermodynamic equilibrium constant (ionization constant) $K_w = (a_{H^+})(a_{OH^-})/(a_{H_2O})$ referring to the ionization reaction represented by $H_2O(l) = H^+(aq) + OH^-(aq)$, where the a's denote activities (based on the hypothetical 1.0 molal standard state for solutes, and on the pure liquid for the solvent water). In addition, they report various derived quantities, such as the standard enthalpy change for the ionization reaction, the heat capacity change, the volume change, etc. For temperatures up to 150 °C (standard state P = 1 atm) the following seven parameter equation for pK_w is recommended:

$$\begin{aligned} \text{p}K_w = {} & 142613.6(T/\text{K})^{-1} + 4229.195 \log(T/\text{K}) - 9.7384(T/\text{K}) \\ & + 0.0129638(T/\text{K})^2 - 1.15068 \times 10^{-5}(T/\text{K})^3 \\ & + 4.602 \times 10^{-9}(T/\text{K})^4 - 8909.483 \end{aligned} \tag{71}$$

In the temperature range 150-300 °C, they regard the values from Sweeton et al.[423] as the "best" available.

D. Solubility Data Which Were Not Used

In screening the literature for gas solubility data we found many references. However, in critically selecting which data to use for the smoothing equations, we also had to reject much data. Since references to such data may be of use, and in the interest of this paper providing a complete set of references, we cite these papers in Table XVI. However, we *do not* claim that Table XVI is exhaustive. The temperature range for each set of data is also cited. The citations for oxygen are broken into two parts: the part marked "chem" is for determinations that were done by chemical methods, and the part marked "phys" is for determinations carried out by physical methods.

E. Recent Developments

In general the cutoff date of this review is fall 1975, although a few references were incorporated in the main body of text as late as April 1976. However, the general field covered has remained highly active since submission of the manuscript, which circumstance prompted us to include this appendix with a brief list of some recent contributions (and several not so recent ones!). See also Wilhelm.[423a]

Yamamoto et al.[424] have determined the solubility of methane in distilled water and seawater, documenting the increasing interest in the oceanic distribution of methane.[376,425-427] The experimental data (Bunsen coefficient β) covered the temperature range −2 to 30 °C and the salinity, S, from 0 to 40 parts per thousand, and were fitted to an equation suggested by Weiss:[71]

$$\begin{aligned} \ln \beta = {} & -67.1962 + 99.1624 \frac{100}{T/\text{K}} + 27.9015 \ln \frac{T/\text{K}}{100} + S \\ & \left[-0.072909 + 0.041674 \frac{T/\text{K}}{100} - 0.0064603 \left(\frac{T/\text{K}}{100} \right) \right]^2 \end{aligned} \tag{72}$$

The results for pure water are in good agreement with those of Bunsen,[59] and Claussen and Polglase,[98] but are higher by 3–5% than those of Winkler,[92] and Morrison and Billett.[82]

Butane has often been suggested as a refrigerant for the freezing process of desalting seawater.[428] Thus, Rice, Gale, and Barduhn[429] report supplemental data to those of Umano and Nakano[430] of butane solubility in pure water, in potassium chloride solutions (3.5 and 7.0 wt %), and in synthetic sea salt solutions (3.5 and 7 wt %), for 0–20 °C. In addition, solubilities were measured under different butane pressures to check the validity of Henry's law. See also Bajolle et al.[431] for a critical examination of literature data on butane solubility in water.

Solubilities of fluorinated hydrocarbons in water have been determined by Battino et al.[432]

A semiempirical correlation for estimating gas solubilities which is based on Alder's[433] perturbed hard-sphere equation of state, has been proposed by Cysewski and Prausnitz.[434] The hard-sphere equation of state is that of Carnahan and Starling;[263] the perturbation is due to a square well potential, the width of which is half of the collision diameter. The expression for Henry's law constant contains two essentially empirical temperature-independent parameters v_{12}^* and T_{12}^*, which characterize the interaction of a solute molecule surrounded by solvent molecules. For water, alcohols, and polar solvents, v_{12}^* was correlated with V_c, the critical volume, by

$$v_{12}^* = -0.379 + 0.177 V_{c1} + 1.595 \times 10^{-5} V_{c2} \tag{73}$$

This equation indicates that v_{12}^* is a strong function of V_{c1}

(solvent) but a weak function of V_{c2} (solute). Correlation of T_{12}^* is considerably more difficult with apparently only a rough correlation with V_{c1}. Henry's law constants are usually predicted within a factor of 2 and often better.

A method to predict solubility of gases (and its temperature dependence as well) which is based on the free-volume theory of liquids was advanced by Gotoh.[435] Estimation of solubility of hydrocarbons, alcohols, etc., in water in terms of molecular surfaces was discussed in detail by Amidon et al.[436]

Hydrophobic interaction continues to attract the attention of many researchers.[437-442] Particularly interesting in the present context are the articles of Tenne and Ben-Naim,[441] and of Hertz and Tutsch.[442] The former measured the solubility of methane, ethane, and propane in aqueous solutions of tetraalkylammonium salts, and subsequently utilized as an approximate relation of the strength of hydrophobic interaction either eq 56, or, exploiting solubility data of propane, the relation[133]

$$\delta G_3^{\mathrm{HI}}(\bar{\sigma}) = \Delta\mu^\circ_{\mathrm{C_3H_8}} - 3\Delta\mu^\circ_{\mathrm{CH_4}} \qquad (74)$$

Perhaps most surprising is their conclusion that δG^{HI} increases with addition of tetraalkylammonium salts; the effect of these salts on HI is more or less the same as the effect of simple salts.[101]

On a more direct level, Hertz and Tutsch[442] measured nuclear magnetic relaxation rates of the CH protons of aqueous solutions of formic acid, of the CH_2 and CH_3 protons of aqueous solutions of acetic, propionic, and butyric acids, respectively, and of ethanol, all as a function of concentration. The salient point is that propionic acid and butyric acid molecules experience a change in the relative pair configuration, with increasing water content, in such a way as to produce a *side-by-side* configuration of the hydrocarbon chains. In ethanol–water mixtures no hydrophobic association is observable.

Lucas and Bury[443] have further elaborated on an improved version of scaled-particle theory[247,444] (for recent advances in SPT see ref 445, 445a,b, and 446), in that thermodynamic quantities referring to transfer from the gaseous phase to water, and from H_2O to D_2O, are discussed with respect to the size of the solutes, and in the latter case also with respect to structural differences between light and heavy water.[447]

The overall deuterium isotope separation factor between hydrogen and liquid water has been measured directly for the first time in the temperature range 280–370 K by Rolston, den Hartog, and Butler.[448] The same problem was treated theoretically (with a correction for the Born–Oppenheimer approximation) by Bardo and Wolfsberg.[449]

A comparatively large number of papers has apped on gas solubility in binary or multicomponent aqueous mixtures, partly of importance to the design of industrial plants. Aqueous solutions of monoethanolamine (MEA) and of diethanolamine are used as absorbants in natural gas sweetening systems to remove hydrogen sulfide and carbon dioxide from plant feed gases. Solubilities pertaining to these systems, plus data on methane and ethane in these solutions, have been given by Lawson and Garst[450,451] (these authors present a comprehensive list of older references and data collections on this topic). Vapor–liquid equilibrium in H_2S–MEA–H_2O systems was also investigated by Lee, Otto, and Mather.[452]

Isobutene solubility in aqueous solutions of $(NH_4)_2SO_4$, in aqueous sulfuric acid, in aqueous solutions of $(NH_4)_2SO_4$ + *tert*-butyl alcohol, as well as in H_2SO_4-*tert*-butyl alcohol-H_2O has been determined by Deckwer.[453]

Careful experimental investigations of gas solubility in water-ethanol and water-*tert*-butyl alcohol mixtures which cover the whole concentration range, have been reported at several temperatures between 4 and 62 °C by Cargill and Morrison[454] (Ar) and Cargill[455] (O_2). The associated thermodynamic functions $\Delta \bar{H}_2^\circ$, $\Delta \bar{S}_2^\circ$, and $\Delta \bar{C}_{P2}^\circ$ are discussed in terms of changes in the structure of water with increasing mole fraction of alcohol. In particular, it was suggested that the observed maximum in the curve $\Delta \bar{C}_{P2}^\circ$ vs. x_{ROH} at very low alcohol concentration may be taken as additional evidence for the stabilizing effect of small amounts of alcohol as well as gas on the hydrogen-bonded network of water. For a comparison between these experimental data and calculations via scaled particle theory, see Lucas and Cargill.[456] The solubility of nitrous oxide in mixtures of various alcohols and water has been measured by Sada et al.[456a]

The chemistry of ozone in the treatment of water has been reviewed by Peleg,[457] a timely article indeed, because of the considerable number of installations operating with ozone as disinfectant for drinking water.

A major contribution to chemical oceanography is the second edition of "Chemical Oceanography", which contains in Vol. 1 and 2 articles dealing with dissolved gases in seawater.[458,459]

Excesses of dissolved ^{3}He (up to 32% relative to the atmospheric ^{3}He/^{4}He ratio) have been reported for Pacific deep water[460-462] and in the Atlantic,[463] and were attributed to a flux of primordial helium and/or in situ decay of tritium from nuclear weapon testing. Along this line, Jenkins and Clarke[464] have established the pattern of ^{3}He excess in the western Atlantic. For additional data on dissolved gases in marine waters, see, for example, ref 464a,b.

As already indicated above, there is a need to establish the baseline concentrations of low-molecular-weight hydrocarbons in sea water. The data can be used to assess the extent of oil pollution in the oceanic environment. The extensive efforts of Swinnerton and Lamontagne[426] have resulted in a detailed picture of the concentration and distribution of methane, ethane, ethylene, propane, and propylene in surface seawater. Against this background an empirical relationship, the "Contamination Index" CI, is proposed to differentiate between open clean water and water contaminated by hydrocarbons:

$$\mathrm{CI} = \tfrac{1}{3}(C_1/C_1^* + C_2/C_2^* + C_3/C_3^*) \qquad (75)$$

Here C_1, C_2, and C_3 are the actual concentrations of methane, ethane, and propane, respectively, while the starred quantities are average baseline concentrations of these hydrocarbons in clean ocean water. See also ref 376, 427, 465, and 466.

Dissolved CO, CH_4 and H_2 in southern ocean surface water was measured by Williams and Bainbridge.[427]

Simultaneous determination of dissolved oxygen, nitrogen, and carbon dioxide in water by membrane diffusion and subsequent gas chromatographic analysis has been developed by Kollig et al.[467]

The effects of dissolved air and natural isotopic distribution[468,469] on the density of water have been determined by Millero and Emmet[470] at 1 atm as function of temperature. Dissolved air was found to decrease the density by $(3.0 \pm 0.2) \times 10^{-6}$ g/cm^3 at 4 °C. The apparent molal volume of air was found to be only slightly dependent of gas concentration and independent of temperature between 0 and 30 °C. See also Bradshaw[471] and Millero and Berner,[472] and ref 44, 94, and 122.

The extensive topic "water in biological systems" has been recently reviewed by Luck,[473] who devotes a considerable part of his work to the structure of aqueous solutions, in particular to the problem of hydrophobic solutes (see also Lauffer[474]).

The effect of ultrasound on water in the presence of dissolved gases has been investigated by Mead et al.[475] Sonolysis at 447 kHz causes a decrease in pH. In the presence of air, the products observed are hydrogen peroxide, nitrous and nitric acids.

In conclusion, a few articles dealing with pure water and seawater will be cited. Hawkins[476] has prepared a comprehensive bibliography on the physical and chemical properties of water, covering the time period 1969–1974. Millero et al.[477] measured the density of seawater at one atmosphere as a function of temperature (0 to 40 °C) and salinity (0.5 to 40‰)

TABLE XVI. Sources of Low-Pressure Solubility Data for Gases in Liquid Water Which Were Not Used for the Smoothing Equations

Temp range, T/K

1 (He)
298[a]
298[b]
273–323[c]
311[d]
311[e]
291–306[f]
298–353[251]
298–353[g]

2 (Ne)
311[h]
274–288[i]
273–283[c]
298[j]
291–307[f]
283–313[k]
293[l]
293[m]
283–313[n]

3 (Ar)
303[o]
273–293[p]
288–298[a]
298–313[q]
283–293[r]
298[b]
273–323[c]
275–313[v]
298–313[s]
298[j]
298[t]
273[u]
298–353[251]
278–323[106]
298–353[g]
298–308[v]
293[w]
313–343[x]

4 (Kr)
274–297[r]
298–318[80]
273–323[c]
274–293[y]

5 (Xe)
273–293[p]
278–298[r]
303[z]
273–323[c]

6 (Rn)
273–353[aa]
294[bb]
273–291[cc]
273–312[dd]
273–333[ee]

7 (H_2)
278–298[ff]
277–297[59]
277–297[61]
293[93]
298[gg]
298[hh]
293[ii]
293–298[jj]
293[kk]
298[ll]
286–292[mm]
275–299[nn]
298[oo]
292–305[f]
298–333[251]
298–333[g]

8 (N_2)
298[pp]
311[n]
298[54]
294[qq]
278–298[ff]
277–297[59]
273–293[60]
277–297[61]
293[93]
298[gg]
273–323[rr]
311[ss]
311[ll]
293[ii]
293–298[jj]
289–291[mm]
298[uu]
293[vv]
298–311[ww]
273–353[88]
311[e]
298[j]

9 (O_2, chem)
298[xx]
275–302[339]
274–308[yy]
278–302[340]
293[zz]
298[aaa]
273–309[bbb]
298[ccc]
273–303[88]
273–333[89]

9 (O_2, phys)
281–302[85]
273–398[p]
285–303[340]
298[54]
293[ddd]
279–297[eee]
294[qq]
279–296[59]
273–293[60]
279–296[61]
293[93]
288–298[fff]
273–323[rr]
288–289[mm]
298[uu]
280–286[nn]
298[j]
296[348]
298–353[251]
298[ggg]
298–353[g]
277–323[hhh]
293–353[iii]

10 (O_3)
288[jjj]

11 (CO)
279–298[59]
273–293[60]
279–295[61]
293–298[jj]

12 (CO_2)
293–311[kkk]
283–303[lll]
293–303[mmm]
298[nnn]
285–350[ooo]
293–348[ppp]
311[qqq]
298–318[80]
278–296[59]
273–293[60]
289[rrr]
293[93]
298[sss]
298[ttt]
298[uuu]
298[vvv]
298[hh]
298[www]
288–298[fff]
298[jj]
273–298[xxx]
298[yyy]
293–307[mm]
273–313[nn]
273–298[zzz]
298[aaaa]
298[uu]
273[bbbb]
298[cccc]
288[dddd]
293[eeee]
311[ffff]
298[oo]
298[gggg]
274–303[hhhh]
303–353[iiii]
298[jjjj]
303[kkkk]
294[llll]
297–308[mmmm]

13 (CH_4)
273–293[p]
298[96]
298[97]
298[54]
278–318[394]
278–297[59]
273–293[60]
278–297[61]
293[93]
311–344[nnnn]
283–303[101]
298–353[g]

14 (C_2H_6)
273[oooo]
273–293[p]
298[96]
298[97]
298[54]
278–318[394]
279–295[59]
273–293[60]
279–295[61]
283–303[pppp]

15 (C_2H_4)
311–361[qqqq]
303[q]
298[97]
298[54]
288[rrrr]
273–293[60]
278–294[61]
298–311[ss]
298[uu]
303[ssss]
298[tttt]

16 (C_2H_2)
311[ss]
298[tttt]
298[uuuu]

17 (propane)
289–361[vvvv]
298[96]
298[97]
293[wwww]

19 (propyne)
298[97]

20 (cyclopropane)
310[382]

21 (*n*-butane)
298[96]
298[97]

22 (isobutane)
298[96]

25 (1,3-butadiene)
311–378[xxxx]

32 (CF_4)
280–312[72]
298[107]

42 (NH_3)
298[yyyy]
333[115]
298[zzzz]
298[aaaaa]
273–298[zzz]
273–313[bbbbb]
298[oo]

46 (N_2O)
309[ccccc]
298[sss]
298[ddddd]
298[uuuu]
298[uu]
278–298[eeeee]
298[fffff]

47 (NO)
293[ggggg]
298[hhhhh]

48 (H_2S)
273–313[61]
298[iiiii]
273–298[xxx]
298[jjjjj]
273[bbbb]
298[kkkkk]

49 (SO_2)
273–333[lllll]
283–305[mmmmm]
273–285[nnnnn]
298[ooooo]
273–313[61]
298–308[lll]
283–300[ppppp]
283–298[zzz]
281–323[113]
278–333[qqqqq]

50 (SF_6)
273–298[a]
284–303[rrrrr]
298–353[251]
298–353[g]

51 (Cl_2)
294[sssss]
287[ttttt]

52 (Cl_2O)
277[uuuuu]

54 (H_2Se)
288–308[vvvvv]

56 (AsH_3)
280–294[wwwww]
293[xxxxx]
293[yyyyy]

57 (air)
294[e]
273–293[59]
273–293[60]
293[337,338]
295–297[zzzzz]

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to a precision of $\pm 3 \times 10^{-6}$ g/cm^3. For a recent determination of high pressure specific volumes (up to 1000 bar) in the same range of temperature and 5 to 40‰ salinity, see Chen and Millero.[478] Compressibility data of distilled water and seawater were also obtained by Bradshaw and Schleicher.[479] For comprehensive articles on the physical chemistry and structure of seawater see ref. 480–482.

High precision absolute sound velocity measurements in pure water and natural seawater of 35‰ salinity (3.3 – 34 °C, atmospheric pressure) have been reported by Kroebel and Mahrt.[483] See also Del Grosso,[374h,484,485] and Millero and Kubinski.[486]

Speed of sound measurements in mixtures of H_2O and D_2O were carried out by Mathieson and Conway,[487] and more extensively by Gupta et al.[488] For pure ordinary water the results of the latter authors agree closely with those of Wilson,[17h] whereas for D_2O somewhat higher values are obtained than Wilson's.[489] However, their results agree closely with the data of McMillan and Lagemann.[490]

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VI. References and Notes

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(16) At low or moderate pressures, the standard state chemical potential of pure liquid at system temperature is usually taken either at $P_{1\sigma}$ (where the subscript σ indicates orthobaric conditions), or else at the total pressure P of the mixture. At conditions remote from critical, the difference between these quantities (the Poynting correction) is small:

$$\mu_1{}^{\circ L}(T,P) = \mu_1{}^{\circ L}(T,P_{1\sigma}) + \int_{P_{1\sigma}}^{P} V_1{}^{\circ L}(T,P)\,dP$$
$$\approx \mu_1{}^{\circ L}(T,P_{1\sigma}) + V_1{}^{\circ L}(T,P = P_{1\sigma})(P - P_{1\sigma})[1 - \beta_T(P - P_{1\sigma})/2]$$

where $V_1^{\circ L}$ denotes the (pressure dependent) molar volume of pure solvent, and $\beta_T = -(\partial V_1^{\circ L}/\partial P)_T/V_1^{\circ L}$ is the isothermal compressibility. Since for low pressures $\beta_T(P - P_{1\sigma})/2 \ll 1$, the condensed phase may often be regarded as incompressible, in which case the relation takes the simple form

$$\mu_1^{\circ L}(T,P) = \mu_1^{\circ L}(T,P_{1\sigma}) + V_{1\sigma}^{\circ L}(P - P_{1\sigma})$$

with $V_{1\sigma}^{\circ L}$ being the molar volume at saturation. However, in high-pressure work great care has to be taken in specifying the appropriate pressure of the standard state.[17]

For a discussion of several aspects of volumetric behavior of dense fluids under hydrostatic compression in general, see Macdonald,[17a] Hayward,[17b] and Wilhelm.[17c,d] High-precision work on water, in particular, was reported by Kell and Whalley,[17e,f] and by Fine and Millero.[17g] The latter authors determined the isothermal compressibility of water from 0 to 100 °C and 0 to 1000 bar from Wilson's[17h] sound velocity measurements which have been normalized to Kell's 1 atm values.[17f] These compressibilities have been fit, with a maximum deviation of ±0.016 10^{-6} bar^{-1}, to an extended secant bulk modulus equation, viz.

$$K = V_0P/(V_0 - V_P) = B + A_1P + A_2P^2$$

where K is the secant bulk modulus (at 1 atm or $P = 0$, $K = B = \beta_T^{-1}$), B, A_1, and A_2 are temperature-dependent parameters, and P is the applied pressure. V_0 and V_P are the specific volumes at an applied pressure of zero and P, respectively. Recently, Tanishita[17i] et al. presented an extensive experimental study of the PVT properties of water in the following ranges: of temperature, 323.15 to 773.15 K, of pressure, 1.673 to 195.165 MPa, and of specific volume, 0.94444 to 31.66 $\text{cm}^3\ \text{g}^{-1}$. The measurements were made with a constant-volume piezometer which was contained within a pressure vessel. The experimental uncertainties with respect to specific volume were estimated to be less than 0.03%.

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$$PV^v/RT = 1 + B/V^v \tag{7c}$$

where B is a function of temperature and composition only. Its composition dependence in an N component mixture is represented exactly by

$$B = \sum_{i=1}^{N}\sum_{j=1}^{N} y_iy_jB_{ij}$$

with B_{ii} and B_{jj} being the second virial coefficients of the pure components, and B_{ij} ($i \neq j$) denotes the second virial cross coefficient.
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$$P = \frac{RT}{V - b} - \frac{a(T)}{T^{1/2}V(V + b)}$$

where b is a constant reflecting molecular size (repulsive interaction), and a reflects attractive intermolecular interaction. Subsequently, $a(T)$ is decomposed into a temperature-independent (representing dispersion forces) and into a temperature-dependent part (reflecting attraction due to hydrogen bonds, permanent dipoles, etc.), that is

$$a(T) = a_0 + a_1(T)$$

By assuming rather simple mixing rules, good results were obtained for mixtures of water with a nonpolar gas. For water-carbon dioxide mixtures there is experimental evidence indicating complex formation in the gas phase.[34] Thus, the second virial cross coefficient (Nothnagel et al.[30]) is decomposed into a physical and chemical part,

$$B_{12} = B_{12}(\text{physical}) - RTK/2$$

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$$y_1 = \frac{(1 - x_2)\phi_1^{\circ}(T,P_{1\sigma})P_{1\sigma}}{\phi_1(T,P)P}\exp\left[\frac{V_{1\sigma}^{\circ L}(P - P_{1\sigma})}{RT}\right]$$

Here, $\overline{V}_1^L$ is the partial molar volume of solvent 1. For water and a partial gas pressure of $(P - P_{1\sigma}) = 1$ atm at 273.15 K, the Poynting correction amounts to 1.0008. Thus, in the low-pressure range, the crucial factor determining the value of y_1 is the nonideality of the vapor phase: Since $x_2 \ll 1$, the vapor-phase solubility is determined primarily by the fugacity coefficient ϕ_1. At elevated temperatures and hence higher pressures, Prausnitz[41] has proposed an iterative trial-and-error scheme for the evaluation of y_1.
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$$U(\mathbf{X}_1,\mathbf{X}_2) = U_{LJ}(r_{12}) + S(r_{12})U_{HB}(\mathbf{X}_1,\mathbf{X}_2)$$

where LJ stands for Lennard-Jones, and HB for hydrogen bond. Both the positional and the orientational coordinates are denoted by $\mathbf{X}_i$. The hydrogen-bonding contribution, $U_{HB}(\mathbf{X}_1,\mathbf{X}_2)$, results solely from the Coulombic interactions among the 16 pairs of point charges. The Lennard-Jones (12,6) part is presumed to be the same as for neon, which is isoelectronic with water. Combination of the two parts of the potential is achieved by a suitably chosen "switching function" $S(r_{12})$, which is unity at large distances r_{12} (U_{HB} is then fully coupled) and vanishes at small distances where only the Lennard-Jones part is effective. Physically it represents the short-range repulsive effects of the high electron densities in the vicinities of the protons.
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(305) For this particular problem only information on $y(R_{12})$ in the range $0 < R_{12} < \sigma$ is needed. Two sources of preliminary information were considered: (a) the Percus–Yevick approximation for hard spheres yields an analytical expression,[306] since for $R_{12} < \sigma$

$$c(R_{12}) = -y(R_{12})$$

with $c(R_{12})$ being the direct correlation function; (b) numerical solutions of the Percus–Yevick equation for real fluids. These two pieces of information on the form of $y(R_{12})$ in the range $0 < R_{12} < \sigma$ were used for an estimate of δA^{HI} $(R_{12} = \sigma)$; that is, $y(R_{12})$ was approximated by a polynomial expression in distance R_{12} of degree 2:

$$y(R_{12}) = a_0 + a_1(R_{12}/\sigma) + a_2(R_{12}/\sigma)^2$$

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