eV. These T values are about 1.5 to 2 eV less than the observed $T = 8.03$ eV. On the other hand, $A^3\Sigma_u^+$ is estimated to yield two $O^+(^4S)$ ions at $T = 7.8$ eV, which is only 0.2 eV less than the observed value.

The recorded spectrum shows no evidence of processes occurring at other than 8.03 eV and is in substantial agreement with theoretical prediction, if the predominant metastable species decomposes from the $A^3\Sigma_u^+$ state. Otherwise, one would conclude that Hurley's $E(R)$ curves are estimated too low by about 2 eV. In this event a clear-cut identification of a metastable state would likely be impossible.

Finally, in $NO \cdot ^{2+}$, the predicted T values of 6.4 and 6.3 eV resulting from $X^2\Sigma^+$ and $A^2\Pi$, respectively, producing $N^+(^2P) + O^+(^4S)$ are only slightly removed from the observed $T = 6.15$ eV.

Hurley was able only to consider doublet states of $NO \cdot ^{2+}$, and so no consideration of possible quartet states can be made here.

It may be noted with the N_2 and O_2 systems that closest agreement with predictions was obtained in our assumed process when the predominant species is a dissociable metastable doubly charged ion assigned to a high vibrational level of the same electronic spin state as the parent neutral diatomic.

Internuclear distances corresponding to maxima in the $E(R)$ curves believed to be significant here may be estimated from Figure 7. They are approximately 1.9, 1.6, and 1.9 Å for N_2^{2+}, O_2^{2+}, and $NO \cdot ^{2+}$, respectively, compared to the upper limits given in Table I as 2.31, 1.79, and 2.34 Å, respectively. Thus can be clearly seen the extent of covalency effects (*e.g.*, interaction with states arising from $A^{2+} + B$) in lowering the purely Coulombic repulsion between the A^+ and B^+ ions at distances approaching normal bond lengths.

Similar agreement between theory and experiment is found among the other cases listed in Table I. In the course of earlier work, Hurley and Maslen[12] calculated theoretical T values for CO^{2+}, Cl_2^{2+}, Br_2^{2+}, and I_2^{2+} of 56.8, 4.70, 4.28, and 3.7 eV, respectively.[13] These results also stand in excellent agreement with corresponding experimental values presented in Table I. Interpretations of the other experimental data should yield to a similar treatment when the appropriate theoretical $E(R)$ calculations become available.

Acknowledgment. J. H. Beynon and R. M. Caprioli thank the U. S. Department of Health, Education, and Welfare, National Institutes of Health, for financial support under Grant No. FR-00354-02.

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Solubility of Water in Compressed Carbon Dioxide, Nitrous Oxide, and Ethane. Evidence for Hydration of Carbon Dioxide and Nitrous Oxide in the Gas Phase[1]

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Abstract: The solubility of water in compressed carbon dioxide, nitrous oxide, and ethane has been measured over pressure ranges of 1–60 atm and temperatures ranging from 25 to 100°. Second cross virial coefficients representing deviations from ideality caused by gas–water pair interactions have been evaluated from these data. The cross virial coefficients involving water with carbon dioxide and nitrous oxide are found to be considerably more negative than those for water with ethane at all temperatures. The anomalously large values of these coefficients for water with carbon dioxide and nitrous oxide are interpreted as indicating that a reversible hydration reaction occurs between these gases and water vapor in the gas phase. Values of K_{eq} and the standard enthalpies and entropies of reaction for these equilibria are estimated.

Hildebrand and Scott[2] have presented considerable evidence based on solubility data for the existence of specific chemical interactions involving carbon dioxide, nitrous oxide, and acetylene with many solvents in the liquid phase. In the CO_2–water system, an acid–base reaction is postulated, resulting in the formation of carbonic acid. Considerably less is known regarding the association of nitrous oxide or acetylene with such solvents. There is some evidence that these gases behave in a similar manner in the gas phase. Prausnitz and coworkers[3a] have examined PVT properties of the ammonia–acetylene system and conclude that weakly bound complexes exist in gaseous mixtures of these two compounds. Other evidence[3b] indicates that CO_2 forms a very weak complex with naphthalene vapor at room temperature while N_2O does not.

This paper reports measurements of the solubility of water in compressed carbon dioxide, nitrous oxide, and ethane which were carried out in order to assess the nature and significance of any chemical forces that

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[1] This work was supported by the National Science Foundation.

[2] J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," Reinhold, New York, N.Y., 1950; reprinted by Dover Publications, New York, N. Y., 1964, p 248.

[3] (a) H. Y. Cheh, J. P. O'Connell, and J. M. Prausnitz, *Can. J. Chem.*, **44**, 429 (1966); (b) A. D. King, Jr., *J. Chem. Phys.*, **49**, 4083 (1968).

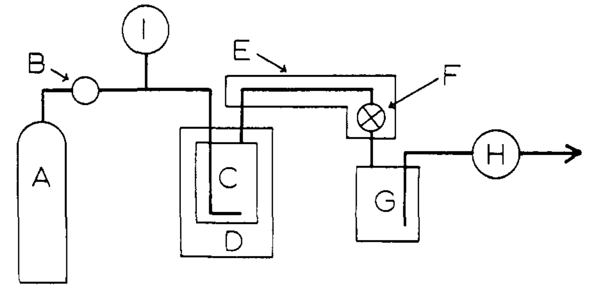

Figure 1. Schematic diagram of equipment.

might exist between water and the gases CO_2 and N_2O in the gas phase. This information is valuable in that it provides thermodynamic quantities useful in interpreting the liquid-phase properties of these same systems. Such an understanding is important considering the biological and industrial importance of these two systems.

The solubility of a liquid in a compressed gas is determined by two factors: variations in the fugacity of the liquid phase, caused by hydrostatic pressure and dissolved gas, and deviations from ideal behavior of the fugacity of the liquid component in the gas phase. At low to moderate pressures the concentrations of gas dissolved in the condensed phase are quite low so that the liquid component in the condensed phase exhibits ideal solution behavior. However, in the gas phase, deviations from ideality caused mainly by pair interactions between molecules of the liquid component and those of the gas are often quite significant. As a consequence of this, solubility determinations for liquids in compressed gases can be used to provide accurate values of second cross virial coefficients representing such deviations from ideality. The magnitude and temperature dependence of these cross virial coefficients provide the information necessary to characterize the weak physical and chemical forces present in the various water–gas systems studied here.

Experimental Section

The experimental technique used here for determining the solubility of water in these compressed gases is a modification of a method used by Prausnitz and Benson[4] and is described in detail in ref 5. The method entails measuring the concentration of water vapor in equilibrium with its liquid phase in the presence of the compressed gas by means of a flow system shown schematically in Figure 1.

The gas to be studied is allowed to flow under high pressure from its storage cyclinder (A) through a Matheson Model 3 pressure regulator (B) into a cylindrical steel equilibrium cell (C) containing water. This cell is identical with that described in ref 5 with the exception of a Pyrex liner added to prevent corrosion. In use, the cell was filled with water to a level approximately 2 in. from the top. The high-pressure gas entering the bottom of this cell is dispersed into small bubbles by a fritted glass sparger (pore size 14 μ) to ensure rapid equilibration between the gas and water as the bubbles pass up through the liquid phase. There were no problems with water entrainment or splashing at the surface provided adequate dead space was maintained over the liquid surface. The temperature of this cell was controlled to within ±0.05° by a constant-temperature oil bath (D).

The vapor–gas mixture leaving the cell passes through a heated section of tubing (E) and is expanded through a heated stainless steel needle valve (F) into a trapping section (G). This trapping section consisted of either three cold traps connected in series and suspended in a cold bath maintained slightly above Dry Ice–acetone temperature (−75°) or a magnesium perchlorate trapping system similar to that used by Rigby and Prausnitz.[6] After leaving the traps, the gas stream passes through an American Meter Co. Model AL-17-1 wet-test meter (H) which measures the volume of diluent gas passing through the system during a given experiment. The pressure of the gas-phase system in the high-pressure section between the regulator (B) and the expansion valve (F) is measured with a 1000-lb/in.^{2} range bourdon gauge (I). This gauge was calibrated against an Aminco Model 47-2221 dead-weight tester.

The experimental procedure followed is very simple. The system containing water is loaded with high-pressure gas and allowed to come to equilibrium for at least 12 hr at the desired temperature. The needle valve (F) is then adjusted to give the appropriate flow rate (0.5–1.0 l./min) and, after a short delay to assure steady-state conditions, the expanded gas–water vapor mixture is directed through the trapping system (G). After a desired period of time, flow of the gas–water vapor mixture through the traps (G) and wet-test meter (H) is stopped and the weight of water trapped and volume of dry gas at ambient temperature and pressure accompanying this water are recorded. The amount of water collected ranged from 0.3 to 2 g depending upon the temperature of the gas–water mixture in the cell and duration of flow. Since the trapping systems used here were very efficient, no effort was made to correct for loss of residual water vapor. No variation of water vapor concentration with flow rate was detected over the ranges used in these experiments, indicating that complete saturation was obtained in the equilibrium cell under these conditions.

The gases ethane (CP grade) and nitrous oxide were obtained from Matheson Gas Products having purities of 99.0 and 98%, respectively. The carbon dioxide was obtained from Selox Corp. with a quoted purity of 99.8%. Ordinary distilled water was used in all experiments.

Results and Discussion

A single determination of the mole fraction of water in a given diluent gas at a known pressure and temperature provides sufficient information for determining the second cross virial coefficient for that system at that temperature if (a) the solubility of the gas in the liquid phase is low and is known at that pressure, (b) the second virial coefficients of pure water vapor and pure diluent gas are known at the temperature of the experiment, and (c) the pressure is not so great as to require the introduction of third and higher virial coefficients to describe the gas-phase properties of the mixture in the equilibrium cell.

The fugacity of water (component 2) in the liquid phase, f_2^L, is related to the mole fraction of dissolved gas (component 1), X_1, and the total hydrostatic pressure of the system, P, by

$$f_2^L = \gamma_2^L(1 - X_1)P_2^0\phi_2^0 \exp\left[\frac{V_2^{0(L)}(P - P_2^0)}{RT}\right] \qquad (1)$$

Here P_2^0 and ϕ_2^0 are the vapor pressure and fugacity coefficient of pure water vapor at temperature T, while γ_2^L and $V_2^{0(L)}$ are the activity coefficient and molar volume of water in the liquid phase, assumed to remain constant over the ranges of pressure encountered here. When the mole fractions of dissolved gas are low as in these experiments, γ_2^L can be taken to be unity without introducing appreciable error. The fugacity of water vapor in the gas phase, f_2^G, is a function of the mole fraction of water in the gas phase, Y_2, its fugacity coefficient, ϕ_2, and the pressure

$$f_2^G = \phi_2 Y_2 P \qquad (2)$$

The condition for equilibrium is $f_2^G = f_2^L$, so that the vapor-phase concentration of water is related to the hy-

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Table I. Vapor Composition in Binary Systems Containing Water

	Temp, °C	Total pressure, atm	Mole fraction of water, Y_2
CO_2	25	22.4	0.00195
		29.4	0.00163
		29.6	0.00167
		36.8	0.00145
		36.9	0.00149
	50	17.1	0.00841
		25.2	0.00595
		25.5	0.00598
		35.9	0.00466
		35.9	0.00463
		45.7	0.00396
	75	23.0	0.0200
		36.9	0.0125
		37.0	0.0126
		50.6	0.0104
		50.8	0.0102
	100	36.3	0.0328
		36.7	0.0323
		44.2	0.0277
		44.2	0.0274
		50.8	0.0248
		50.8	0.0251
N_2O	25	24.0	0.00172
		29.3	0.00158
		31.5	0.00144
		31.6	0.00144
		36.5	0.00127
		36.7	0.00151
		36.7	0.00137
		43.3	0.00124
	50	23.0	0.00659
		29.4	0.00537
		29.6	0.00520
		30.1	0.00510
		36.5	0.00462
		38.4	0.00481
N_2O	75	23.7	0.0189
		23.9	0.0190
		24.0	0.0180
		24.3	0.0177
		29.3	0.0158
		29.4	0.0158
		30.8	0.0149
		35.9	0.0135
		36.0	0.0134
		36.4	0.0129
		36.6	0.0130
		37.2	0.0132
	100	21.9	0.0507
		29.2	0.0404
		29.3	0.0407
		29.4	0.0392
		29.4	0.0377
		34.9	0.0350
		35.9	0.0326
		36.0	0.0329
		43.0	0.0282
		43.0	0.0288
		49.3	0.0251
		49.3	0.0252
C_2H_6	25	24.1	0.00142
		29.3	0.00111
		35.5	0.00090
		35.6	0.00093
	50	22.5	0.00563
		29.3	0.00432
		29.3	0.00432
		29.3	0.00437
		35.3	0.00354
		35.8	0.00354
	75	23.0	0.0175
		23.4	0.0169
		29.9	0.0132
		35.8	0.0109
	100	25.6	0.0414
		28.9	0.0367
		29.5	0.0360
		35.9	0.0296

drostatic pressure of the system by

$$Y_2 = \frac{(1 - X_1)p_2^0}{P}\left(\frac{\phi_2^0}{\phi_2}\right)\exp\left[\frac{V_2^{0(\mathrm{L})}(P - P_2^0)}{RT}\right] \qquad (3)$$

If contributions arising from third and higher virial coefficients are neglected the fugacity coefficient of water in gas mixture can be expressed as

$$\ln \phi_2 = (2/V)[Y_2B_{22}(T) + Y_1B_{12}(T)] - \ln Z \qquad (4)$$

where Y_1 represents the mole fraction of diluent gas in the gas phase, V is the molar volume of the gas mixture, and the symbols $B(T)$ denote second virial coefficients representing deviations from ideality caused by pair interactions between molecules of the species designated by the subscripts. Z represents the compressibility factor of the gaseous mixture.

It is seen in eq 3 that a given experimental measurement of the mole fraction of water vapor in a particular diluent gas at a known temperature and pressure and a knowledge of the mole fraction of gas dissolved in the liquid phase under these conditions are sufficient to evaluate the ratio of fugacity coefficients ϕ_2^0/ϕ_2. The second cross virial coefficient $B_{12}(T)$ for that particular water–gas mixture can then be evaluated from this ratio fugacity coefficients through an iterative procedure using eq 4 and a trial value of $B_{12}(T)$ in the appropriate virial expansions for the molar volume V and compressibility factor Z to make initial estimates of these quantities. In the computations used here gas fugacities along with Henry's law constants obtained from data found in ref 7–10 were used to estimate X_1 of eq 3 as a function of pressure for the various gases involved. Values of pure component second virial coefficients used in solving eq 4 were taken from ref 11–16.

Table I lists the experimentally determined mole fractions of water vapor in the various mixtures. Figure 2 is a graphical representation of the data in Table I. It

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Table II. Second Cross Virial Coefficients for Water with Various Gases

Gas	Temp, °C	$B_{12}(T)$,[a] cm^3/mol	$B^{(\text{disp})}$, cm^3/mol	$B^{\mu-\theta}$, cm^3/mol	$B_{12}(T)_{\text{phys}}$, cm^3/mol	K_p, atm
CO_2	25	−214 ± 6	−93	−19	−112 ± 6	120 ± 11
	50	−151 ± 6	−72	−16	−88 ± 5	210 ± 26
	75	−107 ± 4	−60	−14	−74 ± 4	433 ± 79
	100	−89 ± 2	−51	−12	−63 ± 3	588 ± 79
N_2O	25	−188 ± 9	−103	−9	−112 ± 6	161 ± 23
	50	−152 ± 9	−82	−8	−90 ± 5	214 ± 34
	75	−119 ± 6	−69	−7	−76 ± 4	332 ± 48
	100	−94 ± 7	−59	−6	−65 ± 3	528 ± 138
C_2H_6	25	−125 ± 6	−120 ± 6		−120 ± 6	
	50	−94 ± 3	−95 ± 5		−95 ± 5	
	75	−78 ± 5	−81 ± 4		−81 ± 4	
	100	−72 ± 2	−69 ± 3		−69 ± 3	
Ar[b]	25	−37 ± 6	−40		−40	
	50	−25 ± 5	−27		−27	
	75	−20 ± 4	−21		−21	
	100	−14 ± 3	−16		−16	

[a] Error expressed as average deviation from mean. [b] Data taken from ref 6.

is evident from this figure that the solubility of water is considerably greater in compressed CO_2 and N_2O than in C_2H_6 even though the physical properties of these three gases are very similar. Figure 3 compares the data taken here for the water–CO_2 system with that measured by Wiebe.[7] It is seen that, with the exception of one point at 75°, the agreement is quite good. There are no data available for comparison in the cases of N_2O and C_2H_6.

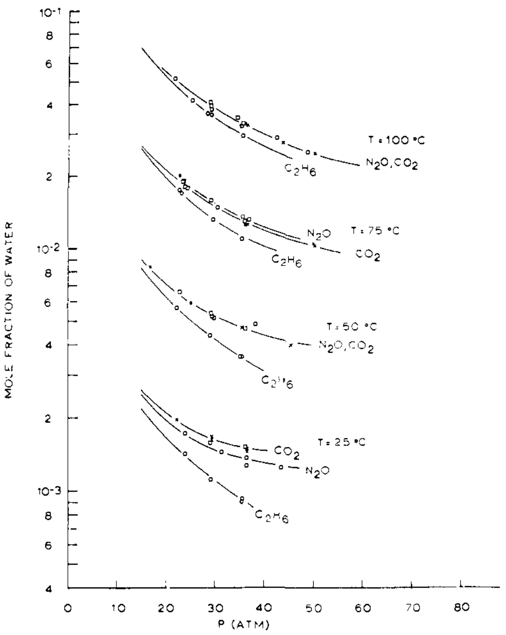

Figure 2. Mole fraction of water in CO_2 (×), N_2O (□), and C_2H_6 (○), as a function of pressure.

Second cross virial coefficients for the various water–gas mixtures have been calculated from the data of Table I. Within experimental error, no trend with pressure was observed among the values of $B_{12}(T)$, calculated for each system at a given temperature. Average values of these $B_{12}(T)$ are listed in column 2 of Table II. The data for CO_2 and C_2H_6 are shown graphically in Figure 4, along with values of second cross virial coefficients of water in methane and argon measured by Rigby and Prausnitz.[6] At a given temperature, the magnitude of the cross virial coefficients involving Ar, CH_4, and C_2H_6 increase with gas critical temperature as expected when intermolecular forces are physical in nature. The cross virial coefficients involving CO_2 with water are considerably more negative than those of ethane at all temperatures, and show a somewhat greater variation with temperature. The $B_{12}(T)$'s of N_2O with water are not included in Figure 4 for the sake of clarity, but are of the same magnitude and show a temperature dependence very similar to those of CO_2.

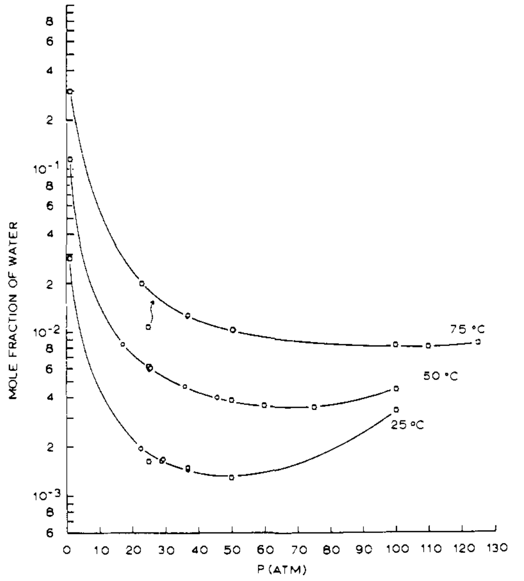

Figure 3. Mole fraction of water in CO_2: ○, this work; □, from ref 7.

Although the nature of the physical interactions between molecules of CO_2, N_2O, and C_2H_6 in the pure state differ somewhat with regard to origin[3b] (CO_2 and N_2O molecules are less polarizable but have much larger quadrupole moments than C_2H_6), the net effect of dispersion and angle dependent forces between these molecules is about the same as evidenced by the similarity in their critical temperatures (304, 310, and 305°K, respectively). Since any effects arising from weak dipole–quadrupole forces between water and the two quadrupolar gases are estimated to be small at these temperatures there is no reason to expect physical forces between water and these three gases to differ appreciably. This suggests that chemical association in the gas phase between water and the gases CO_2 and N_2O is responsible for the large discrepancy between the cross virial coefficients involving these two gases and those with C_2H_6, a conclusion not wholly unexpected in the case of CO_2.

Lambert, Rowlinson, and coworkers[17–19] have shown that orientation-specific interactions such as chemical bonding present in addition to usual physical forces can be treated from a mass action standpoint, allowing the second virial coefficient to be expressed as a sum of two terms, describing the physical and chemical contributions to nonideality separately. For weakly associated mixed systems, the expression for the second cross virial coefficient becomes

$$B_{12}(T) = B_{12}(T)_{\text{phys}} - RT/2K_p \tag{5}$$

where $B_{12}(T)_{\text{phys}}$ represents deviations from ideality caused by physical forces and K_p is the equilibrium constant describing in this case the chemical equilibrium between water, the chemically reactive gas (CO_2 or N_2O), and the resulting complex in terms of the respective partial pressures

$$K_p = P_{H_2O}P_{\text{gas}}/P_{\text{complex}}$$

Various methods have been used to estimate $B(T)_{\text{phys}}$. These include calculating $B(T)_{\text{phys}}$ from the Berthelot equation[17,18,20] or other representations of reduced virial coefficients based upon the principle of corresponding states[3,19] using critical properties, and elaborate calculations based on the Kihara potential with appropriate core parameters and force constants.[3a] These methods cannot be used here, however, because of uncertainties concerning the role hydrogen bonding plays in determining the critical properties and force constants of water vapor.[16]

An alternate approach which avoids these problems is used here. According to Pople[21] and Kielich,[22] virial coefficients of polar gases and their mixtures can be expressed as a series of terms, one for each type of intermolecular interaction occuring between the molecules involved. For the water–gas systems studied here dispersion force $B^{(\text{disp})}$, dipole–quadrupole $B^{(\mu-\theta)}$, and dipole-induced dipole $B^{(\mu-\text{ind }\mu)}$ terms will be important.

$$B_{12}(T)_{\text{phys}} = B^{(\text{disp})} + B^{(\mu-\theta)} + B^{(\mu-\text{ind }\mu)} \tag{6}$$

where

$$B^{(\mu-\theta)} = -\frac{\pi\mu_2{}^2\theta_1{}^2N}{192\sigma_{12}{}^5\epsilon_{12}{}^2}H_8(y) + \text{higher order terms} \tag{7}$$

and

$$B^{(\mu-\text{ind }\mu)} = -\frac{\pi\alpha_1\mu_2{}^2N}{24\sigma_{12}{}^3\epsilon_{12}y^2}H_6(y) + \text{higher order terms} \tag{8}$$

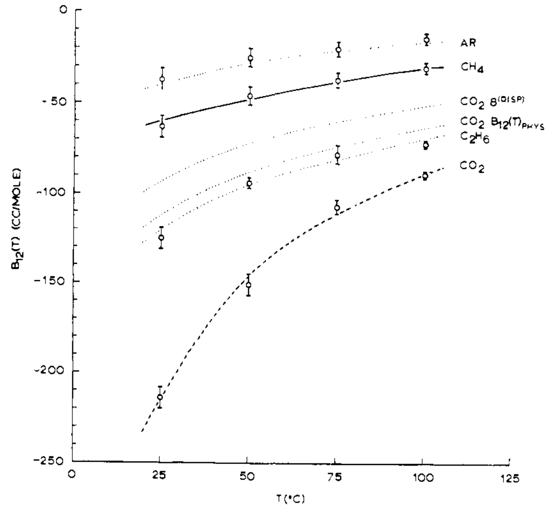

Figure 4. Second cross virial coefficients of water with Ar, CH_4, C_2H_6, CO_2, and N_2O as a function of temperature (Ar and CH_4 data from ref 6). Solid line denotes curve described by 6–12 potential with ϵ_{12}/k = 151°K and σ_{12} = 4.18 Å.

Here μ_2, θ_1, and α_1 are the dipole moment of water, the quadrupole moment, and polarizability of the gas involved.[23] The terms ϵ_{12} and σ_{12} represent Lennard-Jones force constants which describe the dispersion forces between water and gas molecules and $y = 2 \cdot (\epsilon_{12}/kT)^{1/2}$. The functions $H_6(y)$ and $H_8(y)$ are listed in ref 21. The term $B^{(\mu-\text{ind }\mu)}$ contributes least to $B_{12}(T)$ and can be considered to be the same for these gases without introducing appreciable error. The dipole–quadrupole term will make an important contribution in the cases of CO_2 and N_2O but can be neglected for mixtures of water with ethane or argon.

The $B^{(\text{disp})}$ terms for water with CO_2 and N_2O are calculated as follows. Experimental data for a homomorphic gas–water system are used as a reference and corrections are made for the slight differences in dispersion forces of the gas–water systems of interest by expanding at constant temperature about the virial coefficients of the homomorph on the $B(T)$, ϵ/k, σ surface defined by a Lennard-Jones 6–12 potential. An expansion to the first order in covolume b_0 ($b_0 = {}^2/_3\pi \cdot N\sigma^3$) and second order in ϵ/k results in the following expression relating the cross virial coefficient to be calculated, $B_{32}{}^{(\text{disp})}$, to that of the homomorph at the same temperature, $B_{12}{}^{(\text{disp})}$.

$$B_{32}{}^{(\text{disp})} = B_{12}{}^{(\text{disp})} + [(b_{0_{32}}/b_{0_{12}}) - 1]B_{12}{}^{(\text{disp})} + \left(\frac{\epsilon_{12}/k}{\epsilon_{32}/k} - 1\right)b_{0_{12}}T^*(\mathrm{d}B^*/\mathrm{d}T^*) + \frac{1}{2}\left[\left(\frac{\epsilon_{12}/k}{\epsilon_{32}/k}\right)^2 - 2\left(\frac{\epsilon_{12}/k}{\epsilon_{32}/k}\right) + 1\right]b_{0_{12}}T^{*2}(\mathrm{d}^2B^*/\mathrm{d}T^{*2}) \tag{9}$$

The usual combining rules, $\epsilon_{ab} = (\epsilon_a\epsilon_b)^{1/2}$ and $\sigma_{ab} = {}^1/_2 \cdot (\sigma_a + \sigma_b)$ allow the force constants for the gas–water system of interest (ϵ_{32}/k, σ_{32}) to be related to those of the homomorph (ϵ_{12}/k, σ_{12}) in a manner which avoids introducing the force constants of pure water, ϵ_2/k, σ_2

$$\epsilon_{32}/k = (\epsilon_3/\epsilon_1)^{1/2}\epsilon_{12}/k \tag{10}$$

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and

$$\sigma_{32} = \sigma_{12} + {}^1/_2(\sigma_3 - \sigma_1) \qquad (11)$$

Methane–water second cross virial coefficients were used as a reference. A 6–12 potential fit to these data (solid curve, Figure 4) yielded the value $\epsilon_{12}/k = 151°\text{K}$ and $b_{0_{12}} = 91.9\ \text{cm}^3/\text{mol}$ for this system. Force constants for the other gas–water systems were determined through eq 10 and 11 using viscosity force constants for the respective gases found in ref 24. Values for $B^{(\text{disp})}$, $B^{(\mu-\theta)}$, and B_{phys} calculated using these force constants and eq 6, 7, and 9 are listed in Table II. These results are shown as dotted lines in Figure 4 for water with Ar, CO_2, and C_2H_6. The excellent agreement between calculated and experimental values in the Ar–H_2O and C_2H_6–H_2O systems suggests that values of $B^{(\text{disp})}$ calculated using eq 9, 10, and 11 are quite accurate.

Values of K_p calculated from eq 5 for the CO_2–H_2O and N_2O–H_2O systems are listed in Table II. It is apparent that CO_2 and N_2O are associated with water to about the same degree in the gas phase. The standard enthalpy and entropy of hydration (standard state of 1 atm, 298°K) corresponding to these K_p are

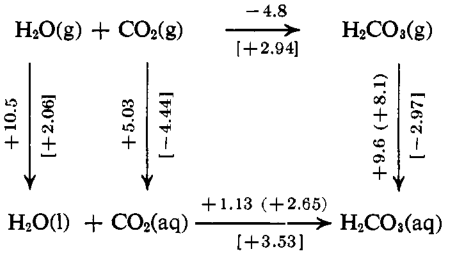
$$CO_2\text{–}H_2O\text{:}\quad \Delta H° = -4.8 \pm 0.4\ \text{kcal/mol}$$
$$\Delta S° = -25.9 \pm 1.1\ \text{eu}$$
$$N_2O\text{–}H_2O\text{:}\quad \Delta H° = -3.5 \pm 0.5\ \text{kcal/mol}$$
$$\Delta S° = -21.6 \pm 1.4\ \text{eu}$$

These data when combined with heats of formation and entropies of the reactants in the appropriate standard states[25] yield the following values for the standard heats of formation and entropies of the hydration products at 298°K

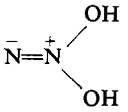
$$CO_2\text{–}H_2O\text{:}\quad \Delta H_f° = -156.7 \pm 0.4\ \text{kcal/mol}$$
$$S° = 70.3 \pm 1.1\ \text{eu}$$
$$N_2O\text{–}H_2O\text{:}\quad \Delta H_f° = -41.8 \pm 0.5\ \text{kcal/mol}$$
$$S° = 76.1 \pm 1.4\ \text{eu}$$

The hydration of CO_2 in the liquid phase is a subject of great interest to biochemists and ecologists by virtue of the central role this reaction plays in respiration and decay processes. Consequently, the equilibrium of CO_2 and its hydrate in the liquid phase has been studied by many investigators using a wide variety of techniques. While the results obtained by the various laboratories are not entirely in agreement,[26] their data indicate that the hydration of CO_2 is endothermic to the extent of about 1 kcal/mol in the liquid phase with a K_{eq} in activity units of the order of 10^{-3}. If it is assumed that the hydration product in the gas phase is the same as that in the liquid phase, namely carbonic acid, then the data assembled here can be combined with those for the liquid phase[27] to give the thermodynamic quantities associated with solvation of carbonic acid. The results are summarized in the thermodynamic cycle shown in Scheme I. The numbers in brackets in Scheme I represent Gibbs free energy changes, while the others are the changes in enthalpy associated with the various steps in this cycle at 298°K. All values are given in kilocalories per mole. The standard state for all components in the gas phase is 1 atm. In the aqueous phase, CO_2(aq) and H_2CO_3(aq) are in Henry's law standard states having mole fractions of unity. The standard state for water is the pure liquid. The data indicate that the degree of solvation for carbonic acid molecules in water is intermediate between that of molecules of CO_2 and molecules of water itself in the aqueous phase.

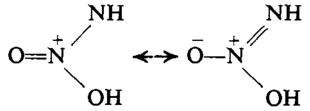
Scheme I



The hydration product of N_2O with H_2O has the same empirical formula as hyponitrous acid (HONNOH) and nitramide (H_2NNO_2). However, it is not likely that either of these compounds is in fact the hydration product since the standard heats of formation of aqueous solutions of these two compounds from their elements ($\Delta H_f°_{298} = -13.7$[25] and -16.9[28] kcal/mol, respectively) are considerably more positive than the heat of formation for the gas-phase hydration product found here. A more likely possibility is that this hydration product is the same as the intermediate thought to exist in the decomposition of nitramide.[29,30] This intermediate can be thought of as having one of several structures (see **1** and **2**), all of which resemble that postulated for carbonic acid. However, the fact that no exchange of oxygen occurs between N_2O and water enriched with ^{18}O[31,32] suggests that structures **2** are the most likely representation for the product resulting from the hydration of N_2O.



1



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