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The O_2/N_2 Ratio Gas Solubility Mystery

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ABSTRACT: Oxygen (O_2) and nitrogen (N_2) are the two most abundant gases in the Earth's atmosphere and have generally similar physical properties, yet O_2 is twice as soluble in water as N_2, a feature that may have physiological and other biological consequences. Furthermore, examination of 47 other solvents shows that the mole-fraction solubility of O_2 always exceeds that of N_2, with O_2/N_2 solubility ratios ranging from 1.20 in *n*-dodecane to 2.31 in nitromethane. The greater solubility of O_2 is especially puzzling since the molecular polarizability of N_2, a feature normally associated with higher solubility, is greater than that of O_2. Several theoretical and empirical approaches are explored in an effort to understand this observation: (1) molecular structure–property relationships, (2) thermodynamic analysis, (3) scaled particle theory, (4) ideal solution theory, and (5) quantum-chemical calculations. Speculations on the causes are offered.

INTRODUCTION

The impetus for the present paper began with a question asked by C. J. Wormald following a presentation by one of us (R.B.) on correlations involving the solubilities of gases in water. The question was, "Why is oxygen about twice as soluble in water as nitrogen?" R.B. had no ready answer. Nitrogen and oxygen are the two most prominent gases in the Earth's atmosphere, and the difference in their solubilities in water could have physiological or biological importance. In addition, a sensible explanation for the difference in the aqueous solubilities of O_2 and N_2 would provide some insight into the factors determining gas solubility in water. Thus, we felt that further examination of this solubility difference would be worth pursuing.

The two gases are alike in many of their physical properties. The most apparent distinction between these two gases is that O_2 is paramagnetic, whereas N_2 is not. However, NO is also paramagnetic while N_2O is not, yet N_2O is almost 13 times more soluble in water than NO. The greater solubility of N_2O also prevails in solvents other than water. There appears to be no persuasive connection between paramagnetism and greater solubility, nor is there any readily apparent mechanism relating paramagnetism to solubility.

In two recent reports, we have examined factors influencing the solubilities of a wide variety of gases in different solvents.[1,2] In several representative nonaqueous solvents, the polarizability of the solute was found to be the dominant factor influencing gas solubility, but in water no comparable simple determinant could be found, and it was necessary to examine different gas categories individually to look for possible explanations of the solubility trends. In this report, we examine the O_2/N_2 solubility question from a variety of theoretical and empirical perspectives.

INVESTIGATIVE BACKGROUND STUDIES

On the basis of data available in IUPAC's Solubility Data Series volumes on the solubilities of oxygen, nitrogen, and oxides of nitrogen[3−5] as well as other sources, Table 1 was assembled. This table gives the mole-fraction solubilities of O_2 in 48 solvents at 101 325 Pa partial pressure of gas and 298.15 K and also the ratios of the O_2 and N_2 solubilities. The table is arranged in order of decreasing ratio of solubilities. No pattern is readily apparent to us in the properties of the solvents with low and high O_2/N_2 ratios—they include polar and nonpolar solvents and a variety of classes of solvents.

Biological Fluids and Solids. Table 2 gives the O_2/N_2 solubility ratios for olive oil,[6] human blood, three solid lipids, and mineral oil (at slightly different temperatures and solubility units). The average ratio was 1.83, with an average deviation of 0.10. There is little spread in the ratio, which leads to the speculation that this observation could be of importance in human physiology. It should be noted that the solubilities in lecithin, cephalin, and cholesterol are values extrapolated to the pure substances using solubilities[7] determined at increasing concentrations of these lipids in benzene and isobutanol at 310.65 K (body temperature).

Solvent Contributions. We next explored possible solvent contributions to the solubility ratio. The following solvent physical properties were collected and tabulated: molar volume, molar mass, normal boiling point (T_B), surface tension (σ), enthalpy of vaporization at 298.15 K, critical temperature (T_c), critical pressure (P_c), critical molar volume (V_c), $V_c^{2/3}$ (a measure of molecular surface area), van der Waals parameters *a* and *b*, dipole moment, and the square of the Hildebrand solubility parameter. These properties, singly and in combinations, were submitted to least-squares analysis. The two physical properties that gave the best fits singly (with *t* and R^2 values in parentheses) were T_c (2.75, 0.123) and σ (2.91, 0.138). When both of these properties were used together, there was a slight improvement in R^2 (0.166), but the *t* values were less significant (T_c, 1.59; σ, 1.84). (Recall that the *t* statistic for a given coefficient should be 4 or greater for that coefficient to be considered significant.) The conclusion from these attempts to find a correlation between the O_2/N_2 solubility ratios and the

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Table 1. O_2 Mole-Fraction Solubilities and O_2/N_2 Solubility Ratios

solvent	O_2 solubility	O_2/N_2
nitromethane	$4.640 \cdot 10^{-4}$	2.31
1,4-dioxane	$5.380 \cdot 10^{-4}$	2.27
chlorobenzene	$8.980 \cdot 10^{-4}$	2.11
hexadecane	$2.470 \cdot 10^{-3}$	2.03
carbon disulfide	$4.390 \cdot 10^{-4}$	1.98
aniline	$2.260 \cdot 10^{-4}$	1.97
m-xylene	$1.196 \cdot 10^{-3}$	1.95
water	$2.301 \cdot 10^{-5}$	1.94
pentadecane	$2.419 \cdot 10^{-3}$	1.92
tetradecane	$2.366 \cdot 10^{-3}$	1.91
sulfinylbismethane (DMSO)	$1.570 \cdot 10^{-4}$	1.88
nitrobenzene	$4.950 \cdot 10^{-4}$	1.88
tetrachloromethane (CCl_4)	$1.200 \cdot 10^{-3}$	1.87
dodecane	$2.295 \cdot 10^{-3}$	1.87
1-decanol	$1.236 \cdot 10^{-3}$	1.86
tridecane	$2.297 \cdot 10^{-3}$	1.85
2,2,4-trimethylpentane	$2.814 \cdot 10^{-3}$	1.84
D_2O	$2.459 \cdot 10^{-5}$	1.81
1-octanol	$1.106 \cdot 10^{-3}$	1.81
benzene	$8.100 \cdot 10^{-4}$	1.81
undecane	$2.263 \cdot 10^{-3}$	1.78
cyclooctane	$1.072 \cdot 10^{-3}$	1.78
cis-1,2-dimethylcyclohexane	$1.543 \cdot 10^{-3}$	1.74
isobutanol	$8.390 \cdot 10^{-4}$	1.73
trans-1,2-dimethylcyclohexane	$1.734 \cdot 10^{-3}$	1.73
decane	$2.080 \cdot 10^{-3}$	1.72
1-butanol	$7.860 \cdot 10^{-4}$	1.71
1-heptanol	$1.042 \cdot 10^{-3}$	1.71
1-pentanol	$8.807 \cdot 10^{-4}$	1.71
2-propanol	$7.820 \cdot 10^{-4}$	1.70
methylcyclohexane	$1.599 \cdot 10^{-3}$	1.69
1-hexanol	$9.752 \cdot 10^{-4}$	1.67
nonane	$2.134 \cdot 10^{-3}$	1.67
ethanol	$5.974 \cdot 10^{-4}$	1.66
1-propanol	$6.741 \cdot 10^{-4}$	1.65
cyclohexane	$1.230 \cdot 10^{-3}$	1.62
octane	$2.110 \cdot 10^{-3}$	1.59
1-nonanol	$1.185 \cdot 10^{-3}$	1.58
toluene	$8.915 \cdot 10^{-4}$	1.55
1-undecanol	$1.314 \cdot 10^{-3}$	1.55
acetone	$8.400 \cdot 10^{-4}$	1.54
diethyl ether	$1.480 \cdot 10^{-3}$	1.51
methanol	$4.154 \cdot 10^{-4}$	1.49
heptane	$1.940 \cdot 10^{-3}$	1.44
pentane	$2.050 \cdot 10^{-3}$	1.41
hexane	$1.980 \cdot 10^{-3}$	1.40
hexafluorobenzene	$2.410 \cdot 10^{-3}$	1.35
1-dodecanol	$1.080 \cdot 10^{-3}$	1.20

Table 2. O_2/N_2 Solubility Ratios for Biological Fluids

fluid or solid	conditions	O_2/N_2
olive oil	298.15 K; mole fraction	1.80
human blood	310 K; Bunsen coefficient	1.72
cephalin[a]	310 K; Ostwald coefficient	1.72
lecithin[a]	310 K; Bunsen coefficient	1.77
cholesterol[a]	310 K; Bunsen coefficient	2.07
mineral oil	297 K; Bunsen coefficient	1.89

[a] Extrapolated value.

physical properties of the solvents is that the physical properties of the solvents play a minor role in the solubility differences.

Structure–Property Relationships. *Gases with O_2/N_2 Solubility Ratios Clustering around O_2 and N_2.* It seemed reasonable to find out whether any of the physical properties of the two molecules could explain the 2-fold greater solubility of O_2 over N_2 in water. That is, what clues could be found by examining the solubilities of gases in water that cluster around O_2 and N_2 solubilities? Table 3 shows data for gases that are about one-third to twice as soluble as O_2 and other gases that have solubilities close to that of N_2. It should be noted that this table goes from Kr to He, with solubility ratios of 0.51 to 3.3 with respect to O_2. The table contains some possibly relevant physical properties of these gases. The volumes ("Vol") and surface areas ("Area") are values obtained from the Spartan'10 quantum-chemical program.[8] Other listed properties are the polarizability ("Pol"), molar mass (MM), normal boiling point (T_B), critical temperature (T_c), critical pressure (P_c), and critical volume (V_c).

Examination of the data in Table 3 does not immediately suggest an explanation for the greater solubility of O_2. Many of the properties listed are quite similar for the two gases. In the normal energy bookkeeping analysis of solvation, one first employs an endergonic term for the energy required to form a cavity for the solute to be placed within the solvent, and then an exergonic term for the energy of interaction between the solute and the solvent. The first term is proportional to the volume of the solute, and since O_2 and N_2 have almost identical molecular volumes, this suggests that the difference in solubility of these two gases must be due in some way to differences in their interaction with the solvent in question (here, water). Interestingly, the polarizability of N_2, normally an indicator of stronger dispersion interactions and greater solubility, is 10% greater than that of O_2.

The ratio of the polarizability of O_2 to that of each gas was considered in an attempt to examine the possible effect of intermolecular forces (as exemplified by the polarizability) on the solubility ratio. The fitting equation is eq 1, and the data are given in Table 4. The *t* values for the coefficients for this fit are reasonable, as are the R^2 and standard deviation (sd) values.

$$\frac{x_{O_2}}{x_{gas}} = (0.9522 \pm 0.146) + (0.3260 \pm 0.0655)\left[\frac{\alpha_{O_2}}{\alpha_{gas}}\right] \tag{1}$$

$$R^2 = 0.6225, \quad sd = 0.50, \quad av\ dev = 0.37$$

The *t* values for the first and second coefficients are 6.50 and 4.97, respectively. The Ar and O_2 solubilities and polarizabilities are about the same. However, CH_4, C_3F_6, and *n*-C_4H_{10} have almost the same solubility as O_2 but much higher polarizabilities, especially the latter two gases. The five gases that we have grouped around the N_2 solubility (*i*-C_4H_{10}, H_2, *neo*-C_5H_{12}, Ne, and He) have quite different polarizabilities than N_2. For example, *neo*-C_5H_{12} has approximately the same solubility as N_2 in water, but

Table 3. Solubilities and Physical Properties (x_2, Mole-Fraction Solubility at 298.15 K and 101 325 Pa; Pol, Molecular Polarizability; Vol, Molar Volume; Area, Molar Surface Area; MM, Molar Mass, T_B, Normal Boiling Point; T_c, Critical Temperature; P_c, Critical Pressure; V_c, Critical Volume) of Selected Gases with Aqueous Solubilities Close to Those of O_2 and N_2

		Pol	Vol	Area	MM	T_B	T_c	P_c	V_c
gas	x_2	Å^3	cm^3·mol^{-1}	cm^2·mol^{-1}	g·mol^{-1}	K	K	MPa	cm^3·mol^{-1}
Kr	$4.5 \cdot 10^{-5}$	2.484	27.08	43.61	83.8	119.9	209.5	5.53	91
NO	$3.5 \cdot 10^{-5}$	1.7	23.32	40.78	30.	121.4	180.	6.48	58
C_2H_6	$3.3 \cdot 10^{-5}$	4.45	51.8	72.38	30.1	184.6	305.3	4.87	145.5
C_2F_4	$2.8 \cdot 10^{-5}$	4.22	66.15	89.88	100.	197.3	306.5	3.94	172
C_3H_8	$2.7 \cdot 10^{-5}$	6.33	70.22	92.64	44.1	231.1	369.8	4.25	203
Ar	$2.5 \cdot 10^{-5}$	1.64	22.09	38.07	39.9	87.3	150.9	4.9	75
CH_4	$2.5 \cdot 10^{-5}$	2.59	33.17	51.31	16.	111.67	190.56	4.60	98.6
O_2	$2.3 \cdot 10^{-5}$	1.58	23.06	40.64	32.	90.2	154.6	5.04	73
n-C_4H_{10}	$2.2 \cdot 10^{-5}$	8.2	88.68	112.94	58.1	272.7	425.2	3.79	255
CO	$1.7 \cdot 10^{-5}$	1.95	33.81	51.49	28.	81.7	132.9	3.49	93
$CClF_3$	$1.7 \cdot 10^{-5}$	5.66	60.99	84.85	104.5	191.8	303	3.87	180
$CH(CH_3)_3$	$1.5 \cdot 10^{-5}$	8.14	88.37	111.75	58.1	261.4	407.9	3.64	255.5
NF_3	$1.4 \cdot 10^{-5}$	3.62	42.15	65.82	71.	144	—	—	—
H_2	$1.4 \cdot 10^{-5}$	0.804	10.49	23.7	2.	20.28	32.97	1.293	65
N_2	$1.2 \cdot 10^{-5}$	1.74	23.59	40.96	28.	77.35	126.2	3.39	90
$C(CH_3)_4$	$1.1 \cdot 10^{-5}$	10.2	106.1	129.48	72.1	282.6	433.7	3.196	307
Ne	$8.1 \cdot 10^{-6}$	0.396	13.03	26.78	20.2	27.1	44.4	2.76	42
He	$7.0 \cdot 10^{-6}$	0.205	6.71	17.2	4.	4.22	5.19	0.227	57

Table 4. O_2/Gas Polarizability Ratios ($\alpha_{O_2}/\alpha_{gas}$) for Various Gases

gas	x_2	α/Å^3	x_{O_2}/x_{gas}	$\alpha_{O_2}/\alpha_{gas}$	abs residual[a]
Kr	$4.494 \cdot 10^{-5}$	2.484	0.511	0.636	0.648
NO (0.15)[b]	$3.477 \cdot 10^{-5}$	1.70	0.661	0.930	0.595
C_2H_6	$3.345 \cdot 10^{-5}$	4.45	0.687	0.355	0.381
C_2F_4	$2.846 \cdot 10^{-5}$	4.22	0.807	0.375	0.267
C_3H_8	$2.704 \cdot 10^{-5}$	6.33	0.850	0.250	0.184
Ar	$2.526 \cdot 10^{-5}$	1.641	0.910	0.963	0.357
CH_4	$2.507 \cdot 10^{-5}$	2.593	0.917	0.610	0.234
O_2	**$2.298 \cdot 10^{-5}$**	**1.581**	**1.000**	**1.000**	**0.278**
C_3F_6	$2.280 \cdot 10^{-5}$	6.17	1.008	0.256	0.028
n-C_4H_{10}	$2.197 \cdot 10^{-5}$	8.20	1.046	0.193	0.031
CO (0.11)[b]	$1.724 \cdot 10^{-5}$	1.95	1.333	0.811	0.116
i-C_4H_{10} (0.10)[b]	$1.463 \cdot 10^{-5}$	8.14	1.571	0.194	0.555
H_2	$1.413 \cdot 10^{-5}$	0.804	1.626	1.966	0.033
N_2	**$1.173 \cdot 10^{-5}$**	**1.74**	**1.959**	**0.909**	**0.711**
neo-C_5H_{12}	$1.077 \cdot 10^{-5}$	10.20	2.134	0.155	1.131
Ne	$8.133 \cdot 10^{-6}$	0.3956	2.826	3.996	0.570
He	$6.983 \cdot 10^{-6}$	0.2050	3.291	7.712	0.176

[a] Absolute residuals for eq 1. [b] The value in parentheses is the dipole moment in D.

Table 5. O_2/N_2 Ratios for Selected Physical Properties (B_{22}, Second Virial Coefficient; P_c, Critical Pressure; d_c, Critical Density; R_G, Radius of Gyration; ε/k, Lennard-Jones Energy Parameter; T_c, Critical Temperature; ΔH_{vap}^{NBP}, Enthalpy of Vaporization at the Normal Boiling Point; α, Molecular Polarizability)

physical property	O_2/N_2
B_{22}/ (cm^3·mol^{-1})	3.476
P_c/bar	1.486
d_c/ (g·cm^{-3})	1.402
R_G/Å	1.243
(ε/k)/K	1.242
T_c/K	1.226
ΔH_{vap}^{NBP}/ (kJ·mol^{-1})	1.224
α/Å^3	0.909

its polarizability is about 6 times greater. We can ask why there are these apparent disparities in solubility and polarizability around these two gases. We had hoped that an examination of the gases grouped around the O_2 and N_2 solubilities would provide a clue about what is going on with these gases and water. To complicate matters further, we note that in Table 4 there are three gases that have small dipole moments (NO, CO, and i-C_4H_{10}). The data in Table 4 could have been fit to higher-order polynomials, yet if there were a strong connection between the polarizability and the solubility, a linear fit should have sufficed.

Ratio of Physical Properties of O_2 and N_2. The next study had to do with searching for a connection between the O_2/N_2 ratios for various physical properties. These O_2/N_2 ratios were calculated for 25 physical properties. Table 5 gives these ratios for properties with the highest ratios (those above 1.2). The most significant property by far appears to be the second virial coefficient (B_{22}) at 298.15 K. This ratio is more than double the next property. On the other hand, an examination of the $B_{22,O_2}/B_{22,gas}$ ratios for the 15 gases clustered around the O_2 and N_2 solubilities showed that this physical property did not correlate at all (except for Ar) with the O_2/gas solubility ratio. Aside from the radius of gyration (R_G), the other six properties can be

Table 6. Temperature Dependence of the O_2/N_2 Mole-Fraction Solubility Ratio at a Gas Partial Pressure of 101 325 Pa

T/K	x_{O_2}	x_{N_2}	x_{O_2}/x_{N_2}
298.15	$2.3009\cdot10^{-5}$	$1.183\cdot10^{-5}$	1.95
308.15	$1.9906\cdot10^{-5}$	$1.047\cdot10^{-5}$	1.90
318.15	$1.7776\cdot10^{-5}$	$0.9585\cdot10^{-5}$	1.86
328.15	$1.6305\cdot10^{-5}$	$0.9033\cdot10^{-5}$	1.81
338.15	$1.5299\cdot10^{-5}$	$0.8735\cdot10^{-5}$	1.75
348.15	$1.4634\cdot10^{-5}$	$0.8644\cdot10^{-5}$	1.69
358.15	$1.4230\cdot10^{-5}$	$0.8732\cdot10^{-5}$	1.63

considered to be related in some way to intermolecular forces. These forces, of course, would have to be stronger the greater the O_2/N_2 solubility ratio.

T and P Dependence of O_2 and N_2 Solubilities. We thought it would be interesting to find out how the O_2/N_2 water solubility ratio depends on temperature and pressure. Table 6 shows these data from (298.15 to 358.15) K for the mole-fraction solubility at a gas partial pressure of 101 325 Pa. It is worthy of note that the ratio decreases regularly as the temperature increases. Also, it is of interest that in general (and contrary to naive expectations), the solubility of gases goes through a minimum as the temperature increases. This minimum solubility is at about 373.15 K for O_2 and 348.39 K for N_2. Aside from pointing out this information at a gas partial pressure of 101 325 Pa, not much else can be said.

Table 7 shows the temperature and pressure dependence of the O_2/N_2 solubility ratio for six sets of $T-P$ data. There are extensive data for the T and P dependence of the N_2 solubility but not the O_2 solubility. It must be the case that researchers were not keen on determining O_2 solubilities at high pressures! To obtain the points in Table 7, some interpolations and extrapolations were required. The O_2/N_2 solubility ratios were consistently greater than 1.0 and approached 2.0 for certain combinations of T and P. At higher temperatures, increasing the pressure reduced the O_2/N_2 solubility ratio.

Ratios of Solubilities for Other Pairs of Gases. In a continuing exploration involving the two groups of gases with solubilities similar to those of O_2 and N_2, the ratios of the solubilities of several gas pairs in all of the solvents for which the data were available are given in Table 8. The gas pairs are O_2/N_2, O_2/Ar, O_2/CH_4, O_2/CO, O_2/C_3H_8, CH_4/Ar, and O_2/N_2 for the six biological fluids and solids. Notably, the O_2/gas ratio tends to decrease for the larger gases. The trends are what would be expected given the earlier tables and studies in this paper. The ratio for the O_2/C_3H_8 pair appears to be unusual, but it should be noted that C_3H_8 is significantly more soluble than O_2 in organic solvents (these values were carefully checked). More food for thought!

As an interesting finding we present Figure 1, which shows the natural logarithms of the x_2 values for the rare gases in water, as well as those for O_2 and N_2, plotted versus their molecular polarizabilities. The rare gases are the purest examples of the role of polarizability in determining solubility, and we wanted to find out how O_2 and N_2 compared with them. Surprisingly, this plot appears to show that O_2 actually behaves "normally" within this framework, while N_2 does not! As a further indicator of this perspective, a plot of ln x_2 versus T_B for these eight gases gave identical results (Figure 2). This suggests that N_2 is the gas that behaves anomalously, while O_2 is "normal." The initial starting point for this paper should have been an attempt to answer a different question, namely, "Why does N_2 show about one-half the solubility of O_2 in water and other solvents?" (The quantum-chemical studies discussed below were one attempt to answer this question.)

Table 7. O_2/N_2 Mole-Fraction Solubility Ratios at Various Temperatures and Partial Pressures

T/K	P/bar	x_{O_2}	x_{N_2}	x_{O_2}/x_{N_2}
353.15	101.3	$0.828\cdot10^{-3}$	$6.98\cdot10^{-4}$	1.19
398.15	101.3	$1.099\cdot10^{-3}$	$8.55\cdot10^{-4}$	1.29
533.1	10.34	$0.555\cdot10^{-3}$	$3.1\cdot10^{-4}$	1.79
533.1	34.47	$1.48\cdot10^{-3}$	$8.9\cdot10^{-4}$	1.66
588.7	10.34	$0.730\cdot10^{-3}$	$0.39\cdot10^{-3}$	1.87
588.7	34.47	$2.66\cdot10^{-3}$	$1.66\cdot10^{-3}$	1.60

Table 8. Mole-Fraction Gas Solubility Ratios at 101 325 Pa Partial Pressure of Gas at 298.15 K for Several Gas Combinations

gas pair	avg ratio
O_2/N_2	1.74
O_2/Ar	0.912
O_2/CH_4	0.473
O_2/CO	1.34
O_2/C_3H_8	0.051
N_2/Ar	0.519
CH_4/Ar	2.00
O_2/N_2[a]	1.83

[a] In six biological fluids or solids.

THEORETICAL STUDIES

Changes in Thermodynamic Properties on Solution. What can the changes in the thermodynamic properties on solution (e.g., $\Delta G°$, $\Delta H°$, and $\Delta S°$) tell us about what is going on regarding the solubilities of O_2 and N_2 in water? Also, since it should be important to compare these changes for the gases that cluster about O_2 and N_2 in solubility, these other gases are included. In Table 9 are data on the thermodynamic functions at 298.15 K gathered from multiple sources; the mole-fraction solubility is included for perspective. The first thing to notice is that the difference between the Gibbs energy of solution for O_2 and N_2 is quite small, merely 1.64 $kJ\cdot mol^{-1}$. This points to the fact that a small change in the Gibbs energy can lead to a noticeable change in solubility: a 1 $kJ\cdot mol^{-1}$ change can cause a 50% increase. The entropy change on solution is essentially the same for both gases, so it is the difference in the enthalpy function that determines the difference in solubility. Examination of the entropy and enthalpy changes for O_2 and n-C_4H_{10}, which have essentially the same solubility, shows that the enthalpy change for n-C_4H_{10} is roughly double that for O_2 and the entropy change is significantly larger for n-C_4H_{10} than O_2. Ar and O_2 have essentially the same solubility and enthalpy and entropy changes. The gases closest to N_2 in solubility, H_2 and *neo*-C_5H_{12}, show considerable differences in their enthalpy and entropy changes. Thus, the data collected for changes in the thermodynamic properties on solution for O_2 and N_2 and the gases clustered around them demonstrate that similar

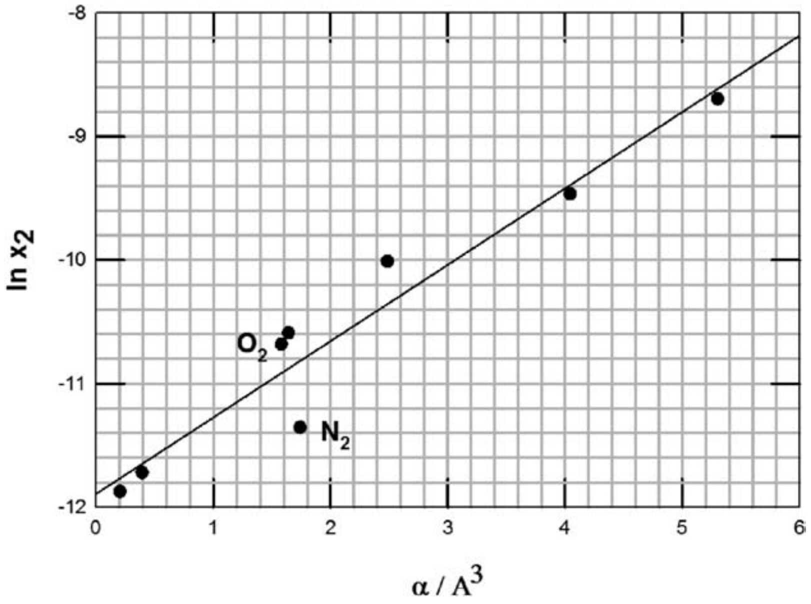

Figure 1. ln x_2 vs molecular polarizability (α) for rare gases, O_2, and N_2 at 298.15 K.

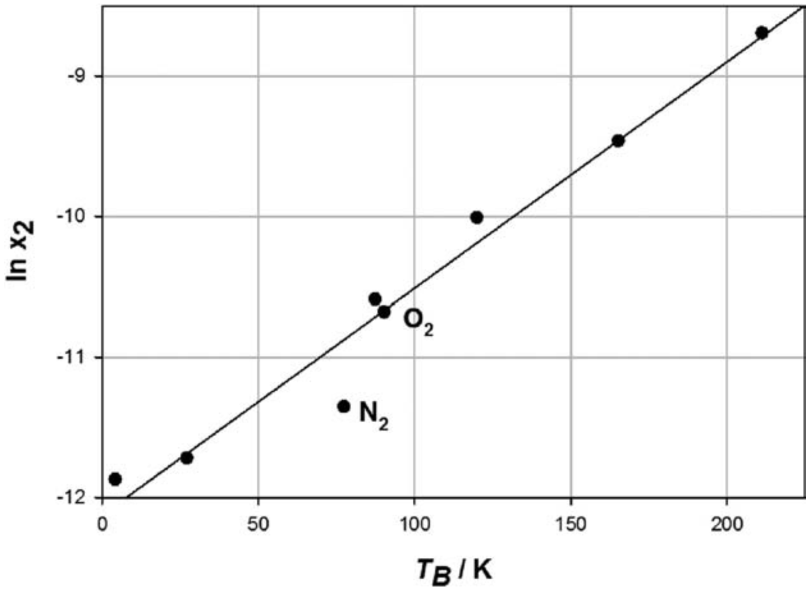

Figure 2. ln x_2 vs normal boiling point (T_B) for rare gases, O_2, and N_2 at 298.15 K.

solubilities can be achieved by different means. A detailed study of the changes in the thermodynamic functions on solution is indicated.

Scaled Particle Theory Calculations of Thermodynamic Functions. Scaled particle theory (SPT)[9−11] can be used to calculate various thermodynamic functions relating to solubility. The Gibbs energy change on solution, from which the mole-fraction solubility can be calculated, is computed as the sum of the Gibbs energy change on forming a cavity for the solute (ΔG_{CAV}), the Gibbs energy change due to the interaction between the solute and the solvent (ΔG_{INT}), and a correction term [$RT \ln (RT/V_m)$].[9,10] For the solubility of a gas in water, this correction term amounts to 17.875 $kJ \cdot mol^{-1}$ at 298.15 K. SPT uses a two-step model for the solubility of a gas in a liquid: First, a cavity of sufficient size to accommodate the solute molecule in the surface of the liquid is formed; this gives the Gibbs energy of cavity formation, ΔG_{CAV}. Next, the solute molecule enters the cavity and interacts with the surrounding solvent molecules, which gives the Gibbs energy of interaction, ΔG_{INT}. Because it would be useful to know separately the contributions of the cavity and interaction terms to the Gibbs energy change on solution, we calculated both of them for O_2 and N_2 *and* the gases that cluster about them in solubility. This information is given in Table 10. We note that SPT gives remarkably accurate solubility estimates for O_2 and N_2, especially the latter.

Examining the values for O_2 and N_2, we see that ΔG_{INT} is roughly the same for both gases and that the primary contributor to the difference in solubility appears to be the difference in

Table 9. Thermodynamic Changes on Solution for Several Gases at 298.15 K

		$\Delta G°$	$\Delta H°$	$\Delta S°$
gas	x_2	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$J \cdot mol^{-1} \cdot K^{-1}$
C_3H_8	$2.732 \cdot 10^{-5}$	26.05	−22.16	−161.7
CH_4	$2.550 \cdot 10^{-5}$	26.22	−13.21	−132.3
Ar	$2.519 \cdot 10^{-5}$	26.25	−12.24	−129.1
O_2	**$2.293 \cdot 10^{-5}$**	**26.48**	**−12.11**	**−129.5**
n-C_4H_{10}	$2.244 \cdot 10^{-5}$	26.54	−25.34	−174.0
CO	$1.774 \cdot 10^{-5}$	27.12	−10.78	−127
i-C_4H_{10}	$1.463 \cdot 10^{-5}$	27.61	−22.51	−168.1
H_2	$1.411 \cdot 10^{-5}$	27.69	−4.10	−106.6
N_2	**$1.183 \cdot 10^{-5}$**	**28.12**	**−10.30**	**−129**
neo-C_5H_{12}	$1.077 \cdot 10^{-5}$	28.38	−25.35	−188.6
Ne	$8.152 \cdot 10^{-6}$	29.05	−3.868	−110.4
He	$6.983 \cdot 10^{-6}$	29.43	−0.761	−101.3
C_3F_6	$5.298 \cdot 10^{-6}$	30.13	−20.23	−168.9

Table 10. Results of Scaled Particle Theory (SPT) Calculations at 298.15 K

	ΔG_{CAV}	ΔG_{INT}	$\Delta G°$	x_2	
gas	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	SPT	exptl
C_3H_8[a]	35.514	−35.279	18.108	$6.721 \cdot 10^{-4}$	$2.732 \cdot 10^{-5}$
CH_4	21.041	−14.305	24.610	$4.880 \cdot 10^{-5}$	$2.550 \cdot 10^{-5}$
Ar	18.368	−10.778	25.460	$3.457 \cdot 10^{-5}$	$2.519 \cdot 10^{-5}$
O_2	**18.874**	**−10.778**	**25.983**	**$2.806 \cdot 10^{-5}$**	**$2.293 \cdot 10^{-5}$**
n-C_4H_{10}[a]	41.279	−44.773	14.380	$3.023 \cdot 10^{-3}$	$2.244 \cdot 10^{-5}$
CO	21.598	−11.410	28.020	$1.232 \cdot 10^{-5}$	$1.774 \cdot 10^{-5}$
i-C_4H_{10}[a]	41.673	−44.108	15.439	$1.974 \cdot 10^{-3}$	$1.463 \cdot 10^{-5}$
H_2	14.096	−4.456	27.518	$1.511 \cdot 10^{-5}$	$1.411 \cdot 10^{-5}$
N_2	**21.041**	**−10.816**	**28.104**	**$1.193 \cdot 10^{-5}$**	**$1.183 \cdot 10^{-5}$**
Ne	13.431	−4.100	27.204	$1.712 \cdot 10^{-5}$	$8.152 \cdot 10^{-6}$
He	12.356	−1.665	28.567	$9.892 \cdot 10^{-6}$	$6.983 \cdot 10^{-6}$

[a] Using Lennard-Jones parameters from Tahery and Modarress.[11]

ΔG_{CAV}. N_2 is a very slightly larger molecule than O_2 and would therefore require a larger cavity. The two Gibbs energy terms for Ar and O_2 are essentially identical, which accounts for their similar solubilities in water. n-Butane, a much larger molecule than O_2, ends up having almost the same solubility, although both of the Gibbs energy terms are much larger (which is to be expected). H_2 is slightly more soluble than N_2, and the Gibbs energy terms are much smaller for H_2. The gases Ne and He, which are slightly less soluble than N_2, again have significantly smaller Gibbs energy terms. The initial hope that studying the two Gibbs energy terms contributing to solubility would provide a clear explanation for the solubility differences being discussed in this paper appears instead to add to the "mystery."

"Ideal" Solubilities for Gases above Their T_c Values. Hildebrand and Scott state that Raoult's law can be used to obtain a reasonable estimate of the solubility of a gas above its critical temperature, T_c (see pp 241−243 in ref 12). The vapor pressure is extrapolated to 298.15 K as ln P versus $1/T$. The "ideal" mole-fraction solubility, which assumes that the gas is well-described by Raoult's law, may then be taken to be $1/(P/101\,325\ \text{Pa})$. (When the vapor pressure has been fitted to the Antoine equation, this may be used for the extrapolation.) We estimated ideal solubilities at 298.15 K and 1 atm partial pressure of gas for eight gases related to this paper. Table 11 contains the relevant data.

Table 11. Ideal Mole-Fraction Solubilities and Critical Temperatures (T_c)

	x_2				
gas	exptl	ideal	$x_{2,O_2}^{ideal}/x_{2,gas}^{ideal}$	x_2^{ideal}/x_2^{exptl}	T_c/K
Kr	$4.494 \cdot 10^{-5}$	$354 \cdot 10^{-5}$	0.373	78.8	209.5
Ar	$2.526 \cdot 10^{-5}$	$160 \cdot 10^{-5}$	0.825	64.0	150.9
CH_4	$2.507 \cdot 10^{-5}$	$350 \cdot 10^{-5}$	0.377	14.0	190.6
O_2	$2.298 \cdot 10^{-5}$	$132 \cdot 10^{-5}$	1.000	57.4	154.6
CO	$1.724 \cdot 10^{-5}$	$128 \cdot 10^{-5}$	1.031	75.3	132.9
H_2	$1.413 \cdot 10^{-5}$	$80 \cdot 10^{-5}$	1.650	57.1	32.97
N_2	$1.173 \cdot 10^{-5}$	$100 \cdot 10^{-5}$	1.320	83.3	126.2
Ne	$8.133 \cdot 10^{-6}$	$3.68 \cdot 10^{-4}$	3.59	45.3	44.4

One first notices that the ideal solubilities determined in this manner are approximately 1 to 2 orders of magnitude greater than the experimental solubilities in water. On the other hand, the solubilities listed in Hildebrand and Scott's Table 4 (p 243 in ref 12) for the gases H_2, N_2, CO, O_2, Ar, CH_4, C_2H_4, C_2H_2, and C_2H_6 are reasonably close to the experimental solubilities for those gases in a variety of *organic solvents*. Generally, the more polar the organic solvent, the poorer the correspondence with the experimental values. However, the *ratios* of the ideal solubility of O_2 to those for the gases Kr, Ar, H_2, and N_2 are similar to the ratios of the experimental solubilities in water. For example, $x_{2,O2}/x_{2,N_2}$ = 1.32 (ideal) versus 1.96 (experimental), and the corresponding values for O_2/Kr are 0.51 and 0.37. Thus, the ideal solubility is apparently a reasonable measure of the *relative* magnitude of the forces contributing to gas solubility, although not the absolute magnitudes. These results were not unexpected given that water is so polar and strongly hydrogen-bonded. Finally, we note that although the extrapolations to 298.15 K from the relevant T_c values are over considerable temperature ranges, the rough correlations are quite remarkable.

Quantum-Chemical Studies. As a final attempt to understand the O_2/N_2 solubility difference, we examined these species using quantum-chemical methods. Computations were performed using density functional theory (DFT) with Chai and Head-Gordon's ωB97X-D functional[13] and Dunning's correlation-consistent polarized cc-pVTZ basis set[14] and also using second-order Møller−Plesset perturbation theory (MP2) with the same basis set. We thought that a clue to the solubility difference might appear in the electrostatic potential surface (ESP) maps for the two compounds. These maps, shown in Figure 3, display the potentials on the 0.002 bohr^{-3} electron density surface as determined at the DFT B3LYP/6-311+G* level. Positive regions on the electron density surface are shown in blue and negative regions in red. It is clear that N_2 shows a more varied ESP map, with negative regions on both ends (corresponding to the N_2 electron lone pairs) and a positive band around the center of the molecule. O_2 displays a more neutral and moderate potential energy surface. Thus, one might expect N_2, with its greater surface potential variations, to interact more strongly with the H_2O solvent and thus exhibit greater solubility, which is contrary to the experimental evidence.

Figure 3. Electrostatic potential surface maps for N_2 and O_2 calculated at the B3LYP/6-311+G* level. The blue areas represent regions with positive potential and the red areas regions with negative potential.

A second approach was to investigate directly the strength of the interactions between the gases and the aqueous solvent. We first attempted to examine the behavior of a variety of gases using two solvation models: the continuum SM5.4 water model of Chambers et al.[15] and the self-consistent reaction-field SM8 model of Marenich et al.[16] Unfortunately, neither solvation model was designed for use with molecules other than closed-shell species, so neither could be applied directly to triplet oxygen. Hence, further results from these calculations will not be reported here.

Next we examined the interactions between explicit water molecules and O_2 and N_2. As a measure of attraction, we evaluated the binding energy between each gas and a single water molecule. The calculations were performed using DFT at the ωB97X-D/cc-pVTZ level and then, as a check, MP2 theory at the MP2/cc-pVTZ level. In both cases, we found several shallow energy-minimum H_2O orientations surrounding the gas solute. (No corrections were applied for basis-set superposition error.) Both the DFT and MP2 calculations showed the interaction energy between N_2 and a single H_2O to be roughly twice as large as that between O_2 and H_2O. The computed N_2-H_2O/O_2-H_2O binding energy ratios were 2.5 (DFT) and 1.9 (MP2) for the strongest binding conformations. It was also observed that there was very little, if any, charge transfer between the solute and water (≤ 1 millielectron). In some situations, especially those involving ions, significant charge transfer between the solute and the aqueous solvent can occur.[17] Ideally, one would prefer to cluster several water molecules around each of these solutes, but because of the much greater H_2O-H_2O attraction (~ 25 $kJ \cdot mol^{-1}$), such an equilibration procedure led preferentially to water–water clusters at the expense of the much weaker attractions to either N_2 or O_2.

One might assume that the stronger N_2-H_2O interaction found above would naturally point to greater solubility in water for N_2 over O_2. However, a number of studies in recent years have considered the aqueous solvation of both small and large hydrophobic compounds,[18−20] the former being of particular interest in this context. Lum et al.[18] have shown that when hydrophobic solutes are sufficiently small, the surrounding water molecules can reorganize with relatively little disruption of their hydrogen-bonding network. Nonetheless, the disruption of the water network by inclusion of small hydrophobic solutes, however minor, does carry some enthalpic and entropic costs. In the present case, N_2 interacts more strongly with water than does O_2, as suggested by both the ESP maps in Figure 3 and the results in Table 12, so one can expect that N_2 will cause more disruption of the surrounding water solvation shell than will the more weakly interacting O_2.

Table 12. Water–Solute Interaction Energies Determined Using Density Functional Theory (DFT ωB97X-D/cc-pVTZ) and Second-Order Møller–Plesset Perturbation Theory (MP2/cc-pTVZ)

method	interaction	energy/ $(kJ \cdot mol^{-1})$
DFT	N_2-H_2O	4.86
DFT	O_2-H_2O	1.93
DFT	H_2O-H_2O	25.87
MP2	N_2-H_2O	6.32
MP2	O_2-H_2O	3.39
MP2	H_2O-H_2O	25.45

DISCUSSION

Since we have approached work on this paper from different perspectives (empirical/experimental vs theoretical), we thought it would be useful to present the discussion in three parts: comments by P.G.S., comments by R.B., and joint comments.

Comments by P.G.S. We have examined the difference in solubility of O_2 and N_2 from a number of perspectives. Examination of the O_2/N_2 solubility ratio in solvents other than water shows that the greater solubility of O_2 persists in all of the solvents examined, although the ratio varies from solvent to solvent. Therefore, the phenomenon is not unique to water, although that is the present focus of attention. The experimentally determined solvation thermodynamic properties of O_2 and N_2 show that the difference in solubility is attributable almost entirely to the (relatively small) difference in the enthalpy change on solvation for these gases. The rather small difference in the Gibbs energy of solution for O_2 and N_2 (roughly 2 $kJ \cdot mol^{-1}$) might be considered to make the studies in this paper inconsequential if it were not for the persistence of the phenomenon in many solvents. SPT, which supplies surprisingly accurate solubility estimates for these gases, suggests that the difference in solubility is due to the cavity formation term (ΔG_{CAV}) rather than the term for interaction with the solvent (ΔG_{INT}). These disparate results lead to several possible explanations.

Recent theoretical studies on hydrophobic solutes in water[18−20] argue that small hydrophobic solutes can enter the bulk water system without severely distorting the hydrogen-bonding network of the surrounding water. However, even small distortions of the water hydration shell, with their accompanying relatively small Gibbs energy changes, can lead to discernible, say 2-fold, differences in solubility. Quantum-chemical analysis indicates that although both O_2 and N_2 interact only weakly with water, the interaction between N_2 and water is approximately twice as strong as that between O_2 and water. The ESP surface maps of the two gases (Figure 3) also support the idea that N_2, with its more varied surface potential, should interact more strongly with a solvent than would O_2. One might propose that N_2, through its albeit weak interaction with its aqueous solvation shell, causes a greater distortion of this hydrogen-bonding network than does O_2, leading to a 2-fold difference in solubility. From the thermodynamic data, in this case the main effect of the distortion difference appears in the enthalpy of solvation, i.e., in a small weakening of the H_2O-H_2O hydrogen bonds, more so by N_2 than by O_2.

A much more plausible explanation for the difference in the solubilities of O_2 and N_2 concerns the effective volumes of the two gases in water and the influence of these volumes on the solution cavity formation terms. In the analyses above, we focused on the Spartan'10-calculated volumes of the two gases, which are almost identical and therefore suggest no difference in the cavity formation terms. However, in an earlier structure—property examination of aqueous solubilities, Abraham et al.[21] employed McGowan characteristic volumes[22] for the cavity terms with considerable success. The McGowan volume of N_2 ($22.22\ \mathrm{cm^3 \cdot mol^{-1}}$) is 21% greater than that of O_2 ($18.30\ \mathrm{cm^3 \cdot mol^{-1}}$), suggesting that more energy is required to form a cavity for N_2 than O_2 in the aqueous solvent. In fact, in Abraham et al.'s approach the cavity formation volumes are the only terms influencing the solubilities of these two gases, since all other terms (dispersion, dipolarity, hydrogen-bonding, etc.) in the regression analysis are zero. This explanation is consistent with both the thermodynamic data given in Table 9 and, more pointedly, the SPT results in Table 10, which show a greater cavity term for N_2 but solute—solvent interaction terms that are almost the same the two gases. Accordingly, if McGowan volumes are more appropriate for this comparison than are the volumes, the O_2/N_2 ratio "mystery" would appear to be solved.

Several additional lines of evidence support the idea that the resolution of the solubility difference between O_2 and N_2 lies in the different sizes of the two molecules. The van der Waals *b* value for N_2 ($0.0387\ \mathrm{Å^3}$), a parameter directly related to the molecular volume, is 21% greater than the *b* value for O_2 ($0.0319\ \mathrm{Å^3}$).[23] It should be noted that the "volume" calculated by the Spartan'10 program is not correctly a van der Waals volume, but rather is a value for use in visualizing space-filling models.[24] In addition, it has been observed that O_2 permeates rubber (as in rubber tires) 3—4 times faster than does N_2, an effect which is also attributed to the smaller size of the O_2 molecule.[25] Moreover, the critical volume of N_2 ($90.1\ \mathrm{cm^3 \cdot mol^{-1}}$) is considerably larger than that of O_2 ($78.0\ \mathrm{cm^3 \cdot mol^{-1}}$), and the polarizability of N_2 ($1.74\ \mathrm{Å^3}$), another feature generally associated with molecular volume, is greater than that of O_2 ($1.58\ \mathrm{Å^3}$). Therefore, one can conclude that O_2 is more soluble than N_2 in water (and other solvents) because it has a smaller volume and hence requires less energy to form a cavity in the solvents.

Comments by R.B. Given the above results, it is just not possible to provide a simple and convincing reason or set of reasons for the exceptionally *lower* solubility of N_2 over O_2 in a large number of solvents and fluids. To put all of this in perspective, it is important to know that the range of solubilities of gases in water extends over a factor of 7 from the very soluble, chemically interactive gases to the inert "Teflon-like" gases. Considering this huge range of solubilities, should one be concerned with a solubility ratio of 2 with sparsely soluble gases? After all, the solubility of O_2 in water is such that there are about two O_2 molecules in 100 000 water molecules. For N_2, this is about one N_2 molecule in 100 000 water molecules. How are the water molecules arranged around molecules of these effectively isolated gases? Would structural evidence help in providing an explanation? It is obvious that there have to be sufficient intermolecular forces for the gas molecules to stay in solution. However, we have not discovered how this can be quantified. After all, the central dispersion forces must be connected to the polarizability of the solute molecules, yet the examination of polarizability and solubility for these two gases does not provide any clues. What is going on, and do we need to be concerned (except that as scientists we love puzzles like this)?

The finding that O_2 is about twice as soluble as N_2 in biological fluids and solids, especially the important lipids of cephalin, lecithin, and cholesterol, was initially greeted with enthusiasm because it might be of great significance in physiology. But is it? Perhaps it is just an interesting curiosity since the important information is really just knowing what the solubilities of these gases are in various biological materials.

Also, any explanations of these solubilities would have to consider why the gases that cluster around the O_2 and N_2 solubilities cluster there. That is, for example, why do Ar, CH_4, C_3F_6, and *n*-C_4H_{10} have effectively the same solubility in water as does O_2, even though they are quite a disparate group of molecules?

Joint Comments. P.G.S. makes convincing arguments that the solubility of N_2 is less than that of O_2 in a large number of solvents because of the larger size of N_2. We both agree that this is a reasonable explanation for these two gases, and that this "answers" the question that initiated this paper. We certainly expect that the insights provided by molecular modeling will be an important contribution to explaining why these gases have their solubilities.

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■ REFERENCES

(1) Campanell, F. C.; Battino, R.; Seybold, P. G. On the Role of Solute Polarizability in Determining the Solubility of Gases in Liquids. *J. Chem. Eng. Data* **2010**, *55*, 37–40.

(2) Battino, R.; Seybold, P. G.; Campanell, F. C. Correlations Involving the Solubility of Gases in Water at 298.15 K and 101 325 Pa. *J. Chem. Eng. Data* **2011**, *56*, 727–732.

(3) *Oxygen and Ozone*; Battino, R., Ed.; Solubility Data Series, Vol. 7; Pergamon Press: New York, 1981.

(4) *Nitrogen and Air*; Battino, R., Ed.; Solubility Data Series, Vol. 10; Pergamon Press: New York, 1982.

(5) *Oxides of Nitrogen*; Young, C. L., Ed.; Solubility Data Series, Vol. 8; Pergamon Press: New York, 1981.

(6) Byrne, J. E.; Battino, R.; Danforth, W. F. The Solubility of Gases in Liquids. 7. The Solubilities of O_2, N_2, Ar, CO, CO_2, and *c*-C_3H_6 in Benzene and Isobutanol Solutions of Cholesterol, Lecithin, and Cephalin at 37.5 °C. *J. Chem. Thermodyn.* **1974**, *6*, 245–250.

(7) Battino, R.; Evans, F. D.; Danforth, W. F. The Solubility of Seven Gases in Olive Oil with Reference to Theories of Transport through the Cell Membrane. *J. Am. Oil Chem. Soc.* **1968**, *45*, 830–833.

(8) *Spartan'10*; Wavefunction, Inc.: Irvine, CA, 2010.

(9) Pierotti, R. A. The Solubility of Gases in Liquids. *J. Phys. Chem.* **1963**, *67*, 1840–1845.

(10) Pierotti, R. A. A Scaled Particle Theory of Aqueous and Nonaqueous Solutions. *Chem. Rev.* **1976**, *76*, 717–726.

(11) Tahery, R.; Modarress, H. Lennard-Jones Energy Parameters for Pure Fluids from Scaled Particle Theory. *Iran. J. Chem. Chem. Eng.* **2007**, *26*, 1–8.

(12) Hildebrand, J. H.; Scott, R. L. *The Solubility of Nonelectrolytes*, 3rd ed.; Reinhold Publishing: New York, 1980.

(13) Chai, J.-D.; Head-Gordon, M. Long-Range Hybrid Density Functionals with Damped Atom—Atom Dispersion Corrections. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615–6620.

(14) Dunning, T. H. Gaussian Basis Sets for Use in Correlated Molecular Calculations. I. The Atoms Boron through Neon and Hydrogen. *J. Chem. Phys.* **1989**, *90*, 1007–1023.

(15) Chambers, C. C.; Hawkins, G. D.; Cramer, C. J.; Truhlar, D. G. Model for Aqueous Solvation Based on Class IV Atomic Charges and First Solvation Shell Effects. *J. Phys. Chem.* **1996**, *100*, 16385–16398.

(16) Marenich, A. V.; Olson, R. M.; Kelly, C. P.; Cramer, C. J.; Truhlar, D. G. Self-Consistent Reaction Field Model for Aqueous and Nonaqueous Solutions Based on Accurate Polarized Partial Charges. *J. Chem. Theory Comput.* **2007**, *3*, 2011–2033.

(17) Ben-Amotz, D. Unveiling Electron Promiscuity. *J. Phys. Chem. Lett.* **2011**, *2*, 1216–1222.

(18) Lum, K.; Chandler, D.; Weeks, J. D. Hydrophobicity at Small and Large Length Scales. *J. Phys. Chem. B* **1999**, *103*, 4570–4577.

(19) Zangi, R. Driving Force for Hydrophobic Interaction at Different Length Scales. *J. Phys. Chem. B* **2011**, *115*, 2303–2311.

(20) Bakulin, A. A.; Pshenichnikov, M. S.; Bakker, H. J.; Peterson, C. Hydrophobic Molecules Slow Down the Hydrogen-Bond Dynamics of Water. *J. Phys. Chem. A* **2011**, *115*, 1821–1829.

(21) Abraham, M. H.; Andonian-Haftvan, J.; Whiting, G. S.; Leo, S.; Taft, R. S. Hydrogen Bonding. Part 34. The Factors That Influence the Solubility of Gases and Vapours in Water at 298 K, and a New Method for Its Determination. *J. Chem. Soc. Perkin Trans. 2* **1994**, 1777–1791.

(22) Abraham, M. H.; McGowan, J. C. The Use of Characteristic Volumes To Measure Cavity Terms in Reversed Phase Liquid Chromatography. *Chromatographia* **1987**, *23*, 243–246.

(23) Atkins, P.; De Paula, J. *Physical Chemistry*, 9th Ed.; W.H. Freeman: New York, 2010; pp 915—916.

(24) Ohlinger, S. Wavefunction, Inc. Personal communication.

(25) Murphy, K. Air Products and Chemicals Co. Are Nitrogen Molecules Really Larger Than Oxygen Molecules? The Correct Answer, with Respect to “Permeation”, Is Yes. http://www.getnitrogen.org/pdf/graham.pdf (accessed Aug 10, 2011).