

# Chemical Reviews

Volume 73, Number 1 February 1973

## Thermodynamic Functions of the Solubilities of Gases in Liquids at 25°C

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Received November 18, 1971 (Revised Manuscript Received June 12, 1972)

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### I. Introduction

The solubilities of gases in liquids have continued to be an area of active interest both from the practical and theoretical standpoints. For the first, interests range from various industrial processes to the composition of artificial atmospheres. For the second, the small solubility and the variety of gases available to use as probes have made the solubilities of gases in liquids an excellent tool to investigate liquid and solution structure and properties. All of these applications require reliable data. In this paper we present solubility data and the entropy and enthalpy changes on solution for some 16 gases in 39 solvents. Also included are some data for several fluorine-containing gases. Some correlations are discussed. This paper supplements the earlier review article by Battino and Clever<sup>2</sup> since that article contained very little data.

The two principal sources for gas solubility data are Seidell's handbook,<sup>3</sup> which does not contain thermodynamic data, and Appendix 3 in Hildebrand, Scott, and Prausnitz's book,<sup>4</sup> which does not provide as extensive coverage as this paper. We surveyed the available literature through the end of 1970. We deliberately omitted water from this work since the solubilities of gases in water is a subject unto itself.

### II. Calculation of Solubility and Thermodynamic Functions

#### A. Units of Gas Solubility

There are many ways to express the solubility of a gas

in a liquid.<sup>2</sup> The Ostwald coefficient  $L$  is defined as

$$L = V_2/V_1 \quad (1)$$

where  $V_2$  is the volume of gas absorbed by the volume  $V_1$  of the solvent. The mole fraction of the dissolved gas  $X_2$  is

$$X_2 = \{(RT/Lp_2V_1^0) + 1\}^{-1} \quad (2)$$

where  $R$  is the gas constant,  $T$  is the Kelvin temperature,  $p_2$  the partial pressure of the gas, and  $V_1^0$  the molar volume of the pure solvent (this equation assumes ideal gas behavior). The Henry's law coefficient  $K_H$  is given by

$$K_H = p_2/X_2 \quad (3)$$

#### B. Calculation of Gas Solubility from Literature Data

Two review articles,<sup>2,5</sup> the literature, and other sources<sup>3,4</sup> were searched for data which were reasonably precise. In general, all the solubility data used were precise to  $\pm 1\%$  or better. We limited the choice of solvents to those for which we evaluated<sup>6</sup> Lennard-Jones pair potential parameters from gas solubility data. If the literature data were not expressed as mole fractions at 1 atm partial gas pressure, they were converted to this unit using eq 1 and 2. Molar volumes for the solvents were taken from Timmermans<sup>7</sup> and other standard sources. In those cases where the temperature dependence was known, the mole fraction solubility at 298.15 K was determined from a least-squares analysis of  $-RT \ln X_2$  vs.  $T$ , i.e.

$$-RT \ln X_2 = A_0 + A_1 T \quad (4a)$$

For the data listed in Tables I and II this was used. However, for some systems where the data were particularly precise over a range of temperatures, the following quadratic expression was used.

$$-RT \ln X_2 = A_0' + A_1' T + A_2' T^2 \quad (4b)$$

Table III contains the constants  $A_0'$ ,  $A_1'$ , and  $A_2'$  for some systems. Our criterion was that the standard deviation for the three-constant fit was at least less than half that of the two-constant fit.

(1) Senior Fulbright Research Scholar, on leave of absence from the University of Vienna, Vienna, Austria.

(2) R. Battino and H. L. Clever, *Chem. Rev.*, **66**, 395 (1966).

(3) A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," 3rd ed. Van Nostrand, New York, N. Y., 1940, and supplements.

(4) J. H. Hildebrand, J. M. Prausnitz, and R. L. Scott, "Regular and Related Solutions," Van Nostrand-Reinhold, New York, N. Y., 1970.

(5) A. E. Markham and K. A. Kobe, *Chem. Rev.*, **28**, 519 (1941).

(6) E. Wilhelm and R. Battino, *J. Chem. Phys.*, **55**, 4012 (1971).

(7) J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Vol. 1, Elsevier, New York, N. Y., 1950.

TABLE I. Solubility of Gases,  $X_2 \times 10^4$ , at 298.15 K and 1 Atm Partial Gas Pressure (Upper Line), Entropy of Solution,  $\Delta\bar{S}^\circ$  (cal mol<sup>-1</sup> K<sup>-1</sup>)

Gas	1-He	2-Ne	3-Ar	4-Kr	5-Xe	6-H <sub>2</sub>	7-D <sub>2</sub>	8-N <sub>2</sub>
$\epsilon/k, K$	6.03	34.9	122	158	229	29.2	31.1	95
$\Delta E_b^\circ, kcal mol^{-1}$	0.017	0.37	1.385	2.00	2.69	0.175	0.247	1.18
1. <i>n</i> -Hexane	2.604 <sup>b</sup> -9.96 1920	3.699 <sup>b</sup> -11.18 1348	25.12 <sup>b</sup> -14.06 -646	69.60 <sup>b</sup> -13.66 -1130	258.7 <sup>c</sup> -15.84 -2556	6.315 <sup>d</sup> -10.55 1219		14.02 <sup>e</sup>
2. <i>n</i> -Heptane	2.498 <sup>b</sup> -10.29 1846	3.553 <sup>b</sup> -11.32 1330	24.87 <sup>b</sup> -12.90 -292	71.17 <sup>b</sup> -14.25 -1318		6.859 <sup>i</sup> -11.44 904	7.014 <sup>i</sup> -11.55 859	13.54 <sup>j</sup>
3. <i>n</i> -Octane	2.397 <sup>b</sup> -10.10 1926	3.626 <sup>b</sup> -10.18 1659	24.26 <sup>b</sup> -12.25 -85	70.66 <sup>b</sup> -13.85 -1194		6.845 <sup>i</sup> -11.24 965	7.003 <sup>i</sup> -11.39 908	13.04 <sup>j</sup>
4. <i>n</i> -Nonane	2.357 <sup>b</sup> -8.83 2316	3.429 <sup>b</sup> -10.81 1503	24.89 <sup>b</sup> -13.09 -349	71.22 <sup>b</sup> -13.55 -1109		6.922 <sup>j</sup>		12.81 <sup>j</sup>
5. <i>n</i> -Decane	2.309 <sup>b</sup> -10.42 1853	3.491 <sup>b</sup> -10.67 1534	25.09 <sup>b</sup> -13.08 -352	71.93 <sup>b</sup> -13.71 -1165				
6. <i>n</i> -Dodecane	2.223 <sup>b</sup> -10.94 1723	3.127 <sup>b</sup> -10.45 1666	25.66 <sup>b</sup> -12.37 -153	75.54 <sup>b</sup> -13.12 -1016	307.2 <sup>c</sup> -14.47 -2251			
7. <i>n</i> -Tetradecane	2.249 <sup>b</sup> -11.97 1408	3.340 <sup>b</sup> -11.19 1406	26.50 <sup>b</sup> -12.97 -352	80.10 <sup>b</sup> -13.86 -1272				
8. 3-Methylheptane	2.495 <sup>b</sup> -10.23 1866	3.743 <sup>b</sup> -11.22 1329	24.71 <sup>b</sup> -11.82 34	71.06 <sup>b</sup> -12.94 -926				
9. 2,3-Dimethylhexane	2.497 <sup>b</sup> -10.82 1688	3.616 <sup>b</sup> -11.05 1399	24.95 <sup>b</sup> -13.24 -396	70.78 <sup>b</sup> -13.07 -965				
10. 2,4-Dimethylhexane	2.740 <sup>b</sup> -8.86 2219	3.974 <sup>b</sup> -11.25 1284	26.84 <sup>b</sup> -12.73 -287	73.43 <sup>b</sup> -12.94 -946				
11. 2,2,4-Trimethylpentane	3.083 <sup>b</sup> -9.92 1833	4.593 <sup>b</sup> -11.66 1078	29.21 <sup>b</sup> -13.41 -542	79.27 <sup>b</sup> -13.99 -1304	273.5 <sup>c</sup> -15.61 -2522	7.832 <sup>i</sup> -11.21 895	7.981 <sup>i</sup> -11.33 849	15.39 <sup>o</sup> -12.25 186
12. Cyclohexane	1.217 <sup>b</sup> -9.79 2421	1.792 <sup>b</sup> -12.24 1461	14.80 <sup>b</sup> -13.68 -218	46.68 <sup>b</sup> -13.45 -831	202.9 <sup>c</sup> -14.76 -2091	4.142 <sup>r</sup> -11.32 1240		7.61 <sup>s</sup> -12.6 511
13. Methylcyclohexane	1.625 <sup>t</sup> -9.44 2356	2.306 <sup>t</sup> -10.04 1969	18.41 <sup>t</sup> -13.46 -283	57.28 <sup>t</sup> -14.73 -1335	227.1 <sup>t</sup> -14.38 -2045			9.46 <sup>u</sup> -12.09 520
14. Benzene	0.771 <sup>b</sup> -10.79 2396	1.118 <sup>b</sup> -8.07 2984	8.815 <sup>b</sup> -12.98 297	27.39 <sup>b</sup> -13.17 -431	116.6 <sup>c</sup> -14.53 -1695	2.580 <sup>i</sup> -11.32 1519	2.656 <sup>i</sup> -11.41 1478	4.461 <sup>v</sup> -11.92 1016
15. Toluene	0.974 <sup>w</sup> -10.01 2487	1.402 <sup>w</sup> -11.03 1968	10.86 <sup>w</sup> -12.78 232	33.46 <sup>w</sup> -14.31 -889	146.1 <sup>w</sup> -15.03 -1976	3.171 <sup>i</sup> -11.92 1218	3.271 <sup>i</sup> -12.07 1155	5.74 <sup>u</sup> -9.88 1475
16. <i>m</i> -Xylene	1.121 <sup>x</sup> -9.96 2420	1.619 <sup>x</sup> -9.28 2403				4.153 <sup>x</sup> -11.44 1203		
17. Perfluoro- <i>n</i> -heptane	8.862 <sup>p</sup> -8.26 1703		53.22 <sup>aa</sup>			14.03 <sup>i</sup> -9.68 1005	14.45 <sup>i</sup> -9.83 945	38.80 <sup>e</sup> -11.59 -165

(Second Line), Enthalpy of Solution,  $\Delta\bar{H}^\circ$  (cal mol<sup>-1</sup>) (Third Line), and Reference (Superscript on First Line)

9-O <sub>2</sub>	10-CO	11-CO <sub>2</sub>	12-CH <sub>4</sub>	13-C <sub>2</sub> H <sub>6</sub>	14-C <sub>2</sub> H <sub>4</sub>	15-CF <sub>4</sub>	16-SF <sub>6</sub>	Solvent <sup>a</sup> V <sub>1</sub> <sup>0</sup> δ <sub>1</sub> <sup>2</sup> σ
118 1.45	100 1.28	195	157 1.73	236 3.15	230 2.90	134 2.72	201 (4.08)	
19.3 <sup>f</sup>			50.37 <sup>g</sup> -12.32 -539	320 <sup>h</sup>	229.5 <sup>d</sup> -13.48 -1782			131.62 53.3 17.90
21.66 <sup>j</sup>	17.24 <sup>k</sup>	120.2 <sup>i</sup> -16.53 -2309	34.53 <sup>m</sup> -14.30 -906	319.6 <sup>h</sup> -15.78 -2666		21.50 <sup>n</sup> -13.48 -381	101.3 <sup>n</sup> -15.75 -1977	147.46 54.8 19.80
20.83 <sup>j</sup>			29.27 <sup>m</sup> -14.84 -970	342.5 <sup>j</sup>		19.66 <sup>15</sup> -12.45 -21	95.88 <sup>15</sup> -15.92 -1993	163.54 56.3 21.25
21.12 <sup>j</sup>				342.0 <sup>j</sup>				179.70 59.3 22.40
			18.42 <sup>m</sup> -15.68 -945	351 <sup>h</sup>				195.94 59.3 23.40
								228.60 62.4 24.95
								261.31 64.0 26.30
								162.78 53.3 20.80
								161.34 54.8 19.70
								164.08 51.8 19.90
28.14 <sup>p</sup> -12.94 -378		138.7 <sup>q</sup> -16.02 -2241	29.66 <sup>m</sup> -14.59 -901	292.6 <sup>p</sup> -17.13 -3014		29.09 <sup>n</sup> -13.78 -648	153.0 <sup>p</sup> -15.60 -2174	166.10 47.6 18.40
12.48 <sup>s</sup> -13.1 58	9.91 <sup>s</sup> -13.1 202	76.0 <sup>s</sup> -14.1 -1327	32.75 <sup>g</sup> -13.34 -588	235.9 <sup>r</sup> -16.24 -2621		10.34 <sup>n</sup> -13.26 119	54.19 <sup>n</sup> -14.99 -1377	108.75 67.2 24.50
15.99 <sup>u</sup> -14.04 224	12.41 <sup>u</sup> -13.52 -66	92.8 <sup>u</sup> -17.52 -2451	39.6 <sup>u</sup> -15.01 -1197			13.71 <sup>u</sup> -11.77 397	70.51 <sup>n</sup> -15.59 -1713	128.35 60.8 23.29
8.165 <sup>v</sup> -12.76 409	6.680 <sup>v</sup> -12.40 635	97.30 <sup>i</sup> -16.69 -2230	20.77 <sup>v</sup> -13.30 -305	148.7 <sup>v</sup> -15.74 -2200	123.3 <sup>v</sup> -15.95 -2151	5.748 <sup>n</sup> -13.02 540	26.38 <sup>n</sup> -14.41 -778	89.41 84.6 28.25
9.09 <sup>u</sup> -14.44 -143	8.11 <sup>u</sup> -12.64 447	101.3 <sup>u</sup> -17.56 -2515	24.14 <sup>u</sup> -16.05 -1214	154.1 <sup>d</sup> -15.44 -2130	146.3 <sup>d</sup> -15.43 -2096	6.93 <sup>u</sup> -9.67 1427	33.73 <sup>n</sup> -15.56 -1266	106.86 79.2 27.94
11.96 <sup>y</sup>					138.7 <sup>z</sup> -17.57 -2703			123.47 77.4 28.33
55.08 <sup>k</sup>	38.75 <sup>k</sup>	208.2 <sup>p</sup> -14.77 -2111	82.56 <sup>p</sup> -12.95 -1019	210.2 <sup>j,aa</sup>			222.6 <sup>p</sup> -15.15 -2261	227.33 36.0 12.78

TABLE I (Continued)

Gas	1-He	2-Ne	3-Ar	4-Kr	5-Xe	6-H <sub>2</sub>	7-D <sub>2</sub>	8-N <sub>2</sub>
$\epsilon/k, K$	6.03	34.9	122	158	229	29.2	31.1	95
$\Delta E_0^v, kcal mol^{-1}$	0.017	0.37	1.385	2.00	2.69	0.175	0.247	1.18
18. Perfluoromethyl- cyclohexane	7.498 <sup>t</sup> -10.85 1028	11.25 <sup>t</sup> -10.71 829	44.65 <sup>t</sup> -12.54 -532	84.82 <sup>t</sup> -12.89 -1016	169.4 <sup>t</sup> -14.07 -1778			32.66 <sup>e</sup>
19. Perfluoro- benzene	2.137 <sup>cc</sup> -1.55 4544	3.455 <sup>cc</sup> -6.31 2841	23.98 <sup>cc</sup> -13.06 -318	59.00 <sup>cc</sup> -13.47 -974				17.95 <sup>cc</sup> -12.60 -10
20. (C <sub>4</sub> F <sub>9</sub> ) <sub>3</sub> N	11.67 <sup>4</sup>	16.79 <sup>4</sup>	61.0 <sup>4</sup>	111.2 <sup>4</sup>				34.90 <sup>p</sup> -11.76 -153
21. CCl <sub>4</sub>			13.51 <sup>ee</sup> -13.47 -103			3.349 <sup>i</sup> -11.41 1340	3.284 <sup>i</sup> -11.62 1287	6.480 <sup>v</sup> -12.70 564
22. 1,1,2,2-Tetra- chloroethane	1.079 <sup>x</sup> -11.48 1989	1.495 <sup>x</sup> -10.85 1984				4.059 <sup>x</sup> -12.77 818		
23. 1,1,2-Trichloro- 1,2,2-trifluoro- ethane		4.848 <sup>ff</sup> -11.03 1233	30.95 <sup>q</sup> -13.10 -481		214.7 <sup>ff</sup> -14.90 -2166	6.572 <sup>ff</sup> -10.60 1181		19.58 <sup>q</sup> -11.96 128
24. Fluorobenzene	1.144 <sup>w</sup> -11.69 1890	1.575 <sup>w</sup> -11.60 1730	11.48 <sup>w</sup> -13.57 -35	33.22 <sup>w</sup> -13.92 -770	130.3 <sup>w</sup> -14.87 -1863			
25. Chlorobenzene	0.691 <sup>w</sup> -11.00 2397	0.979 <sup>w</sup> -10.63 2299	8.609 <sup>w</sup> -13.66 107	27.26 <sup>w</sup> -14.18 -730	123.2 <sup>w</sup> -15.71 -2078	2.609 <sup>v</sup> -12.40 1192		4.377 <sup>v</sup> -13.42 581
26. Bromobenzene	0.536 <sup>w</sup> -10.57 2675	0.787 <sup>w</sup> -12.06 2002	6.800 <sup>w</sup> -13.74 223	22.78 <sup>w</sup> -14.53 -726	108.2 <sup>w</sup> -15.04 -1802			
27. Iodobenzene	0.373 <sup>w</sup> -9.54 3196	0.525 <sup>w</sup> -11.17 2507	5.011 <sup>w</sup> -12.97 636	16.84 <sup>w</sup> -14.10 -421	88.10 <sup>w</sup> -15.01 -1673			
28. Nitromethane	0.386 <sup>hh</sup>	0.541 <sup>hh</sup>	3.198 <sup>hh</sup>	8.376 <sup>hh</sup>	25.09 <sup>hh</sup>			2.007 <sup>hh</sup>
29. Nitrobenzene	0.350 <sup>w</sup> -9.52 3240	0.436 <sup>w</sup> -9.35 3162	4.448 <sup>w</sup> -13.47 557	13.83 <sup>w</sup> -13.41 -97	58.38 <sup>w</sup> -14.36 -1233			
30. Methanol	0.595 <sup>jj</sup> -13.24 1817	0.814 <sup>jj</sup> -14.88 1143	4.491 <sup>jj</sup> -16.01 -206					2.747 <sup>o</sup> -15.89 120
31. Ethanol	0.769 <sup>jj</sup> -13.01 1733	1.081 <sup>jj</sup> -13.42 1408	6.231 <sup>jj</sup> -14.97 -92			2.067 <sup>nn</sup> -13.87 891		3.593 <sup>o</sup> -15.40 109
32. 2-Methyl-1- propanol (isobutyl alcohol)	1.015 <sup>14</sup> -14.34 1172	1.527 <sup>14</sup> -14.10 1001	9.518 <sup>14</sup> -15.43 -478	25.49 <sup>14</sup> -16.74 -1453				4.837 <sup>14</sup> -15.33 -48
33. Cyclohexanol	0.473 <sup>jj</sup> -10.53 2761	0.718 <sup>jj</sup> -12.25 2001	5.299 <sup>jj</sup> -13.55 430			1.689 <sup>oo</sup>		2.655 <sup>11</sup>
34. Acetone	1.081 <sup>jj</sup> -8.93 2747	1.577 <sup>jj</sup> -9.33 2405	9.067 <sup>jj</sup> -12.38 461			2.996 <sup>v</sup> -12.49 1084		5.395 <sup>v</sup> -13.56 417

9-O <sub>2</sub>	10-CO	11-CO <sub>2</sub>	12-CH <sub>4</sub>	13-C <sub>2</sub> H <sub>6</sub>	14-C <sub>2</sub> H <sub>4</sub>	15-CF <sub>4</sub>	16-SF <sub>6</sub>	Solvent <sup>a</sup>
118	100	195	157	236	230	134	201	V <sub>1</sub> <sup>0</sup>
1.45	1.28		1.73	3.15	2.90	2.72	(4.08)	δ <sub>1</sub> <sup>2</sup>
								σ
						106.1 <sup>bb</sup>		195.88
						-14.81		37.2
						-1722		15.20
24.18 <sup>cc</sup>	21.2 <sup>cc</sup>	220 <sup>cc</sup>	38.42 <sup>cc</sup>			45.61 <sup>cc</sup>		115.79
-12.81			-13.25			-14.33		68.9
-250			-656			-1078		21.80
52.01 <sup>p</sup>		199.0 <sup>p</sup>	68.8 <sup>4</sup>	332.6 <sup>p</sup>			729.3 <sup>q</sup>	358.49
-12.31		-14.63		-15.18			-16.17	34.8
-553		-2041		-2510			-3270	19.35 <sup>pdd</sup>
12.01 <sup>v</sup>	8.763 <sup>v</sup>	105.3 <sup>l,v</sup>	28.70 <sup>v</sup>	208.2 <sup>v</sup>	145.0 <sup>v</sup>	11.84 <sup>n</sup>	65.31 <sup>n</sup>	97.09
-13.34	-12.98		-14.03	-16.52	-16.10	-12.92	-15.57	74.0
8	302		-714	-2630	-2292	141	-1662	26.17
								105.80
								86.5
								34.9
		183.0 <sup>q</sup>	50.47 <sup>q</sup>	286.1 <sup>ff</sup>		48.17 <sup>n</sup>	297.3 <sup>q</sup>	119.84
		-16.71	-13.28	-15.46		-14.05	-15.57	50.4
		-2611	-827	-2503		-1027	-2559	21.28 <sup>p</sup>
15.08 <sup>y</sup>								94.31
								82.8
								26.87
7.910 <sup>v</sup>	6.468 <sup>v</sup>	98.06 <sup>gg</sup>	20.47 <sup>v</sup>	146.5 <sup>v</sup>	118.9 <sup>v</sup>			102.27
-13.68	-13.81		-14.34	-16.31	-16.17			92.2
152	232		-609	-2360	-2195			32.58
7.48 <sup>y</sup>								105.51
								100.0
								35.72
5.10 <sup>y</sup>								111.91
								104.0
								37.70
							8.310 <sup>hh</sup>	53.96
								(154.3) <sup>ii</sup>
								36.7
4.95 <sup>y</sup>	3.724 <sup>gg</sup>	99.80 <sup>gg</sup>						102.72
								(117.9)
								43.75
4.147 <sup>o</sup>	3.761 <sup>kk</sup>	55.78 <sup>ll</sup>	8.695 <sup>g</sup>	38.81 <sup>mm</sup>	43.60 <sup>mm</sup>			40.73
-16.24	-15.14	-18.88	-16.90					(210.3)
-229	157	-2555	-862					22.12
5.841 <sup>o</sup>	4.843 <sup>kk</sup>	63.66 <sup>ll</sup>	12.80 <sup>g</sup>	68.37 <sup>mm</sup>	61.03 <sup>mm</sup>			58.68
-15.77	-14.89	-20.30	-16.31					(163.8)
-291	84	-3056	-915					21.88
8.397 <sup>14</sup>	6.524 <sup>14</sup>	69.63 <sup>14</sup>						92.88
-15.83	-15.72	-18.36						(118.8)
-522	-341	-2530						22.55
		44.28 <sup>pp</sup>	12.55 <sup>g</sup>	82.02 <sup>11</sup>				105.94
		-17.89	-15.53					33.96
		-2124	-673					
8.383 <sup>v</sup>	7.719 <sup>v</sup>	185.3 <sup>ll</sup>	18.35 <sup>v</sup>	96.29 <sup>v</sup>	109.1 <sup>v</sup>			74.01
-13.98	-14.04	-26.08	-14.78	-16.14	-16.25			(96.4)
30	59	-5414	-674	-2062	-2168			21.92

TABLE I (Continued)

Gas	1-He	2-Ne	3-Ar	4-Kr	5-Xe	6-H <sub>2</sub>	7-D <sub>2</sub>	8-N <sub>2</sub>
$\epsilon/k, K$	6.03	34.9	122	158	229	29.2	31.1	95
$\Delta E_b^v, kcal\ mol^{-1}$	0.017	0.37	1.385	2.00	2.69	0.175	0.247	1.18
35. N-Methyl- acetamide	0.491 <sup>aa</sup> -12.02 2296		4.434 <sup>aa</sup> -15.12 67					2.396 <sup>aa</sup> -14.93 488
36. Hydrazine	0.05227 <sup>rr</sup> -19.93 1264		0.1239 <sup>rr</sup> -15.60 2043					0.07254 <sup>rr</sup> -15.60 2361
37. Methyl- hydrazine	0.252 <sup>rr</sup> -14.68 1897		1.784 <sup>rr</sup> -14.98 648					0.920 <sup>rr</sup> -14.71 1121
38. Dimethyl- hydrazine	0.934 <sup>rr</sup> -11.37 2107		6.858 <sup>rr</sup> -13.68 239					3.735 <sup>rr</sup> -13.00 800
39. Dimethyl sulfoxide	0.284 <sup>r</sup>	0.368 <sup>r</sup>	1.54 <sup>r</sup>	4.46 <sup>r</sup>	17.0 <sup>r</sup>	0.761 <sup>r</sup>	0.799 <sup>r</sup>	0.833 <sup>r</sup>

<sup>a</sup>Solvent properties: first line, molar volume  $V_1^0$  ( $cm^3\ mol^{-1}$ ); second line, Hildebrand solubility parameter  $\delta_1^2$  ( $cal\ cm^{-3}$ ); third line, surface tension  $\sigma_1$  ( $dynes\ cm^{-2}$ ). <sup>b</sup>H. L. Clever, R. Battino, J. H. Saylor, and P. M. Gross, *J. Phys. Chem.*, **61**, 1078 (1957). <sup>c</sup>H. L. Clever, *ibid.*, **62**, 375 (1958). <sup>d</sup>J. A. Waters, G. A. Mortimer, and H. E. Clements, *J. Chem. Eng. Data*, **15**, 174 (1970). <sup>e</sup>J. C. Gjaldbaek and J. H. Hildebrand, *J. Amer. Chem. Soc.*, **71**, 3147 (1949). <sup>f</sup>D. Guerry, Ph.D. Thesis, Vanderbilt University, Nashville, Tenn., 1944. <sup>g</sup>A. Lannung and J. C. Gjaldbaek, *Acta Chem. Scand.*, **14**, 1124 (1960). <sup>h</sup>W. Hayduk and S. C. Cheng, *Can. J. Chem. Eng.*, **48**, 93 (1970). <sup>i</sup>M. W. Cook, D. N. Hanson, and B. J. Alder, *J. Chem. Phys.*, **26**, 748 (1957). <sup>j</sup>E. S. Thomsen and J. C. Gjaldbaek, *Acta Chem. Scand.*, **17**, 127 (1963). <sup>k</sup>J. C. Gjaldbaek, *ibid.*, **6**, 623 (1952). <sup>l</sup>J. C. Gjaldbaek, *ibid.*, **7**, 534 (1953). <sup>m</sup>K. Onda, E. Sada, and S. Shinno, *Kogyo Kagaku Zasshi*, **61**, 702 (1958). <sup>n</sup>G. Archer and J. H. Hildebrand, *J. Phys. Chem.*, **67**, 1830 (1963). <sup>o</sup>C. B. Kretschmer, J. Nowakowska, and R. Wiebe, *Ind. Eng. Chem.*, **38**, 506 (1946). <sup>p</sup>Y. Kobatake and J. H. Hildebrand, *J. Phys. Chem.*, **65**, 331 (1961). <sup>q</sup>H. Hiraoka and J. H. Hildebrand, *ibid.*, **68**, 213 (1964). <sup>r</sup>J. H. Dymond, *ibid.*, **71**, 1829 (1967). <sup>s</sup>E. Wilhelm and R. Battino, to be published. <sup>t</sup>H. L. Clever, J. H. Saylor, and P. M. Gross, *J. Phys. Chem.*, **62**, 89 (1958). <sup>u</sup>L. Field, R. Battino, and E. Wilhelm, to be published. <sup>v</sup>J. Horvut, *Sci.*

TABLE II. Solubility of Some Fluorocarbon Gases in Several Solvents<sup>a</sup>

Gas	CF <sub>4</sub>	C <sub>2</sub> F <sub>6</sub>	C <sub>3</sub> F <sub>8</sub>	c-C <sub>4</sub> F <sub>8</sub>	SF <sub>6</sub>	CF <sub>3</sub> Cl	CF <sub>2</sub> Cl <sub>2</sub>
$\epsilon/k, K$	134	255	266	223	201	222	286
$\Delta E_b^v, kcal/mol$	2.72	3.47	4.22	5.00	(4.08)	3.33	4.29
n-Heptane	21.50 <sup>b</sup> -13.48 -381				101.3 <sup>b</sup> -15.75 -1977	167.5 <sup>c</sup> -18.4 -3070	1252 <sup>c</sup> -19.3 -4520
n-Octane	19.66 <sup>c</sup> -12.45 -21				95.88 <sup>c</sup> -15.92 -1993	162.5 <sup>c</sup> -15.7 -2250	1296 <sup>c</sup> -17.8 -4080
Cyclohexane	10.34 <sup>b</sup> -13.26 119	24.46 <sup>d</sup> -13.47 -452	60.90 <sup>d</sup> -15.23 -1519	216.6 <sup>d</sup> -16.72 -2715	54.19 <sup>b</sup> -14.99 -1377	99.6 <sup>c</sup> -16.5 -2220	939 <sup>c</sup> -20.5 -4720
Benzene	5.748 <sup>b</sup> -13.02 540	11.1 <sup>e</sup>	24.4 <sup>e</sup>	100 <sup>e</sup>	26.38 <sup>b</sup> -14.41 -778	60.9 <sup>c</sup> -14.2 -1200	717 <sup>c</sup> -20.1 -4440
Perfluorobenzene	45.61 <sup>e</sup> -14.33 -1078	155 <sup>e</sup>	520 <sup>e</sup>				
(C <sub>4</sub> F <sub>9</sub> ) <sub>3</sub> N			1497 <sup>f</sup>		729.3 <sup>g</sup> -16.17 -3270		
CCl <sub>4</sub>	11.84 <sup>b</sup> -12.92 141				65.31 <sup>b</sup> -15.57 -1662	108.5 <sup>c</sup> -17.5 -2540	1016 <sup>c</sup> -22.2 -5260
CCl <sub>2</sub> FCClF <sub>2</sub>	48.17 <sup>b</sup> -14.05 -1027	150.3 <sup>h</sup> -15.58 -2159			275.3 <sup>g</sup> -16.81 -2883		

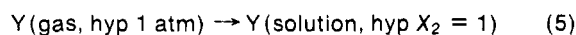
<sup>a</sup>Numbers have the same significance as in Table I. <sup>b</sup>G. Archer and J. H. Hildebrand, *J. Phys. Chem.*, **67**, 1830 (1963). <sup>c</sup>E. Wilhelm and R. Battino, *J. Chem. Thermodyn.*, **3**, 379 (1971). <sup>d</sup>K. W. Miller, *J. Phys. Chem.*, **72**, 2248 (1968). <sup>e</sup>F. D. Evans and R. Battino, *J. Chem. Thermodyn.*, **3**, 753 (1971). <sup>f</sup>J. H. Hildebrand, J. M. Prausnitz, and R. L. Scott, "Regular and Related Solutions," Van Nostrand-Reinhold, New York, N. Y., 1970. <sup>g</sup>H. Hiraoka and J. H. Hildebrand, *J. Phys. Chem.*, **68**, 213 (1964). <sup>h</sup>R. G. Linford and J. H. Hildebrand, *ibid.*, **73**, 4410 (1969).

9-O <sub>2</sub>	10-CO	11-CO <sub>2</sub>	12-CH <sub>4</sub>	13-C <sub>2</sub> H <sub>6</sub>	14-C <sub>2</sub> H <sub>4</sub>	15-CF <sub>4</sub>	16-SF <sub>6</sub>	Solvent <sup>a</sup> V <sub>1</sub> <sup>0</sup> δ <sub>1</sub> <sup>2</sup> σ
118	100	195	157	236	230	134	201	
1.45	1.28		1.73	3.15	2.90	2.72	(4.08)	
				47.45 <sup>qq</sup>				77.59
				-18.07				86.5
				2216				34.32P
								31.94
								(327.63)
								70.61
								52.97
								42.82P
								76.65
								29.41P
1.57 <sup>r</sup>		90.8 <sup>r</sup>	3.86 <sup>r</sup>	17.8 <sup>r</sup>				71.37
								(163.1)
								42.86

Pap. Inst. Phys. Chem. Res. Tokyo, **17**, 125 (1931). <sup>uu</sup>J. H. Saylor and R. Battino, *J. Phys. Chem.*, **62**, 1334 (1958). <sup>xx</sup>W. J. de Wet, *J. S. Afr. Chem. Inst.*, **17**, 9 (1964). <sup>yy</sup>N. K. Naumenko, N. N. Mukhin, and V. B. Aleskovskii, *Zh. Prikl. Khim. (Leningrad)*, **42**, 2522 (1969); *Chem. Abstr.*, **72**, 71206 (1970). <sup>zz</sup>E. Nakamura, K. Koguchi, and T. Amemiya, *Kogyo Kagaku Zasshi*, **69**, 1940 (1966). <sup>aaa</sup>J. C. Gjaldbaek and H. Niemann, *Acta Chem. Scand.*, **12**, 611 (1958). <sup>bbb</sup>L. W. Reeves and J. H. Hildebrand, *J. Phys. Chem.*, **67**, 1918 (1963). <sup>ccc</sup>F. D. Evans and R. Battino, *J. Chem. Thermodyn.*, **3**, 753 (1971). <sup>ddd</sup>Estimated from parachor. <sup>eee</sup>L. W. Reeves and J. H. Hildebrand, *J. Amer. Chem. Soc.*, **79**, 1313 (1957). <sup>fff</sup>R. G. Linford and J. H. Hildebrand, *Trans. Faraday Soc.*, **66**, 577 (1970). <sup>ggg</sup>J. C. Gjaldbaek and E. K. Anderson, *Acta Chem. Scand.*, **8**, 1398 (1954). <sup>hhh</sup>H. L. Friedman, *J. Amer. Chem. Soc.*, **76**, 3294 (1954). <sup>iii</sup>Calculated for polar solvents (in parentheses) although not strictly applicable. <sup>jjj</sup>A. Lannung, *J. Amer. Chem. Soc.*, **52**, 68 (1930). <sup>kkk</sup>J. C. Gjaldbaek, *Kgl. Dan. Vidensk. Selsk. Mat. Fys. Medd.*, **13**, 24 (1948). <sup>lll</sup>W. Kunerth, *Phys. Rev.*, **19**, 512 (1922). <sup>mmm</sup>F. L. Boyer and L. J. Bircher, *J. Phys. Chem.*, **64**, 1330 (1960). <sup>nnn</sup>E. B. Maxted and C. H. Moon, *Trans. Faraday Soc.*, **32**, 769 (1936). <sup>ooo</sup>S. Kruyer and A. P. P. Nobel, *Recl. Trav. Chim. Pays-Bas*, **80**, 1145 (1961). <sup>ppp</sup>J. W. Begley, H. J. R. Maget, and B. Williams, *J. Chem. Eng. Data*, **10**, 4 (1965). <sup>qqq</sup>R. H. Wood and D. E. DeLaney, *J. Phys. Chem.*, **72**, 4652 (1968). <sup>rrr</sup>E. T. Chang, N. A. Gokcen, and T. M. Poston, *ibid.*, **72**, 638 (1968).

### C. Choice of Standard States and Calculation of Thermodynamic Functions

We define  $\Delta\bar{G}^\circ$ ,  $\Delta\bar{H}^\circ$ , and  $\Delta\bar{S}^\circ$  as the change in respectively Gibbs energy, enthalpy, and entropy in the process



for 1 mol of Y, where  $X_2$  is the mole fraction of Y in solution. Assuming ideal behavior of the gas and validity of the laws for ideal dilute solutions, then we have the (approximate) relation

$$\Delta\bar{G}^\circ \cong -RT \ln X_2(\text{sat}) \quad (6)$$

where  $X_2(\text{sat})$  is the value of  $X_2$  when the solution is in equilibrium with gaseous Y at a partial pressure of 1 atm, estimated from the total pressure by neglecting the non-ideality of the mixture of gaseous Y and the solvent vapor. Subject to the same approximation we also have (cf. also Sherwood and Prausnitz<sup>8</sup>)

$$\Delta\bar{H}^\circ = RT \left( \frac{\partial \ln X_2(\text{sat})}{\partial \ln T} \right) \quad (7)$$

$$\Delta\bar{S}^\circ = R \left[ \left( \frac{\partial \ln X_2(\text{sat})}{\partial \ln T} \right) + \ln X_2(\text{sat}) \right] \quad (8)$$

In Tables I and II we give the data for  $10^4 X_2(\text{sat})$  and for the approximate values of  $\Delta\bar{H}^\circ$  and  $\Delta\bar{S}^\circ$  (all at 298.15 K and 1 atm partial pressure of gas) obtained from the experimental results by application of eq 7 and 8, respec-

tively. In a few cases where no temperature-dependent data were available only values of  $X_2$  were reported. Using the two-constant eq 4a it follows that  $\Delta\bar{S}^\circ = -A$  and  $\Delta\bar{H}^\circ = A_0$ . Then  $\Delta\bar{G}^\circ$  may be calculated from the tables via  $\Delta\bar{G}^\circ = \Delta\bar{H}^\circ - T\Delta\bar{S}^\circ$ . For not too large temperature intervals where  $\Delta\bar{H}^\circ$  can be regarded as being constant, the mole fraction  $X_2(T_2)$  at a temperature  $T_2$  may be calculated from

$$\ln X_2(T_2) - \ln X_2(298.15) = \frac{\Delta\bar{H}^\circ}{R} \left( \frac{T_2 - 298.15}{298.15T_2} \right) \quad (9)$$

with reasonable accuracy.

The Hildebrand<sup>4</sup> entropy of solution is given by (same approximations as above)

$$\Delta\bar{S}_H = R(\partial \ln X_2 / \partial \ln T)_{\text{sat}, P} \quad (10)$$

However, it refers to the change in entropy for the process of transferring 1 mol of gaseous Y (1 atm, ideal gas) to a solution at equilibrium mole fraction  $X_2$ , above which the gas partial pressure is 1 atm. This is a solution of different mole fraction for each gas and each temperature. To convert the partial molar entropies of solution obtained via eq 10 to entropies corresponding to the process shown in eq 5, you add the entropy necessary to increase the mole fraction from  $X_2$  to  $X_2 = 1$ . This is, according to Henry's law, equal to the entropy of compressing the gas from 1 atm to atm/ $X_2$  or just  $R \ln X_2$ . Hence

$$\Delta\bar{S}^\circ = \Delta\bar{S}_H + R \ln X_2 \quad (11)$$

To convert  $\Delta\bar{S}^\circ$  values to the standard state  $X_2 = 10^{-4}$ , add  $18.30 \text{ cal K}^{-1} \text{ mol}^{-1}$  ( $\Delta\bar{S}(X_2 = 10^{-4}) = \Delta\bar{S}^\circ - R \ln 10^{-4}$ ).

(8) A. E. Sherwood and J. M. Prausnitz, *AIChE J.*, **8**, 519 (1962).

TABLE III. Coefficients<sup>a</sup> for the Polynomial  $\Delta G^\circ = -RT \ln X_2 = A_0' + A_1' T + A_2' T^2$ 

	H <sub>2</sub>	D <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>	CO	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>
<i>n</i> -Heptane	-0.59385 <sup>b</sup> 1.8550 -1.3007 238-308 (7)	-1.1870 <sup>b</sup> 1.8765 -1.3208 238-308 (7)						
<i>n</i> -Octane	5.6235 <sup>b</sup> 1.4161 -0.52484 248-308 (4)	3.8755 <sup>b</sup> 1.5159 -0.67756 248-308 (4)						
2,2,4-Trimethyl- pentane	3.9966 <sup>b</sup> 1.4801 -0.64575 248-308 (4)	3.5839 <sup>b</sup> 1.4883 -0.63944 248-308 (4)						
Benzene	2.5304 <sup>c</sup> 1.9778 -1.4177 280-336 (4)		-7.1941 <sup>c</sup> 2.3282 -1.8506 280-333 (4)		-6.5835 <sup>c</sup> 2.0791 -1.3562 285-333 (4)	-1.2980 <sup>c</sup> 1.9731 -1.0385 286-333 (4)	-26.319 <sup>c</sup> 1.8620 -0.47868 278-323 (10)	-27.795 <sup>c</sup> 2.0142 -0.69728 278-323 (10)
Toluene	8.5169 <sup>b</sup> 1.4524 -0.45898 258-308 (4)	7.5364 <sup>b</sup> 1.4921 -0.50265 258-308 (4)						
Perfluoro- <i>n</i> - heptane	3.6132 <sup>b</sup> 1.4346 -0.83925 248-308 (5)	2.7727 <sup>b</sup> 1.4663 -0.87085 248-308 (5)						
Carbontetra- chloride			-2.0614 <sup>c</sup> 1.7998 -0.90344 253-333 (5)		-5.6792 <sup>c</sup> 1.8964 -1.0207 253-333 (5)	-11.603 <sup>c</sup> 1.7100 -0.52427 253-333 (5)		
Chlorobenzene	6.6911 <sup>c</sup> 1.6036 -0.62048 232-354 (7)		-1.7143 <sup>c</sup> 1.8644 -0.89006 233-353 (7)	-2.2920 <sup>c</sup> 1.6133 -0.39088 273-353 (9)	-5.5612 <sup>c</sup> 1.9301 -0.93664 233-354 (7)	-12.374 <sup>c</sup> 1.8598 -0.70276 232-373 (8)	-29.472 <sup>c</sup> 2.0081 -0.60232 273-353 (17)	-30.794 <sup>c</sup> 2.1771 -0.88068 298-363 (19)
Acetone	6.5848 <sup>c</sup> 1.5948 -0.68569 191-313 (7)		-2.0834 <sup>c</sup> 1.8594 -0.99043 195-314 (7)	-7.0543 <sup>c</sup> 1.9902 -1.1642 195-313 (9)	-6.8504 <sup>c</sup> 2.0068 -1.1891 193-313 (7)	-13.975 <sup>c</sup> 2.0607 -1.1443 197-313 (7)		

<sup>a</sup>In each column the numbers have the following significance: first row,  $A_0' \times 10^{-2}$ ; second row,  $A_1' \times 10^{-1}$ ; third row,  $A_2' \times 10^2$ ; fourth row, temperature range in °K, number in parentheses is the number of data points. <sup>b</sup>M. W. Cook, D. N. Hanson, and B. J. Alder, *J. Chem. Phys.*, **26**, 748 (1957). <sup>c</sup>J. Horvuti, *Sci. Pap. Inst. Phys. Chem. Res., Tokyo*, **17**, 125 (1931).



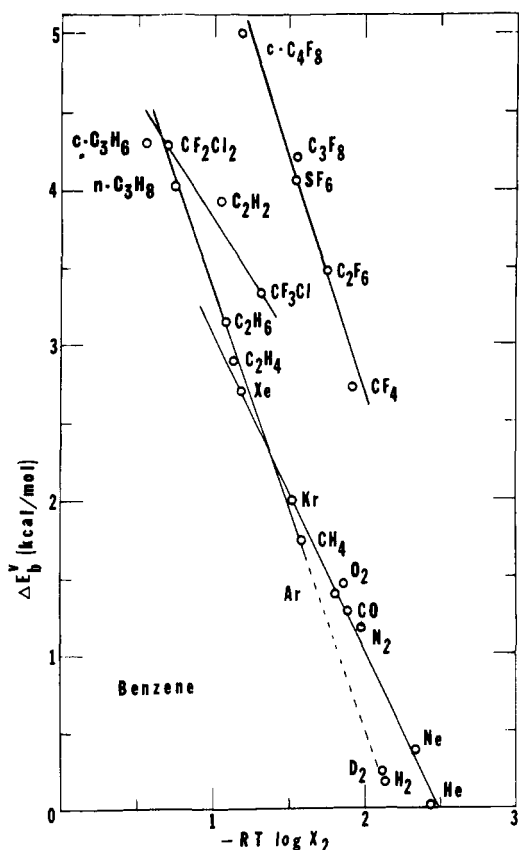


Figure 1. Energy of vaporization of the gas at its normal boiling point against solubility in benzene at 25°C.

### III. Discussion

Many correlations for gas solubilities have been proposed. In almost all of these correlations some function of solubility is plotted against a parameter characteristic of the gas or of the solvent. Three commonly used plots of the former type<sup>9</sup> are  $\log X_2$  vs.  $\epsilon/k$  (Lennard-Jones force parameter),  $\log X_2$  vs.  $\alpha$  (polarizability), and  $-RT \log X_2$  vs.  $\Delta E_b^v$  (energy of vaporization of the gas at its normal boiling point). As has been pointed out by Hildebrand, *et al.*,<sup>4</sup>  $\Delta E_b^v$  as a gas parameter is to be preferred to the others. Figure 1 (benzene) serves as an illustration in which we can distinguish four distinct lines: the permanent gases, hydrocarbon gases, perfluorinated gases, and mixed halogenated gases ( $\text{CF}_3\text{Cl}$  and  $\text{CF}_2\text{Cl}_2$ ). Examples of correlations of the latter type are  $\log X_2$  vs.  $\delta_1$  or  $\delta_1^2$  (Hildebrand solubility parameter; *cf.*, for example, ref 10), and  $\log L$  vs.  $\sigma_1$  (surface tension; *cf.*, for exam-

(9) *Cf.* also H. L. Friedman, *J. Amer. Chem. Soc.*, **76**, 3294 (1954), who gives a relation of the form  $\log X_2 = a + bg$ , where  $a$  and  $b$  depend only on the solvent and  $g$  depends only on the gas.

(10) J. M. Prausnitz and F. H. Shair, *AIChE J.*, **7**, 682 (1961).

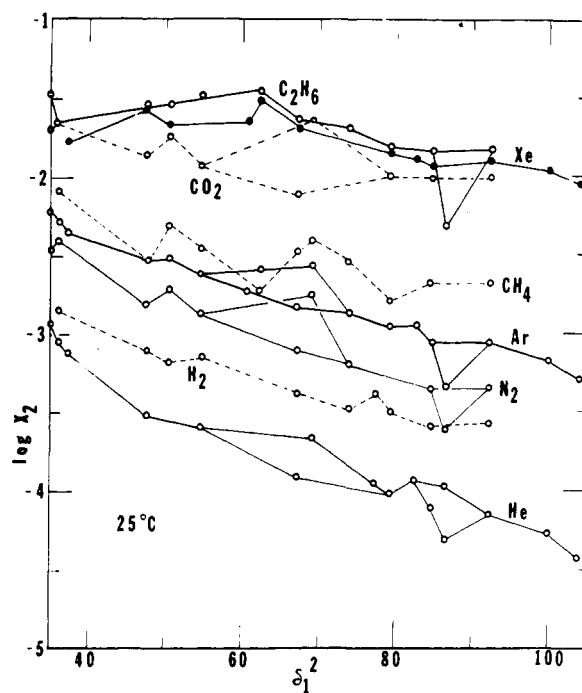


Figure 2. Mole fraction solubility of several gases against Hildebrand solubility parameter squared at 25°C.

ple, ref 11). Figure 2 shows a graph of  $\log X_2$  vs.  $\delta_1^2$  for several gases. All points for a given gas are connected for clarity.

Finally, we want to mention the successful application of the scaled particle theory to gas solubilities as advanced by Reiss, *et al.*,<sup>12</sup> Pierotti,<sup>13</sup> and Wilhelm and Battino.<sup>6,14-16</sup> This theory allows the prediction of solubility and the derived thermodynamic properties  $\Delta \bar{S}^\circ$ ,  $\Delta \bar{H}^\circ$ , etc. It also makes possible the discussion of specific solute-solvent interactions,<sup>6,16,17</sup> *e.g.*, the interaction between  $\text{CO}_2$  and benzene and the resulting enhanced solubility.<sup>16</sup>

In conclusion, we would like to note two things. The first is the excellent chapter on gas solubilities in Hildebrand, Prausnitz, and Scott's new book.<sup>4</sup> The second is to call attention to the many gaps in Table I. Of particular note is the absence of solubility data for He, Ne, Kr, and Xe in carbon tetrachloride.

*Acknowledgment.* The support of the Public Health Service via Grant No. GM 14710-04 is acknowledged.

(11) J. C. Gjaldbaek and H. Niemann, *Acta Chem. Scand.*, **12**, 1015 (1958).

(12) H. Reiss, H. L. Frisch, E. Helfand, and J. L. Lebowitz, *J. Chem. Phys.*, **32**, 119 (1960).

(13) R. A. Pierotti, *J. Phys. Chem.*, **67**, 1840 (1963); **69**, 281 (1965).

(14) R. Battino, F. D. Evans, W. F. Danforth, and E. Wilhelm, *J. Chem. Thermodyn.*, **3**, 743 (1971).

(15) E. Wilhelm and R. Battino, *J. Chem. Thermodyn.*, **3**, 379 (1971).

(16) E. Wilhelm and R. Battino, *J. Chem. Thermodyn.*, **3**, 761 (1971).

(17) E. Wilhelm and R. Battino, *J. Chem. Phys.*, **56**, 563 (1972).