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

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Contents

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[2] since that article contained very little data.

The two principal sources for gas solubility data are Seidell's handbook,[3] which does not contain thermodynamic data, and Appendix 3 in Hildebrand, Scott, and Prausnitz's book,[4] 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.[2] The Ostwald coefficient L is defined as

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

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

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

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

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

B. Calculation of Gas Solubility from Literature Data

Two review articles,[2,5] the literature, and other sources[3,4] were searched for data which were reasonably precise. In general, all the solubility data used were precise to ±1% or better. We limited the choice of solvents to those for which we evaluated[6] 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[7] 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.*

$$-RT \ln X_2 = A_0 + A_1T \qquad (4a)$$

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.

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

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.

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[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^{-1} K^{-1})

Gas	1-He	2-Ne	3-Ar	4-Kr	5-Xe	6-H_2	7-D_2	8-N_2
ϵ/k, K	6.03	34.9	122	158	229	29.2	31.1	95
ΔE_b^v, kcal mol^{-1}	0.017	0.37	1.385	2.00	2.69	0.175	0.247	1.18
1. *n*-Hexane	2.604^{b}	3.699^{b}	25.12^{b}	69.60^{b}	258.7^{c}	6.315^{d}		14.02^{e}
	−9.96	−11.18	−14.06	−13.66	−15.84	−10.55		
	1920	1348	−646	−1130	−2556	1219		
2. *n*-Heptane	2.498^{b}	3.553^{b}	24.87^{b}	71.17^{b}		6.859^{i}	7.014^{i}	13.54^{j}
	−10.29	−11.32	−12.90	−14.25		−11.44	−11.55	
	1846	1330	−292	−1318		904	859	
3. *n*-Octane	2.397^{b}	3.626^{b}	24.26^{b}	70.66^{b}		6.845^{i}	7.003^{i}	13.04^{j}
	−10.10	−10.18	−12.25	−13.85		−11.24	−11.39	
	1926	1659	−85	−1194		965	908	
4. *n*-Nonane	2.357^{b}	3.429^{b}	24.89^{b}	71.22^{b}		6.922^{j}		12.81^{j}
	−8.83	−10.81	−13.09	−13.55				
	2316	1503	−349	−1109				
5. *n*-Decane	2.309^{b}	3.491^{b}	25.09^{b}	71.93^{b}				
	−10.42	−10.67	−13.08	−13.71				
	1853	1534	−352	−1165				
6. *n*-Dodecane	2.223^{b}	3.127^{b}	25.66^{b}	75.54^{b}	307.2^{c}			
	−10.94	−10.45	−12.37	−13.12	−14.47			
	1723	1666	−153	−1016	−2251			
7. *n*-Tetradecane	2.249^{b}	3.340^{b}	26.50^{b}	80.10^{b}				
	−11.97	−11.19	−12.97	−13.86				
	1408	1406	−352	−1272				
8. 3-Methylheptane	2.495^{b}	3.743^{b}	24.71^{b}	71.06^{b}				
	−10.23	−11.22	−11.82	−12.94				
	1866	1329	34	−926				
9. 2,3-Dimethylhexane	2.497^{b}	3.616^{b}	24.95^{b}	70.78^{b}				
	−10.82	−11.05	−13.24	−13.07				
	1688	1399	−396	−965				
10. 2,4-Dimethylhexane	2.740^{b}	3.974^{b}	26.84^{b}	73.43^{b}				
	−8.86	−11.25	−12.73	−12.94				
	2219	1284	−287	−946				
11. 2,2,4-Trimethylpentane	3.083^{b}	4.593^{b}	29.21^{b}	79.27^{b}	273.5^{c}	7.832^{i}	7.981^{i}	15.39^{o}
	−9.92	−11.66	−13.41	−13.99	−15.61	−11.21	−11.33	−12.25
	1833	1078	−542	−1304	−2522	895	849	186
12. Cyclohexane	1.217^{b}	1.792^{b}	14.80^{b}	46.68^{b}	202.9^{c}	4.142^{r}		7.61^{s}
	−9.79	−12.24	−13.68	−13.45	−14.76	−11.32		−12.6
	2421	1461	−218	−831	−2091	1240		511
13. Methylcyclohexane	1.625^{t}	2.306^{t}	18.41^{t}	57.28^{t}	227.1^{t}			9.46^{u}
	−9.44	−10.04	−13.46	−14.73	−14.38			−12.09
	2356	1969	−283	−1335	−2045			520
14. Benzene	0.771^{b}	1.118^{b}	8.815^{b}	27.39^{b}	116.6^{c}	2.580^{i}	2.656^{i}	4.461^{v}
	−10.79	−8.07	−12.98	−13.17	−14.53	−11.32	−11.41	−11.92
	2396	2984	297	−431	−1695	1519	1478	1016
15. Toluene	0.974^{w}	1.402^{w}	10.86^{w}	33.46^{w}	146.1^{w}	3.171^{i}	3.271^{i}	5.74^{u}
	−10.01	−11.03	−12.78	−14.31	−15.03	−11.92	−12.07	−9.88
	2487	1968	232	−889	−1976	1218	1155	1475
16. *m*-Xylene	1.121^{x}	1.619^{x}				4.153^{x}		
	−9.96	−9.28				−11.44		
	2420	2403				1203		
17. Perfluoro-*n*-heptane	8.862^{p}		53.22^{aa}			14.03^{i}	14.45^{i}	38.80^{e}
	−8.26					−9.68	−9.83	−11.59
	1703					1005	945	−165

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

9-O_2 118 1.45	10-CO 100 1.28	11-CO_2 195	12-CH_4 157 1.73	13-C_2H_6 236 3.15	14-C_2H_4 230 2.90	15-CF_4 134 2.72	16-SF_6 201 (4.08)	Solvent[a] V_1^0 δ_1^2 σ
19.3[f]			50.37[g] −12.32 −539	320[h]	229.5[d] −13.48 −1782			131.62 53.3 17.90
21.66[j]	17.24[k]	120.2[l] −16.53 −2309	34.53[m] −14.30 −906	319.6[h] −15.78 −2666		21.50[n] −13.48 −381	101.3[n] −15.75 −1977	147.46 54.8 19.80
20.83[j]			29.27[m] −14.84 −970	342.5[j]		19.66[15] −12.45 −21	95.88[15] −15.92 −1993	163.54 56.3 21.25
21.12[j]				342.0[j]				179.70 59.3 22.40
								195.94 59.3 23.40
			18.42[m] −15.68 −945	351[h]				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[p] −12.94 −378		138.7[q] −16.02 −2241	29.66[m] −14.59 −901	292.6[p] −17.13 −3014		29.09[n] −13.78 −648	153.0[p] −15.60 −2174	166.10 47.6 18.40
12.48[s] −13.1 58	9.91[s] −13.1 202	76.0[s] −14.1 −1327	32.75[g] −13.34 −588	235.9[r] −16.24 −2621		10.34[n] −13.26 119	54.19[n] −14.99 −1377	108.75 67.2 24.50
15.99[u] −14.04 224	12.41[u] −13.52 −66	92.8[u] −17.52 −2451	39.6[u] −15.01 −1197			13.71[u] −11.77 397	70.51[n] −15.59 −1713	128,35 60.8 23.29
8.165[v] −12.76 409	6.680[v] −12.40 635	97.30[l] −16.69 −2230	20.77[v] −13.30 −305	148.7[v] −15.74 −2200	123.3[v] −15.95 −2151	5.748[n] −13.02 540	26.38[n] −14.41 −778	89.41 84.6 28.25
9.09[u] −14.44 −143	8.11[u] −12.64 447	101.3[u] −17.56 −2515	24.14[u] −16.05 −1214	154.1[d] −15.44 −2130	146.3[d] −15.43 −2096	6.93[u] −9.67 1427	33.73[n] −15.56 −1266	106.86 79.2 27.94
11.96[y]					138.7[z] −17.57 −2703			123.47 77.4 28.33
55.08[k]	38.75[k]	208.2[p] −14.77 −2111	82.56[p] −12.95 −1019	210.2[j,aa]			222.6[p] −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_2	7-D_2	8-N_2
ϵ/k, K	6.03	34.9	122	158	229	29.2	31.1	95
ΔE_b^v, kcal mol^{-1}	0.017	0.37	1.385	2.00	2.69	0.175	0.247	1.18
18. Perfluoromethylcyclohexane	7.498^{t} −10.85 1028	11.25^{t} −10.71 829	44.65^{t} −12.54 −532	84.82^{t} −12.89 −1016	169.4^{t} −14.07 −1778			32.66^{e}
19. Perfluorobenzene	2.137^{cc} −1.55 4544	3.455^{cc} −6.31 2841	23.98^{cc} −13.06 −318	59.00^{cc} −13.47 −974				17.95^{cc} −12.60 −10
20. $(C_4F_9)_3N$	11.67^{4}	16.79^{4}	61.0^{4}	111.2^{4}				34.90^{p} −11.76 −153
21. CCl_4			13.51^{ee} −13.47 −103			3.349^{i} −11.41 1340	3.284^{i} −11.62 1287	6.480^{v} −12.70 564
22. 1,1,2,2-Tetrachloroethane	1.079^{x} −11.48 1989	1.495^{x} −10.85 1984				4.059^{x} −12.77 818		
23. 1,1,2-Trichloro-1,2,2-trifluoroethane		4.848^{ff} −11.03 1233	30.95^{q} −13.10 −481		214.7^{ff} −14.90 −2166	6.572^{ff} −10.60 1181		19.58^{q} −11.96 128
24. Fluorobenzene	1.144^{w} −11.69 1890	1.575^{w} −11.60 1730	11.48^{w} −13.57 −35	33.22^{w} −13.92 −770	130.3^{w} −14.87 −1863			
25. Chlorobenzene	0.691^{w} −11.00 2397	0.979^{w} −10.63 2299	8.609^{w} −13.66 107	27.26^{w} −14.18 −730	123.2^{w} −15.71 −2078	2.609^{v} −12.40 1192		4.377^{v} −13.42 581
26. Bromobenzene	0.536^{w} −10.57 2675	0.787^{w} −12.06 2002	6.800^{w} −13.74 223	22.78^{w} −14.53 −726	108.2^{w} −15.04 −1802			
27. Iodobenzene	0.373^{w} −9.54 3196	0.525^{w} −11.17 2507	5.011^{w} −12.97 636	16.84^{w} −14.10 −421	88.10^{w} −15.01 −1673			
28. Nitromethane	0.386^{hh}	0.541^{hh}	3.198^{hh}	8.376^{hh}	25.09^{hh}			2.007^{hh}
29. Nitrobenzene	0.350^{w} −9.52 3240	0.436^{w} −9.35 3162	4.448^{w} −13.47 557	13.83^{w} −13.41 −97	58.38^{w} −14.36 −1233			
30. Methanol	0.595^{jj} −13.24 1817	0.814^{jj} −14.88 1143	4.491^{jj} −16.01 −206					2.747^{o} −15.89 120
31. Ethanol	0.769^{jj} −13.01 1733	1.081^{jj} −13.42 1408	6.231^{jj} −14.97 −92			2.067^{nn} −13.87 891		3.593^{o} −15.40 109
32. 2-Methyl-1-propanol (isobutyl alcohol)	1.015^{14} −14.34 1172	1.527^{14} −14.10 1001	9.518^{14} −15.43 −478	25.49^{14} −16.74 −1453				4.837^{14} −15.33 −48
33. Cyclohexanol	0.473^{jj} −10.53 2761	0.718^{jj} −12.25 2001	5.299^{jj} −13.55 430			1.689^{oo}		2.655^{11}
34. Acetone	1.081^{jj} −8.93 2747	1.577^{jj} −9.33 2405	9.067^{jj} −12.38 461			2.996^{v} −12.49 1084		5.395^{v} −13.56 417

9-O_2 118 1.45	10-CO 100 1.28	11-CO_2 195	12-CH_4 157 1.73	13-C_2H_6 236 3.15	14-C_2H_4 230 2.90	15-CF_4 134 2.72	16-SF_6 201 (4.08)	Solvent[a] V_1^0 δ_1^2 σ
						106.1[bb]		195.88
						−14.81		37.2
						−1722		15.20
24.18[cc]	21.2[cc]	220[cc]	38.42[cc]			45.61[cc]		115.79
−12.81			−13.25			−14.33		68.9
−250			−656			−1078		21.80
52.01[p]		199.0[p]	68.8[4]	332.6[p]			729.3[q]	358.49
−12.31		−14.63		−15.18			−16.17	34.8
−553		−2041		−2510			−3270	19.35P[dd]
12.01[v]	8.763[v]	105.3[l,v]	28.70[v]	208.2[v]	145.0[v]	11.84[n]	65.31[n]	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[q]	50.47[q]	286.1[ff]		48.17[n]	297.3[q]	119.84
		−16.71	−13.28	−15.46		−14.05	−15.57	50.4
		−2611	−827	−2503		−1027	−2559	21.28P
15.08[y]								94.31
								82.8
								26.87
7.910[v]	6.468[v]	98.06[gg]	20.47[v]	146.5[v]	118.9[v]			102.27
−13.68	−13.81		−14.34	−16.31	−16.17			92.2
152	232		−609	−2360	−2195			32.58
7.48[y]								105.51
								100.0
								35.72
5.10[y]								111.91
								104.0
								37.70
							8.310[hh]	53.96
								(154.3)[ii]
								36.7
4.95[y]	3.724[gg]	99.80[gg]						102.72
								(117.9)
								43.75
4.147[o]	3.761[kk]	55.78[ll]	8.695[g]	38.81[mm]	43.60[mm]			40.73
−16.24	−15.14	−18.88	−16.90					(210.3)
−229	157	−2555	−862					22.12
5.841[o]	4.843[kk]	63.66[ll]	12.80[g]	68.37[mm]	61.03[mm]			58.68
−15.77	−14.89	−20.30	−16.31					(163.8)
−291	84	−3056	−915					21.88
8.397[14]	6.524[14]	69.63[14]						92.88
−15.83	−15.72	−18.36						(118.8)
−522	−341	−2530						22.55
		44.28[pp]	12.55[g]	82.02[11]				105.94
		−17.89	−15.53					
		−2124	−673					33.96
8.383[v]	7.719[v]	185.3[ll]	18.35[v]	96.29[v]	109.1[v]			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_2	7-D_2	8-N_2
ϵ/k, K	6.03	34.9	122	158	229	29.2	31.1	95
ΔE_b^v, kcal mol^{-1}	0.017	0.37	1.385	2.00	2.69	0.175	0.247	1.18
35. *N*-Methyl-	0.491^{qq}		4.434^{qq}					2.396^{qq}
acetamide	−12.02		−15.12					−14.93
	2296		67					488
36. Hydrazine	0.05227^{rr}		0.1239^{rr}					0.07254^{rr}
	−19.93		−15.60					−15.60
	1264		2043					2361
37. Methyl-	0.252^{rr}		1.784^{rr}					0.920^{rr}
hydrazine	−14.68		−14.98					−14.71
	1897		648					1121
38. Dimethyl-	0.934^{rr}		6.858^{rr}					3.735^{rr}
hydrazine	−11.37		−13.68					−13.00
	2107		239					800
39. Dimethyl sulfoxide	0.284^{r}	0.368^{r}	1.54^{r}	4.46^{r}	17.0^{r}	0.761^{r}	0.799^{r}	0.833^{r}

[a] Solvent properties: first line, molar volume V_1^0 (cm^3 mol^{-1}); second line, Hildebrand solubility parameter δ_1^2 (cal cm^{-3}); third line, surface tension σ_1 (dynes cm^{-2}). [b] H. L. Clever, R. Battino, J. H. Saylor, and P. M. Gross, *J. Phys. Chem.*, **61**, 1078 (1957). [c] H. L. Clever, *ibid.*, **62**, 375 (1958). [d] J. A. Waters, G. A. Mortimer, and H. E. Clements, *J. Chem. Eng. Data*, **15**, 174 (1970). [e] J. C. Gjaldbaek and J. H. Hildebrand, *J. Amer. Chem. Soc.*, 71, 3147 (1949). [f] D. Guerry, Ph.D. Thesis, Vanderbilt University, Nashville, Tenn., 1944. [g] A. Lannung and J. C. Gjaldbaek, *Acta Chem. Scand.*, **14**, 1124 (1960). [h] W. Hayduk and S. C. Cheng, *Can. J. Chem. Eng.*, **48**, 93 (1970). [i] M. W. Cook, D. N. Hanson, and B. J. Alder, *J. Chem. Phys.*, **26**, 748 (1957). [j] E. S. Thomsen and J. C. Gjaldbaek, *Acta Chem. Scand.*, 17, 127 (1963). [k] J. C. Gjaldbaek, *ibid.*, **6**, 623 (1952). [l] J. C. Gjaldbaek, *ibid.*, 7, 534 (1953). [m] K. Onda, E. Sada, and S. Shinno, *Kogyo Kagaku Zasshi*, **61**, 702 (1958). [n] G. Archer and J. H. Hildebrand, *J. Phys. Chem.*, **67**, 1830 (1963). [o] C. B. Kretschmer, J. Nowakowska, and R. Wiebe, *Ind. Eng. Chem.*, **38**, 506 (1946). [p] Y. Kobatake and J. H. Hildebrand, *J. Phys. Chem.*, **65**, 331 (1961). [q] H. Hiraoka and J. H. Hildebrand, *ibid.*, **68**, 213 (1964). [r] J. H. Dymond, *ibid.*, 71, 1829 (1967). [s] E. Wilhelm and R. Battino, to be published. [t] H. L. Clever, J. H. Saylor, and P. M. Gross, *J. Phys. Chem.*, **62**, 89 (1958). [u] L. Field, R. Battino, and E. Wilhelm, to be published. [v] J. Horiuti, *Sci.*

TABLE II. Solubility of Some Fluorocarbon Gases in Several Solvents[a]

Gas	CF_4	C_2F_6	C_3F_8	*c*-C_4F_8	SF_6	CF_3Cl	CF_2Cl_2
ϵ/k, K	134	255	266	223	201	222	286
ΔE_b^v, kcal/mol	2.72	3.47	4.22	5.00	(4.08)	3.33	4.29
n-Heptane	21.50^{b}				101.3^{b}	167.5^{c}	1252^{c}
	−13.48				−15.75	−18.4	−19.3
	−381				−1977	−3070	−4520
n-Octane	19.66^{c}				95.88^{c}	162.5^{c}	1296^{c}
	−12.45				−15.92	−15.7	−17.8
	−21				−1993	−2250	−4080
Cyclohexane	10.34^{b}	24.46^{d}	60.90^{d}	216.6^{d}	54.19^{b}	99.6^{c}	939^{c}
	−13.26	−13.47	−15.23	−16.72	−14.99	−16.5	−20.5
	119	−452	−1519	−2715	−1377	−2220	−4720
Benzene	5.748^{b}	11.1^{e}	24.4^{e}	100^{e}	26.38^{b}	60.9^{c}	717^{c}
	−13.02				−14.41	−14.2	−20.1
	540				−778	−1200	−4440
Perfluorobenzene	45.61^{e}	155^{e}	520^{e}				
	−14.33						
	−1078						
$(C_4F_9)_3N$			1497^{f}		729.3^{g}		
					−16.17		
					−3270		
CCl_4	11.84^{b}				65.31^{b}	108.5^{c}	1016^{c}
	−12.92				−15.57	−17.5	−22.2
	141				−1662	−2540	−5260
CCl_2FCClF_2	48.17^{b}	150.3^{h}			275.3^{g}		
	−14.05	−15.58			−16.81		
	−1027	−2159			−2883		

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

9-O_2	10-CO	11-CO_2	12-CH_4	13-C_2H_6	14-C_2H_4	15-CF_4	16-SF_6	Solvent[a] V_1^0
118	100	195	157	236	230	134	201	δ_1^2
1.45	1.28		1.73	3.15	2.90	2.72	(4.08)	σ
				47.45[qq]				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[r]		90.8[r]	3.86[r]	17.8[r]				71.37
								(163.1)
								42.86

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C. Choice of Standard States and Calculation of Thermodynamic Functions

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

$$\mathrm{Y(gas,\ hyp\ 1\ atm)} \longrightarrow \mathrm{Y(solution,\ hyp}\ X_2 = 1) \qquad (5)$$

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

$$\Delta\bar{G}° \cong -RT \ln X_2(\mathrm{sat}) \qquad (6)$$

where X_2(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 nonideality of the mixture of gaseous Y and the solvent vapor. Subject to the same approximation we also have (*cf.* also Sherwood and Prausnitz[8])

$$\Delta\bar{H}° = RT\left(\frac{\partial \ln X_2(\mathrm{sat})}{\partial \ln T}\right) \qquad (7)$$

$$\Delta\bar{S}° = R\left[\left(\frac{\partial \ln X_2(\mathrm{sat})}{\partial \ln T}\right) + \ln X_2(\mathrm{sat})\right] \qquad (8)$$

In Tables I and II we give the data for 10^4X_2(sat) and for the approximate values of $\Delta\bar{H}°$ and $\Delta\bar{S}°$ (all at 298.15 K and 1 atm partial pressure of gas) obtained from the experimental results by application of eq 7 and 8, respectively. 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 $\Delta\bar{S}° = -A$ and $\Delta\bar{H}° = A_0$. Then $\Delta\bar{G}°$ may be calculated from the tables *via* $\Delta\bar{G}° = \Delta\bar{H}° - T\Delta\bar{S}°$. For not too large temperature intervals where $\Delta\bar{H}°$ can be regarded as being constant, the mole fraction $X_2(T_2)$ at a temperature T_2 may be calculated from

$$\ln X_2(T_2) - \ln X_2(298.15) = \frac{\Delta H°}{R}\left(\frac{T_2 - 298.15}{298.15T_2}\right) \qquad (9)$$

with reasonable accuracy.

The Hildebrand[4] entropy of solution is given by (same approximations as above)

$$\Delta\bar{S}_{\mathrm{H}} = R(\partial \ln X_2/\partial \ln T)_{\mathrm{sat,P}} \qquad (10)$$

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

$$\Delta\bar{S}° = \Delta\bar{S}_{\mathrm{H}} + R \ln X_2 \qquad (11)$$

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

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

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

	H_2	D_2	N_2	O_2	CO	CH_4	C_2H_6	C_2H_4
n-Heptane	−0.59385[b]	−1.1870[b]						
	1.8550	1.8765						
	−1.3007	−1.3208						
	238–308 (7)	238–308 (7)						
n-Octane	5.6235[b]	3.8755[b]						
	1.4161	1.5159						
	−0.52484	−0.67756						
	248–308 (4)	248–308 (4)						
2,2,4-Trimethylpentane	3.9966[b]	3.5839[b]						
	1.4801	1.4883						
	−0.64575	−0.63944						
	248–308 (4)	248–308 (4)						
Benzene	2.5304[c]		−7.1941[c]		−6.5835[c]	−1.2980[c]	−26.319[c]	−27.795[c]
	1.9778		2.3282		2.0791	1.9731	1.8620	2.0142
	−1.4177		−1.8506		−1.3562	−1.0385	−0.47868	−0.69728
	280–336 (4)		280–333 (4)		285–333 (4)	286–333 (4)	278–323 (10)	278–323 (10)
Toluene	8.5169[b]	7.5364[b]						
	1.4524	1.4921						
	−0.45898	−0.50265						
	258–308 (4)	258–308 (4)						
Perfluoro-*n*-heptane	3.6132[b]	2.7727[b]						
	1.4346	1.4663						
	−0.83925	−0.87085						
	248–308 (5)	248–308 (5)						
Carbontetrachloride			−2.0614[c]		−5.6792[c]	−11.603[c]		
			1.7998		1.8964	1.7100		
			−0.90344		−1.0207	−0.52427		
			253–333 (5)		253–333 (5)	253–333 (5)		
Chlorobenzene	6.6911[c]		−1.7143[c]	−2.2920[c]	−5.5612[c]	−12.374[c]	−29.472[c]	−30.794[c]
	1.6036		1.8644	1.6133	1.9301	1.8598	2.0081	2.1771
	−0.62048		−0.89006	−0.39088	−0.93664	−0.70276	−0.60232	−0.88068
	232–354 (7)		233–353 (7)	273–353 (9)	233–354 (7)	232–373 (8)	273–353 (17)	298–363 (19)
Acetone	6.5848[c]		−2.0834[c]	−7.0543[c]	−6.8504[c]	−13.975[c]		
	1.5948		1.8594	1.9902	2.0068	2.0607		
	−0.68569		−0.99043	−1.1642	−1.1891	−1.1443		
	191–313 (7)		195–314 (7)	195–313 (9)	193–313 (7)	197–313 (7)		

[a] 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. [b] M. W. Cook, D. N. Hanson, and B. J. Alder, *J. Chem. Phys.*, **26**, 748 (1957). [c] J. Horiuti, *Sci. Pap. Inst. Phys. Chem. Res., Tokyo*, 17, 125 (1931).

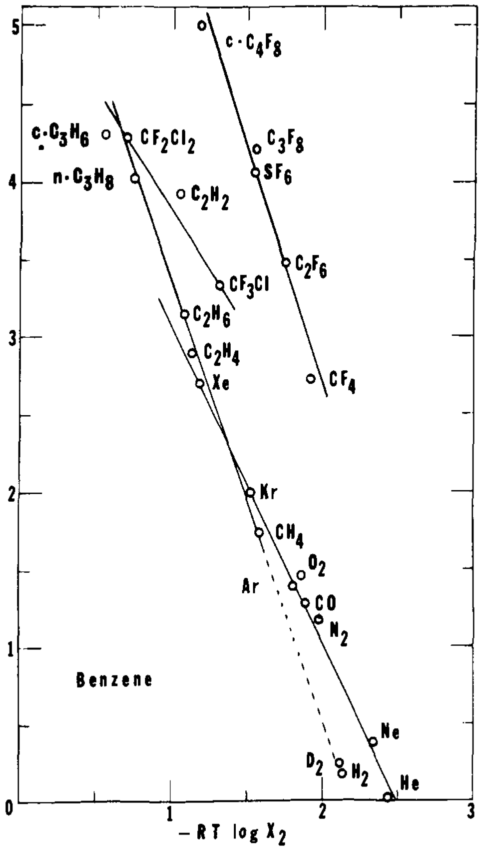

Figure 1. Energy of vaporization of the gas at its normal boiling point against solubility in benzene at 25°C.

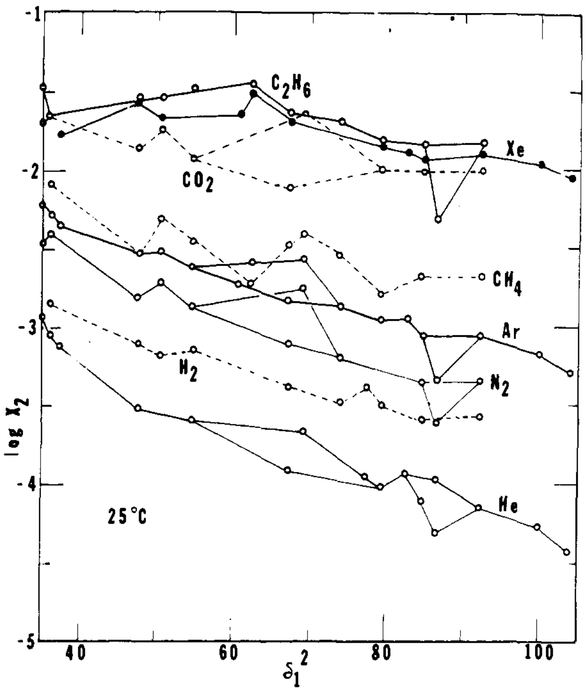

Figure 2. Mole fraction solubility of several gases against Hildebrand solubility parameter squared at 25°C.

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[9] are log X_2 vs. ϵ/k (Lennard-Jones force parameter), log X_2 vs. α (polarizability), and $-RT$ log X_2 vs. ΔE_b^v (energy of vaporization of the gas at its normal boiling point). As has been pointed out by Hildebrand, *et al.*,[4] ΔE_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 (CF_3Cl and CF_2Cl_2). Examples of correlations of the latter type are log X_2 vs. δ_1 or δ_1^2 (Hildebrand solubility parameter; *cf.*, for example, ref 10), and log L vs. σ_1 (surface tension; *cf.*, for example, ref 11). Figure 2 shows a graph of log X_2 vs. δ_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.*,[12] Pierotti,[13] and Wilhelm and Battino.[6,14-16] This theory allows the prediction of solubility and the derived thermodynamic properties $\Delta\bar{S}°$, $\Delta\bar{H}°$, etc. It also makes possible the discussion of specific solute-solvent interactions,[6,16,17] *e.g.*, the interaction between CO_2 and benzene and the resulting enhanced solubility.[16]

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.[4] 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.

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[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.

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

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