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Free Energies, Enthalpies, and Entropies of Solution of Gaseous Nonpolar Nonelectrolytes in Water and Nonaqueous Solvents. The Hydrophobic Effect

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Abstract: Values of the standard free energy, enthalpy, and entropy of solution of a large number of gaseous nonpolar nonelectrolytes in a wide range of nonaqueous solvents and in water have been tabulated. For solution in nonaqueous solvents, all the results may be correlated through equations of type $\Delta P°_s = lR + d$ where $P = G$, H, and S, R is a parameter characteristic of the solute, and l and d characterize the solvent. These equations reproduce 489 $\Delta G°_s$ values to within 0.08 kcal mol^{-1} and 280 $\Delta H°_s$ and $T\Delta S°_s$ values each to within 0.35 kcal mol^{-1}. The parameters for solution of the rare gases and the inorganic gases H_2, N_2, CO, and O_2 in water are also well correlated by the linear equations. From an analysis of $\Delta G°_s$, $\Delta H°_s$, and $\Delta S°_s$ values for *n*-alkanes, the methylene contribution to the processes alkane (gas) → alkane (solvent) and alkane (solvent) → alkane (water) has been obtained for transfers involving 10 nonaqueous solvents. It is shown that both the transfer processes are enthalpy dominated. Through use of the "rare gas lines" as a standard, the methylene increment for alkane (gas) → alkane (water) has been factored to yield a hydrophobic increment of 0.54 kcal mol^{-1} in $\Delta G°$, 0.30–0.44 kcal mol^{-1} in $\Delta H°$, and 0.10–0.24 kcal mol^{-1} in $-T\Delta S°$. It is concluded that the hydrophobic effect of a methylene group in *n*-alkanes is primarily an enthalpic effect that arises through a more endothermic methylene/water interaction than expected. It is also shown that entropic effects of flexible alkanes on their entropies of solution are small and comparatively unimportant. The hydrophobic effect of a methyl group in *n*-alkanes has similarly been estimated as 0.33 kcal mol^{-1} in $\Delta G°$, this being totally an entropic effect, with $-T\Delta S° \simeq 0.33$ kcal mol^{-1}.

A knowledge of the thermodynamic parameters for solution of gaseous nonelectrolytes is essential for any quantitative discussion of the so-called hydrophobic effect. Many workers have analyzed this effect, especially the increment due to the methylene unit, in terms of free energies of solution,[1-9] but there have been but few analyses using enthalpies or entropies of solution.[10-12] It has been suggested[13-15] that water restricts the motion of flexible molecules and that this effect is the main contributor to the entropy change that takes place on solution of such solutes. Wertz,[16] however, has put forward the interesting postulate that all molecules, not just flexible molecules, lose the same fraction of their entropy on dissolution in water and that this loss of entropy is due to loss of internal and external degrees of freedom of the solute. According to Wertz,[16] changes in the entropy of the solvent water contribute little to the observed entropy of solution. On the other hand, Berendson et al.[17] have concluded from dielectric relaxation measurements on alcohols in water that the solute itself makes a positive contribution to the entropy of solution and that this effect is outweighed by a very large negative contribution by the water solvent molecules—a conclusion diametrically opposed to that of Wertz.[16] Pratt and Chandler[18,19] have applied their microscopic theory of solvation to hydrophobic solutes in water and hydrocarbon solvents; since the theory deals with solute–solvent and solvent–solvent functions, it seems also to be incompatible with the proposition of Wertz. Pratt and Chandler[18] took into account the nonrigidity of the higher *n*-alkanes and concluded that these molecules are actually stabilized in water by about 2 cal K^{-1} mol^{-1}

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for *n*-butane and 8 cal K^{-1} mol^{-1} for *n*-octane as compared to a rigid molecule. This result is quite opposite to the suggestion[14] that the solution of flexible (nonrigid) molecules in water is characterized by extra negative entropies of solution. For transfer of *n*-alkanes from a hydrocarbon solvent to water, Pratt and Chandler[18,19] calculated that there was considerable cancellation of the nonrigid effect so that values of ΔS°_t or ΔG°_t are not greatly affected by the flexibility of the solute molecule (cf. the opposite conclusion by Osinga[15]). There is, therefore, little agreement as to the origin or nature of the entropic effects that arise on dissolution of gaseous nonelectrolytes in, especially, water, and it seemed timely to analyze entropies of solution, ΔS°_s, by the method used previously for free energies.[9]

It should be noted that values of ΔS°_s depend on the standard states adopted. Thus an observation that ΔS°_s may have some particular value cannot by itself be used to deduce anything about loss of degrees of freedom, etc., simply because by changing the standard states ΔS°_s may take any value (positive or negative). Even the stratagem of choosing standard states that correspond to the same (nominal) value in gas and solution, e.g., 1 mol dm^{-3} in each phase, does not resolve the problem, because it is not clear what loss of solute translational freedom arises due to restriction of the solute particle to the solvent free volume or solvent fluxional volume.[20] In the present work, standard states adopted will be 1-atm gas and unit mole fraction solution so that ΔG°_s, ΔH°_s, and ΔS°_s in kcal mol^{-1} or cal K^{-1} mol^{-1} refer to the process

$$\text{solute (ideal gas, 1 atm)} \rightarrow \text{solute (ideal solution, unit mole fraction)} \quad (1)$$

In order to avoid the difficulty of the dependence of ΔS°_s or ΔG°_s on the standard states, only comparisons will be made. Thus for solution in a given solvent [ΔS°_s for solute A − ΔS°_s for solute B] is a constant, no matter what the standard states are.

Standard Free Energy of Solution of Gaseous Solutes. It was shown previously[9] that ΔG°_s values for rare gases and alkanes in nonaqueous solvents could be correlated through eq 2. The

$$\Delta G^\circ_s \text{ (in solvent)} = lR_G + d \quad (2)$$

parameter R_G is characteristic of a given solute,[21] and *l* and *d* characterize a given solvent. Other inert solutes such as the inorganic gases H_2, N_2, CO, and O_2 as well as CF_4 and SF_6 can also be included in the correlations, and since further results are available for other solutes,[22-25] it seemed useful to collect all the data and to process the results through eq 2. Values of ΔG°_s are in Table I; unless otherwise stated, they have been taken from recent compilations,[9,26-29] supplemented by data from Seidell.[30] Values of R_G are in Table II,[31] and the analysis of the R_G values through eq 2 is in Table III wherein are given *l*, *d*, *σy*, and the correlation constant *ρ*. The corresponding *t* values or confidence limits have not been listed in Table III because the latter are all greater than 99.9999%. There are a few differences from the previous compilation.[9] The new ΔG°_s values in 1-octanol are derived from direct measurements and are not taken from partition experiments. More importantly, the extended results for ethylene glycol now show that this solvent is well behaved and that there are no anomalous ΔG°_s values in ethylene glycol.

The inorganic gases and also CF_4 and SF_6 conform to eq 2 so that for the nonaqueous solvents in Table I there are 489 ΔG°_s values in the 31 solvents that are correlated through eq 2. For all these 489 values, eq 2 reproduces the observed ΔG°_s values with an average deviation of no more than 0.08 kcal mol^{-1}, corresponding to 0.06 units in log K^H (where K^H is Henry's law constant).

Values of ΔG°_s in water are in Table IV. For the rare gases, the inorganic gases, CF_4, SF_6, the alkanes up to *n*-butane, and Me_4C, the ΔG°_s values as well as the enthalpy and entropy of solution have been taken from the critical review of Wilhelm, Battino, and Wilcock.[32] For the *n*-alkanes, pentane to octane, in water, solubilities recorded by Hine and Mookerjee[33] and Rytting et al.[7] and those determined by Rudakov and Lutsyk[34] and Nelson and de Ligny[35] are all in good agreement, and values of ΔG°_s calculated from the solubilities are in Table IV. The corresponding ΔH°_s and ΔS°_s values are subject to greater uncertainty: for *n*-pentane and *n*-hexane I have taken average values from several sets of workers,[35-37] while for *n*-heptane and *n*-octane I have used those obtained by Nelson and de Ligny.[35] For the remaining solutes, ΔG°_s values are known for cyclopentane,[33] tetramethyltin,[22] cyclohexane,[33,34] and Et_4C,[9] but only for cyclohexane has a value of ΔH°_s, and hence ΔS°_s, been determined.[36,37] Abraham and Nasehzadeh[22] have estimated these values for tetramethyltin and Et_4C, but these estimates must be viewed with caution. Recent work on CF_4 in water[38] has confirmed the parameters listed before.[32]

Comparison of ΔG°_s values for the rare gases and inorganic gases in water and in the nonaqueous solvents shows clearly that no special effect whatsoever is required to interpret these ΔG°_s values in water. For example, ΔG°_s for argon, or the solubility of argon (Table V), gradually varies along a series of hydroxylic solvents such that greater the cohesive energy (i.e., the solvent–solvent forces) the less the solubility, exactly as expected. The actual solubility of argon in water is less than in ethylene glycol by a factor of only 3.4 (Table V), whereas the equivalent factor for *n*-heptane solute is about 1800. Thus if no special (i.e., hydrophobic) effect is needed to account for the rare gas and inorganic gas ΔG°_s values in water, then by the principle of Occam's razor,[39] there are no grounds for assuming such an effect.

Standard Enthalpy and Entropy of Solution of Gaseous Solutes. Values of ΔH°_s and ΔS°_s for solution in water are in Table IV and for solution in a number of nonaqueous solvents are in Table VI. Most of the data in Table VI for the rare gases, the inorganic gases, CF_4, SF_6, and the alkanes up to *n*-butane are from literature compilations,[26-29] supplemented by values calculated from recorded solubilities.[30] For the lower alkanes, ΔH°_s values have been reported by Jadot,[40-42] Battino and Marsh,[43] and Kretschmer and Wiebe.[44] In the case of solutes that are liquid at room tem-

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Table I. Standard Free Energies of Solution of Gaseous Solutes (kcal mol^{-1}) at 298 K[a]

solvent	He	Ne	Ar	Kr	Xe	Rn	H_2	N_2	CO	O_2	CH_4	C_2H_6	C_3H_8	$i\text{-}C_4H_{10}$	$n\text{-}C_4H_{10}$	$n\text{-}C_5H_{12}$	$n\text{-}C_6H_{14}$	$n\text{-}C_7H_{16}$	$n\text{-}C_8H_{18}$[b]	CF_4	SF_6	Me_4C	$cy\text{-}C_5H_{10}$	Me_4Sn[c]	$cy\text{-}C_6H_{12}$	Et_4C	Et_4Sn[d]	Et_4Pb[d]
hexadecane[e]	4.97	4.76	3.53	2.76	2.21		4.18				3.05	1.96	1.19	0.75	0.41	−0.28	−1.04	−1.72							−1.36		−3.84	
decane	4.94	4.72	3.55	2.91	2.19			3.98	3.78	3.63	3.11	1.97	1.16	0.63	0.42	−0.25	−0.98	−1.68	−2.53	3.72	2.81				−1.26			
hexane	4.89	4.67	3.54	2.94	2.16	1.55	4.37	3.89	3.77	3.70	3.14	2.06	1.30	0.76	0.55	−0.20	−0.96	−1.66	−2.36	3.64	2.72	0.32[f]	−0.60	−1.04	−1.33			
OMCTS[g]	4.45	4.14	3.16	2.60			3.89	3.54	3.39	3.23	2.76	1.74	1.05	0.62	0.43	−0.34	−1.00	−1.65	−2.30	3.29	2.34		−0.69		−1.28			
cyclohexane	5.34	5.13	3.86	3.18	2.30		4.61	4.25	4.10	3.96	3.39	2.22	1.40	0.88	0.56	−0.10	−0.87	−1.61	−2.43	4.07	3.09		−0.52	−1.02	−1.22[h]			
CCl_4			3.91	3.43	2.56		4.74	4.35	4.16	3.98	3.47	2.28	1.46	0.91	0.61	0.06	−0.79	−1.47	−1.97	4.00	2.98			−0.89	−1.12[h]		−3.80	−4.46
diethyl ether						1.71	4.44[i]	3.96[i]	3.78[i]	3.70[i]	3.20[i]	2.20[i]							−2.39					−0.80				
toluene	5.47	5.26	4.05	3.37	2.50	1.78	4.77	4.42	4.22	4.15	3.57	2.47	1.55						−2.16	4.31	3.37			−0.61				
benzene	5.61	5.37	4.17	3.49	2.64	1.90	4.90	4.57	4.33	4.21	3.66	2.49	1.72	1.24	0.93	0.20	−0.52	−1.17	−2.02	4.42	3.52	0.82	−0.21	−0.66	−0.91[h]	−2.50	−3.69	−4.25
PhCl	5.67	5.47	4.19	3.49	2.60		4.89	4.58	4.35	4.23	3.71	2.50	1.60				−0.53		−1.91					−0.66	−0.98		−3.72	
PhBr	5.81	5.61	4.32	3.60	2.70					4.26	3.83	2.59	1.80						−1.95					−0.52				
Ph I	6.02	5.82	4.51	3.78	2.80					4.49	4.02	2.58	1.68						−1.52									
$PhNO_2$	6.09	5.95	4.58	3.89	3.05		5.19[i]	4.88[i]	4.68	4.51	4.06	2.88	2.24	1.89	1.55	0.92	0.26	−0.38	−0.93					0.20	−0.18[j]			
ethyl acetate						2.16[i]	4.74[i]		4.08[i]			2.60[i]							−1.44					−0.35				
methyl acetate							4.79	4.40	4.18	4.16	3.68	2.68																
butanone										4.09[k]						0.50[l]	−0.14[l]	−0.79[l]	−1.33									
acetone	5.41	5.19	4.15	3.53	2.75	2.41	4.81	4.46	4.25	4.20	3.73	2.75	2.05			0.75	0.15		−0.93			1.32		0.08	−0.20	−1.42	−2.46	−2.76
NM Pyrrol											4.10	2.96	2.40	2.08	1.73	1.17	0.54	0.08	−0.35					0.27	0.09[j]			
DMF									4.86[m]		4.15[m]		2.61[n]			1.36[o]	0.72[p]		−0.36					0.47			−1.92	
MeCN			4.41												2.12	1.54	0.96	0.42	0.06				1.11[q]	0.81	0.67[q]		−1.36	−1.63
PC											4.17	3.23	2.77	2.49	2.16	1.84	1.38	0.82	0.32					1.09	0.71[j]			
nitromethane	6.02	5.82	4.77	4.20	3.55			5.04								2.12	1.33		0.47		4.20						−1.04	
DMSO	6.20	6.05	5.20	4.57	3.78		5.61	5.56		5.19	4.62	3.53	3.10	2.93	2.47	2.21	1.67	1.18	0.62					1.30	1.04[j]		−1.01	−1.24
1-decanol[r]	5.20	5.05	3.87	3.24				4.33	4.11	3.97	3.42									4.24	3.36							
1-octanol	5.34[r]	5.15[r]	3.96[r]	3.31[r]				4.39[r]	4.19[r]	4.02[r]	3.50[r]	2.41[n]					−0.26[s]	−1.07[s]	−1.61	4.30[r]	3.39[r]			−0.26				
isobutyl alcohol	5.45	5.21	4.12	3.54		2.10	4.68	4.52	4.35	4.20							0.16[s]	−0.61[s]										
1-butanol			4.15				4.37	4.55[t]	4.37	4.23[t]	3.73[u]	2.69[u]	1.96[v]			0.60	0.01[s]	−0.69	−1.14					−0.08	−0.43[j]		−2.60	
2-propanol			4.22[w]			2.33		4.60[x]	4.39	4.24[x]	3.88[n]		2.09[y]	1.70[y]	1.41[y]			−0.39[z]	−0.99					0.08	−0.41[aa]		−2.50	
1-propanol			4.24					4.66[x]	4.45[i]	4.31	3.83	2.82					0.23[s]	−0.45[s]	−0.96					0.11			−2.40	−2.95
ethanol	5.61	5.41	4.37	3.81[ab]		2.56	5.03	4.70	4.52	4.41	3.95	2.98	2.33	1.93	1.65	1.15	0.52	−0.13	−0.66			1.51	0.79	0.46	0.09	−1.18	−2.06	−2.63
methanol	5.76	5.58	4.57	4.02		2.86	5.19[i]	4.86	4.67	4.61	4.18	3.28	2.66	2.33	2.06	1.71	1.00	0.31	−0.01			2.00	1.18	0.88	0.48	−0.50	−1.53	−1.86
$(CH_2OH)_2$			5.56				5.99[ac]	6.08[ad]			5.13	4.46[ad]	3.56	3.42	3.31		2.86[p]	2.46						2.49	2.25[ae]			

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[a] Values from ref 9 and 26–29 unless shown otherwise. [b] Data from L. Rohrschneider, *Anal. Chem.*, **45**, 1241 (1973). [c] Reference 22. [d] M. H. Abraham, *J. Chem. Soc. A*, 1061 (1971); M. H. Abraham and P. L. Grellier, *J. Chem. Soc., Perkin Trans. 2*, 1856 (1975); M. H. Abraham, unpublished work. [e] Values for the rare gases are for solvent tetradecane;[27–29] other values are for solvent hexadecane from I. Kikic and H. Renon, *Sep. Sci.*, 11, 45 (1976); D. Richon and H. Renon, *J. Chem. Eng. Data*, **25**, 59 (1980); P. M. Cukor and J. M. Prausnitz, *J. Phys. Chem.*, 76, 598 (1972). [f] From data for solvent *n*-pentane by A. Höpfner, U. T. Kreibich, and Kl. Schäfer, *Ber. Bunsenges. Phys. Chem.*, **74**, 1016 (1970). [g] Octamethylcyclotetrasiloxane. Values from ref 24 and 25 and from T. M. Letcher, *J. Chem. Thermodyn.*, 12, 297 (1980). [h] From results by J. A. V. Butler and P. Harrower, *Trans. Faraday Soc.*, **33**, 171 (1937). [i] From data in ref 30. [j] J.-P. Monfort, J. Vidal, and H. Renon, *J. Chim. Phys.*, **67**, 748 (1970). [k] G. B. Bub and W. A. Hillebrand, *J. Chem. Eng. Data*, **24**, 315 (1979). [l] G. J. Pierotti, C. H. Deal, and E. L. Derr, *Ind. Eng. Chem.*, **51**, 95 (1959). [m] From results by E. Haidegger, I. Szebényi, and A. Székely, *Magy. Kem. Foly.*, **64**, 365 (1958). [n] W. Gerrard, *J. Appl. Chem.*, **23**, 1 (1973). [o] H. M. Smiley, *J. Chem. Eng. Data*, **15**, 413 (1970). [p] C. H. Deal and E. L. Derr, *Ind. Eng. Chem. Process Des. Dev.*, **3**, 394 (1964). [q] D. C. Locke, *J. Chromatogr.*, **35**, 24 (1968). [r] Reference 23. [s] M. H. Abraham and L. E. Xodo, unpublished work. [t] C. B. Kretschmer, J. Nowakowska, and R. Wiebe, *Ind. Eng. Chem.*, **38**, 506 (1946). [u] M. Yaacobi and A. Ben-Naim, *J. Phys. Chem.*, 78, 175 (1974). [v] W. Hayduk and R. Casteneda, *Can. J. Chem. Eng.*, 51, 353 (1973). [w] G. A. Krestov, V. I. Vinogradov, and V. I. Parfenyuk, *Russ. J. Inorg. Chem.*, **25**, 323 (1980). [x] From results by J. Tokunaga, *J. Chem. Eng. Data*, **20**, 41 (1975). [y] Reference 44. [z] H. C. Van Ness, C. A. Soczek, G. L. Peloquin, and R. Machado, *J. Chem. Eng. Data*, 12, 217 (1967). [aa] K. Nakanishi, *J. Chem. Eng. Jpn.*, 2, 14 (1969). [ab] F.-t. Chiang, Ph.D. Thesis, University of Minnesota, 1967. [ac] E. Brunner, *J. Chem. Thermodyn.*, **12**, 993 (1980). [ad] J. Chr. Gjaldbaek and H. Niemann, *Acta Chem. Scand.*, 12, 1015 (1958). [ae] T. M. Letcher, *J. Chromatogr.*, **166**, 257 (1978).

Table II. Values of the Solute Parameters R_G and R_{HS}

solute	R_G	no.	R_{HS}	no.
He	1.32	19	1.32	17
Ne	1.39	19	1.39	14
Ar	1.75	25	1.79	21
Kr	1.95	20	1.95	11
Xe	2.19	14	2.16	8
Rn	2.39	10	2.34	10
H_2	1.54	18	1.49	14
N_2	1.64	23	1.64	19
CO	1.71	22	1.74	18
O_2	1.74	24	1.76	19
CH_4	1.90	27	1.90	18
C_2H_6	2.26	24	2.16	16
C_3H_8	2.47	22	2.42	13
i-C_4H_{10}	2.61	15	2.54	9
n-C_4H_{10}	2.70	16	2.68	9
n-C_5H_{12}	2.89	19	2.93	12
n-C_6H_{14}	3.11	24	3.15	15
n-C_7H_{16}	3.32	21	3.37	14
n-C_8H_{18}	3.52	27	3.61	6
CF_4	1.70	9	1.72	8
SF_6	1.98	10	2.13	9
Me_4C	2.73	5	2.73	2
c-C_5H_{10}	3.02	7	3.08	3
Me_4Sn	3.14	23	3.20	18
c-C_6H_{12}	3.24	19	3.19	15
Et_4C	3.68	4	3.43	4
Et_4Sn	4.02	14	3.98	4
Et_4Pb	4.17	8		

Table III. Analysis of ΔG°_s Values in Terms of R_G

solvent	no.	l	d	σy^a	ρ^b
hexadecane	16	−3.2991	9.3239	0.066	−0.99968
decane	20	−3.3534	9.4521	0.073	−0.99950
hexane	25	−3.3033	9.3642	0.079	−0.99938
OMCTS	21	−3.0430	8.5096	0.078	−0.99934
cyclohexane	23	−3.5022	10.0218	0.053	−0.99977
CCl_4	22	−3.4431	9.9852	0.093	−0.99946
diethyl ether	9	−3.3364	9.5548	0.136	−0.99854
toluene	17	−3.4494	10.1061	0.078	−0.99930
benzene	28	−3.4652	10.2537	0.050	−0.99985
PhCl	17	−3.4765	10.2754	0.042	−0.99990
PhBr	11	−3.5110	10.4560	0.053	−0.99978
PhI	10	−3.4900	10.5690	0.141	−0.99818
$PhNO_2$	20	−3.1762	10.1336	0.088	−0.99927
ethyl acetate	6	−3.1200	9.5362	0.103	−0.99928
methyl acetate	6	−2.8626	9.1295	0.049	−0.99822
butanone	5	−3.0639	9.4003	0.045	−0.99984
acetone	22	−2.8952	9.2152	0.059	−0.99974
NM pyrrol	11	−2.8394	9.4133	0.128	−0.99630
DMF	8	−2.9010	9.7397	0.093	−0.99928
acetonitrile	11	−2.5151	8.8035	0.074	−0.99906
PC	11	−2.3922	8.6838	0.105	−0.99648
nitromethane	11	−2.5335	9.2494	0.120	−0.99875
Me_2SO	21	−2.6256	9.6854	0.133	−0.99833
1-decanol	10	−3.0320	9.2577	0.087	−0.99245
1-octanol	15	−3.1696	9.5700	0.074	−0.99953
isobutyl alcohol	11	−3.0003	9.3915	0.071	−0.99943
1-butanol	14	−3.0485	9.5186	0.071	−0.99960
2-propanol	14	−2.9938	9.4911	0.070	−0.99958
1-propanol	12	−2.9820	9.5124	0.046	−0.99988
ethanol	25	−2.8691	9.4138	0.036	−0.99989
methanol	25	−2.6686	9.2655	0.062	−0.99927
$(CH_2OH)_2$	12	−2.1500	9.2814	0.234	−0.98757
water	6^c	−1.7331	9.328	0.043	−0.99867
	10^d	−1.7614	9.414	0.096	−0.98849
	26^e	−0.1170	6.725	0.574	−0.14512

[a] $\sigma y = \{[\Delta G^\circ_s(\text{calcd}) - \Delta G^\circ_s(\text{obsd})]^2/(n-2)\}^{1/2}$. [b] Correlation constant. [c] Rare gases. [d] Rare gases plus inorganic gases. [e] All solutes in Table IV.

Table IV. Thermodynamics of Solution of Solutes in Water at 298 K[a]

solute	ΔG°	ΔH°	ΔS°
He	7.03	−0.16	−24.1
Ne	6.94	−0.90	−26.3
Ar	6.27	−2.93	−30.9
Kr	5.93	−3.71	−32.3
Xe	5.60	−4.58	−34.1
Rn	5.15	−5.10	−34.4
H_2	6.62	−0.96	−25.4
N_2	6.73	−2.49	−30.9
CO	6.50	−2.66	−30.7
O_2	6.33	−2.88	−30.9
CH_4	6.28	−3.30	−32.1
C_2H_6	6.11	−4.72	−36.3
C_3H_8	6.23	−5.38	−38.9
i-C_4H_{10}	6.59	−5.38	−40.2
n-C_4H_{10}	6.35	−6.21	−42.1
n-C_5H_{12}	6.61^b	-6.5^c	-44^d
n-C_6H_{14}	6.82^b	-7.5^e	-48^d
n-C_7H_{16}	6.90^b	−8.1	-50.3^d
n-C_8H_{18}	7.16^b	−9.5	-55.9^d
CF_4	7.39	−3.60	−36.9
SF_6	7.31	−4.78	−40.5
Me_4C	6.78	−6.65	−45.1
c-C_5H_{10}	5.48^f		
Me_4Sn	6.48^g	-8.1^h	-49.0^h
c-C_6H_{12}	5.50^i	-7.93^j	−45.0
Et_4C	6.50^k	-9.8^h	-55.0^h

[a] For process 1; ΔG° and ΔH° in kcal mol^{-1} and ΔS° in cal K^{-1} mol^{-1}. Values from ref 32 unless shown otherwise. [b] Reference 7. [c] From ref 35 and 37. [d] Calculated from ΔG° and ΔH°. [e] From ref 35–37. [f] From ref 35. [g] Reference 22. [h] Estimated values from ref 22. [i] References 33 and 34. [j] Reference 37. [k] References 9 and 22.

Table V. Values of ΔG°_s and Solubility for Argon at 298 K[a]

solvent	ΔG°_s	mole fraction solubility
hexane	3.54	25.2×10^{-4}
1-decanol	3.87	14.7×10^{-4}
1-octanol	3.96	12.6×10^{-4}
1-butanol	4.15	9.06×10^{-4}
1-propanol	4.24	7.77×10^{-4}
ethanol	4.37	6.26×10^{-4}
methanol	4.57	4.47×10^{-4}
ethylene glycol	5.56	0.85×10^{-4}
water	6.27	0.25×10^{-4}

[a] References as in Table I. Standard state 1-atm gas and unit mole fraction solution. ΔG°_s in kcal mol^{-1}

perature and pressure, ΔH°_s values are most conveniently obtained by combination of calorimetrically determined enthalpies of solution of the liquid solutes with enthalpies of vaporization of the solute to the ideal gas. Several sets of workers[45-48] have reported such enthalpies of solution of liquid solutes, from which I have calculated the ΔH°_s and ΔS°_s value for the required process (eq 1). These values may then be correlated with the R_G parameter through sets of linear equations (eq 2). Good correlations are obtained for the ΔH°_s and ΔS°_s values against R_G for all the nonaqueous solvents for which there is a sufficient number and spread of results. Somewhat better correlations are found if the values of ΔH°_s and ΔS°_s are plotted against a new set of R values denoted as R_{HS} (Table II). The relevant equations are then

$$\Delta H^\circ_s \text{ (in solvent)} = l_H R_{HS} + d_H \tag{3}$$

$$-T\Delta S^\circ_s \text{ (in solvent)} = l_S R_{HS} + d_S \tag{4}$$

The values of R_{HS} differ but little from the R_G values, and hence the correlations with R_{HS} are always quite close to those with R_G.

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(46) P. P. S. Saluja, T. M. Young, R. F. Rodewald, F. H. Fuchs, D. Kohli, and R. Fuchs, *J. Am. Chem. Soc.*, **99**, 2949 (1977).

(47) B. N. Solomonov; I. S. Antipin, V. V. Gorbachuk, and A. I. Konovalov, *Dokl. Akad. Nauk. SSSR*, **243**, 1087 (1978).

(48) A. V. Ockhin, T. N. Vinetskaya, and Yu. G. Frolov, *Khim. Khim. Tekhnol. (Alma-Ata, 1962)*, **17**, 677 (1974).

The analysis of the ΔH°_s and $-T\Delta S^\circ_s$ correlations with R_{HS} is in Table VII. There are 280 values of ΔH°_s that are reproduced by eq 3 with an average deviation of only 0.30 kcal mol^{-1}, and the 280 values of $-T\Delta S^\circ_s$ are reproduced to within 0.35 kcal mol^{-1}, that is to 1.2 cal K^{-1} mol^{-1} in ΔS°_s. This latter figure compares quite well with results of the factor analysis method of de Ligny et al.,[49] who were able to correlate ΔS°_s values for permanent gases in a wide range of solvents to within 0.9 cal K^{-1} mol^{-1}. The factor analysis method, however, uses a four-constant equation whereas eq 4 contains but three constants. It might be noted (Table VII) that all the values of ΔH°_s and $-T\Delta S^\circ_s$ in water are quite well correlated by eq 3 and 4, in contrast to values of ΔG°_s for which the correlation constant is -0.1451 for 26 solutes (see Table III).[50]

Inspection of the ΔH°_s values in Tables IV and VI shows that the solubility of argon in water decreases with temperature (ΔH°_s negative) whereas in most nonaqueous solvents the solubility varies but little with temperature ($\Delta H^\circ_s \simeq 0$). However, in all solvents, including water, values of ΔH°_s are always negative for large solutes, and thus the solubility of, say, radon decreases with temperature in nonaqueous solvents as well as in water. For any given solvent, as the solute size decreases, ΔH°_s always becomes more positive, the changeover from negative to positive values usually taking place at $R_{HS} = 1.7-1.9$ in nonaqueous solvents, corresponding to $\Delta H^\circ_s \simeq 0$ for argon and krypton. Water behaves in exactly the same way, except that the changeover occurs at $R_{HS} = 1.2$, now corresponding more nearly to $\Delta H^\circ_s \simeq 0$ for helium. Whether or not water is anomalous with respect to ΔH°_s and ΔS°_s values for the rare gases must therefore be decided from the overall general pattern rather than from one single comparison. Both the ΔH°_s and the ΔS°_s values for rare gases in water are quite well correlated through eq 3 and 4, the main obvious difference between water and nonaqueous solvents being that the parameters l and d in the $-T\Delta S^\circ$ correlation are considerably more positive for water, thus reflecting the more negative entropies of solution of the rare gases. A recent calculation of the thermodynamic parameters for solution of the rare gases in water has been carried out, using SPT to estimate the cavity term and the Lennard-Jones method to calculate the interaction term.[22] For the five rare gases He–Xe, the total solution parameters were obtained with an average deviation from the experimental values of 0.14 kcal mol^{-1} in ΔG°_s, 0.44 kcal mol^{-1} in ΔH°_s, and 0.37 kcal mol^{-1} in $-T\Delta S^\circ_s$.[22] Thus a general theory of solution, applicable (at least for the rare gases) to various nonaqueous solvents, can be used to account for the solution thermodynamics of the rare gases in water. Together with the good correlations through eq 2–4, this suggests that there is no unusual effect operative and that for the rare gases in water there is no need to invoke a special hydrophobic effect.

Hydrophobic CH_2 Increment in *n*-Alkanes. The unfavorable ΔG°_t value for transfer of a methylene group from a solvent such as hexane to water may be divided into contributions from the hexane → gas phase transfer and the gas phase → water transfer.[9] In a similar way, the ΔH°_t and $-T\Delta S^\circ_t$ methylene increment for the hexane → water transfer can be obtained from the ΔH°_s and ΔS°_s values in Tables IV and VI and can then be divided into the constituent transfers. Because the values of ΔH°_s and ΔS°_s for *n*-octane in water seem to be quite out of line with those for the other *n*-alkanes, I have obtained the methylene increments in water through plots of ΔH°_s or ΔH°_t (similarly for $-T\Delta S^\circ$) against the carbon number for the *n*-alkanes from ethane to *n*-heptane. Values of these increments for the hexane → water transfer and the constituent transfers are in Table VIII. The unfavorable free energy of transfer of a methylene group from hexane to water (0.92 kcal mol^{-1}) is very largely an enthalpic effect (0.69 kcal mol^{-1}); the methylene $-T\Delta S^\circ_t$ value is comparatively small. This observation might appear strange in view of the large negative entropies of solution of alkanes in water and the smaller negative entropies of solution in hexane. However, the methylene increment is obtained from the variation of the entropy with carbon number, and this mostly cancels out between the two solvents. The breakdown of the hexane → water transfer into the hexane → gas and gas → water transfers is also in Table VIII. The unfavorable ΔH°_t methylene increment for hexane → water is entirely due to the hexane → gas transfer, since for the gas → water transfer the methylene increment is favorable in terms of enthalpy ($\Delta H^\circ = -0.67$ kcal mol^{-1}) but unfavorable entropically ($-T\Delta S^\circ = 0.85$ kcal mol^{-1}). Several workers have previously obtained a number of the methylene increments shown in Table VIII, although not usually for the entire set of C_2–C_7 *n*-alkanes. Thus Rytting et al.[7] have derived almost identical values for the heptane–water–gas phase system to those in Table VIII, but only in terms of free energy, whereas Cabani and Gianni[10] have recorded similar, though not identical values, for the gas phase → water transfer only, in free energy, enthalpy, and entropy.

It then remains to be deduced from the observed gas → water increments whether or not these are "normal" by comparison to those for other gas → solvent transfers or whether the observed increments contain some unusual effect, special to water or aqueous solutions, that might be denoted as the hydrophobic effect.[51–53] Since the thermodynamic parameters (ΔG°_s, ΔH°_s, and ΔS°_s) for solution of the rare gases and inorganic gases in water are well correlated by the solute parameters R_G and R_{HS}, one method of obtaining a measure of a normal effect is to use the "rare gas lines" as a standard. Although in general ΔH°_s and ΔS°_s values are a little better correlated with R_{HS} than with R_G, for thermodynamic consistency it is desirable to use equations in terms of R_G to define the rare gas lines for all three parameters:

$$\Delta G^\circ_s(\text{rare gas in water}) = -1.7331R_G + 9.3278 \quad (5)$$

$$\Delta H^\circ_s(\text{rare gas in water}) = -4.5866R_G + 5.5044 \quad (6)$$

$$-T\Delta S^\circ_s(\text{rare gas in water}) = 2.8518R_G + 3.8254 \quad (7)$$

Correlation constants are 0.9868 and 0.9656 for eq 6 and 7 as compared to 0.9932 and 0.9765 for corresponding plots against R_{HS} (Table VII). If eq 5–7 are used to calculate the expected values for solution, then any unusual effect may be deduced and defined by eq 8 in which $P = G$, H, or S. Values of ΔG°_h, ΔH°_h,

$$\Delta P^\circ_h = \Delta P^\circ_s(\text{obsd}) - \Delta P^\circ_s(\text{calcd}) \quad (8)$$

and $-T\Delta S^\circ_h$ obtained in this way are in Table IX, and from these, hydrophobic methylene increments for the gas → water transfer may be obtained (see Table VIII). Thus the observed increment for the gas → water transfer is now broken down into a "true" hydrophobic increment and a normal gas → water solvent effect. On this basis, the unfavorable observed free energy increment of 0.18 kcal mol^{-1} is composed of a favorable normal solvent effect and a very unfavorable (0.54 kcal mol^{-1}) hydrophobic effect,[9] whereas the favorable observed enthalpic increment (-0.67 kcal mol^{-1}) is actually the net result of a very favorable normal solvent effect and an unfavorable (0.30 kcal mol^{-1}) hydrophobic enthalpic effect. Furthermore, the true hydrophobic free energy contribution of 0.54 kcal mol^{-1} is predominantly an enthalpic effect (0.30 kcal mol^{-1}) rather than an entropic effect (0.24 kcal mol^{-1}).

Calculations have also been carried out by using as a basis the rare gas lines with R_{HS} as the solute parameter:

$$\Delta H^\circ_s(\text{rare gas in water}) = -4.8294R_{HS} + 5.917 \quad (9)$$

$$-T\Delta S^\circ_s(\text{rare gas in water}) = 3.0167R_{HS} + 3.543 \quad (10)$$

In this way, the methylene increment to the true hydrophobic effect is calculated as 0.50 kcal mol^{-1} in ΔH°_h and only 0.11 kcal mol^{-1} in $-T\Delta S^\circ_h$ so that again the dominant feature is the very large enthalpic contribution. Because R_{HS} plots have been used to obtain ΔH°_h and $-T\Delta S^\circ_h$ and R_G plots to obtain ΔG°_h, there is an

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(49) C. L. de Ligny, N. G. van der Veen, and J. C. van Houwelingen, *Ind. Eng. Chem. Fundam.*, **15**, 336 (1976).

(50) The difference in behavior is not due to differences between R_G and R_{HS}, which are very small, but to the quite different behavior of ΔG°_s as compared to ΔH°_s and ΔS°_s.

(51) The term "hydrophobic effect" is not used with any connotation as to microscopic mechanism[52,53] but merely to denote an unusual effect that seems specific to aqueous solutions of hydrocarbon and hydrocarbon-like solutes.

(52) J. H. Hildebrand, *Proc. Natl. Acad. Sci. U.S.A.*, **76**, 194 (1979).

(53) C. Tanford, *Proc. Natl. Acad. Sci. U.S.A.*, **76**, 4175 (1979).

Table VI. Enthalpies (kcal mol^{-1}) and Entropies (cal K^{-1} mol^{-1}) of Solution of Gaseous Solutes at 298 K[a]

solvent	He	Ne	Ar	Kr	Xe	Rn	H_2	N_2	CO	O_2	CH_4	C_2H_6	C_3H_8	i-C_4H_{10}	n-C_4H_{10}	n-C_5H_{12}	n-C_6H_{14}	n-C_7H_{16}	n-C_8H_{18}	CF_4	SF_6	Me_4C	cy-C_5H_{10}	Me_4Sn	cy-C_6H_{12}	Et_4C	Et_4Sn
hexadecane	1.51	1.41	-0.40	-1.27			1.09				-0.55	-2.27				-6.00[b]	-7.00[b]	-7.95[b]							-7.05[b]		
	-11.6	-11.2	-13.2	-13.9			-10.4				-12.1	-14.2				-19.2	-20.0	-20.9							-19.1		
decane	1.64	1.56	-0.39					-0.07	0.09	-0.06	-1.03	-1.86[c]	-3.28[c]	-3.98[c]	-4.85[c]						-1.89						
	-11.1	-10.6	-13.2					-13.6	-12.4	-12.4	-13.9	-12.8	-14.9	-15.5	-17.7						-15.8						
hexane	1.92	1.30	-0.65	-1.13	-2.56	-3.03	1.22	0.19[j]		-0.23[d]	-0.54	-1.99[c]	-3.37[c]	-4.51[c]	-4.90[c]	-6.39[e]	-7.54[f]	-8.74[g]	-9.92[g]	-0.38[h]	-1.98[h]	-5.15[i]		-7.40	-7.75[j]		
	-10.0	-11.3	-14.1	-13.7	-15.8	-15.4	-10.6	-12.4		-13.2	-12.3	-13.6	-15.7	-17.7	-18.3	-20.8	-22.1	-23.7	-15.4	-13.5	-15.8	-18.4		-21.3	-21.5		
OMCTS[k]	1.56		-0.26				1.02	0.09	0.07	-0.35	-0.84	-2.53	-3.62	-4.10	-4.42					-0.84	-1.91						
	-9.7		-11.5				-9.6	-11.6	-11.1	-12.0	-12.1	-14.3	-15.7	-15.8	-16.3					-13.7	-14.2						
cyclohexane	2.42	1.46	-0.22	-0.85	-2.39		1.24	0.51	0.20	0.06	-0.72[l]	-2.66[l]	-3.98[l]			-6.13[m]	-7.27[m]	-8.35[m]	-9.48[m]	0.12	-1.38		-6.82[m]	-7.36	-7.90[n]	-9.61[m]	
	-9.8	-12.2	-13.7	-13.5	-15.7		-11.3	-12.6	-13.1	-13.1	-13.8	-16.4	-18.0			-20.2	-21.5	-22.6	-23.6	-13.3	-15.0		-21.0[e]	-21.3	-22.4	-22.6[e]	
CCl_4			-0.10				1.34	0.56	0.30	0.01	-0.71	-2.20[o]	-3.45[c]	-3.86[o]	-4.42[o]		-7.36[p]			0.14	-1.67			-7.57	-7.73[j]		-11.76[g]
			-13.5				-11.4	-12.7	-13.0	-13.3	-14.0	-15.0	-16.5	-16.0	-16.9		-22.0			-12.9	-15.6			-22.4	-22.2		-26.7
diethyl ether						-2.77	1.44[q]	0.38[q]	0.10[q]	0.01[q]	-0.80[q]													-6.97			
						-15.0	-9.9	-12.0	-12.4	-12.4	-13.4													-20.7			
toluene	2.42	1.97	0.23	-0.89	-1.98	-3.03	1.22	1.48	0.45	-0.14	-1.21	-2.13								1.43	-1.27				-7.35[j]		
	-10.2	-11.0	-12.8	-14.3	-15.0	-16.1	-11.9	-9.9	-12.6	-14.4	-16.0	-15.5								-9.7	-15.6				-21.1[r]		
benzene	2.46	2.50	0.30	-0.46	-1.70	-3.18	1.52	1.02	0.64	0.41	-0.30	-2.00[o]	-3.20[o]	-3.70[o]	-4.16[o]	-5.32[m]	-6.37[m]	-7.41[m]	-8.48[m]	0.54	-0.78		-6.16[m]	-6.70	-7.03[m]	-8.25[m]	
	-10.6	-9.6	-13.0	-13.3	-14.5	-17.0	-11.3	-11.9	-12.4	-12.8	-13.3	-15.0	-16.5	-16.6	-17.1	-18.5	-19.6	-20.9	-21.7	-13.0	-14.4		-20.0	-20.3	-20.5	-19.3	
PhCl	2.40	2.30	0.11	-0.73	-2.08		1.19	0.58	0.23	0.15	-0.61	-2.36	-3.77[s]				-6.94[j]							-7.34	-7.31[j]		
	-11.0	-10.6	-13.7	-14.2	-15.7		-12.4	-13.4	-13.8	-13.7	-14.4	-16.3	-18.0				-21.5[r]							-22.4	-21.2		
PhBr	2.67	2.00	0.24	-0.73	-1.80																						
	-10.6	-12.1	-13.7	-14.5	-15.1																						
PhI	3.19	2.51	0.67	-0.44	-1.67																						
	-9.5	-11.2	-12.9	-14.2	-15.0																						
$PhNO_2$	3.24	3.16	0.59	-0.10	-1.23												-6.25[t]							-6.46	-6.49[j]		
	-9.5	-9.4	-13.4	-13.4	-14.4												-21.8							-22.3	-21.2		
methyl acetate[q]							1.23	0.68	0.34	0.34	-0.33	-2.06															
							-12.0	-12.5	-12.9	-12.8	-13.5	-16.0															
acetone	2.70	2.40	0.46			-2.51	1.08	0.42	0.06	0.03	-0.67	-2.06	-3.84[s]			-4.68[u]	-5.77[j]	-6.97[v]						-6.05	-6.27[j]		-9.68[g]
	-9.1	-9.3	-12.4			-16.5	-12.5	-13.6	-14.0	-14.0	-14.8	-16.1	-19.7			-18.2	-19.9	-22.0[e]						-20.6	-20.4		-24.2
DMF																-4.77[m]	-5.65[m]	-6.56[m]	-7.20[m]				-5.37[m]	-6.07	-6.06	-6.92[m]	
																-20.6	-21.4	-22.4[r]	-22.9				-21.3[r]	-21.9	-21.5[r]	-20.1[r]	
acetonitrile																-4.37[w]	-5.15[w]	-5.96[w]						-5.49	-5.74[j]		-9.58[g]
																-19.8	-20.5	-21.4						-21.1	-21.5		-27.6
PC												-1.37[x]	-1.54[x]	-2.32[x]	-2.59[x]	-4.20[w]	-5.02[w]	-5.90[w]						5.69	-5.78[w]		
												-15.4	-14.7	-16.1	-16.1	-20.2	-21.5	-22.5						-22.7	-21.8		
DMSO							2.30[y]									-3.64[w]	-4.36[w]	-5.12[w]						-5.14	-5.18[w]		
							-11.1									-19.6	-20.2	-21.1						-21.6	-20.9		
1-decanol[z]	1.49		-0.13					0.39	0.23	-0.11	-0.88									0.15	-1.45						
	-12.5		-13.4					-13.2	-13.0	-13.7	-14.4									-13.7	-16.1						
1-octanol[z]	0.94		-0.16					0.60	0.05	-0.28	-0.93									0.22	-1.57			-7.24			
	-14.8		-13.8					-12.7	-13.9	-14.4	-14.9									-13.7	-16.7			-23.4			
isobutyl alcohol	1.17	1.00	-0.48	-1.45		-2.74		-0.05	-0.34	-0.52																	
	-14.3	-14.1	-15.4	-16.7		-16.2		-15.3	-15.7	-15.8																	

1-butanol			-0.57			-0.34	-0.39^{aa}	-0.34^{ab}	-0.29^{aa}	-0.90^{ac}	-2.00^{ac}	-4.23^{ad}			-6.14^{w}	-7.21^{w}	-8.32^{w}				-7.30			
			-15.8			-15.8	-14.0	-15.8	-15.2	-15.6	-15.7	-20.7			-22.6	-24.2	-25.6				-24.2			
2-propanol			-0.89		-2.48		0.71	-0.50	0.07			-3.38^{ac}	-4.28^{ae}	-4.63^{ae}			-7.80^{af}		-4.90^{ag}					
			-17.1		-16.1		-13.0	-16.4	-14.0			-18.3	-20.0	-20.2			-24.9		-20.9^{r}					
1-propanol			-0.40				0.28^{ah}	-0.41^{ab}	0.12^{ah}	-0.50^{ac}	-2.47^{ac}						-8.07^{af}				-7.28			
			-15.6				-14.7	-16.3	-14.1	-14.5	-17.7						-25.6				-24.8			
ethanol	1.73	1.41	-0.14		-2.84	0.89	0.11	0.08	-0.29	-0.91	-2.10^{ac}	-3.36^{ae}	-4.25^{ae}	-4.62^{ae}	-6.00^{w}	-6.94^{w}	-7.96^{w}	-9.15^{ai}			-7.06			
	-13.0	-13.4	-15.1		-18.1	-13.9	-15.4	-14.9	-15.8	-16.3	-17.1	-19.1	-20.7	-21.0	-24.0	-25.0	-26.3	-28.5			-25.2			
methanol	1.40	1.15	-0.20	-1.17	-3.82		0.12	0.16	-0.23	-0.86	-1.90^{ac}	-3.13^{ac}	-3.91^{ae}	-4.49^{ae}	$-5.43^{m,w}$	$-6.38^{m,w}$	$-7.39^{m,w}$	-8.34^{m}		-5.91^{m}	-6.75	-6.72^{m}	-8.34^{m}	-10.27^{g}
	-14.6	-14.9	-16.0	-17.4	-22.4		-15.9	-15.1	-16.2	-16.9	-17.4	-19.4	-20.9	-22.0	-23.9	-24.8	-25.8	-27.9		-23.8	-25.6	-24.1	-26.3	-29.3

[a] Enthalpies in kcal mol^{-1} (top line) and entropies in cal K^{-1} mol^{-1} (bottom line) for each solvent. Values from ref 26-29 unless shown otherwise. All values for Me_4Sn from ref 22. [b] $\Delta H°_s$ values from A. B. Littlewood, *Anal. Chem.*, **36**, 1441 (1964). [c] References 40 and 41. [d] These are values for isooctane solvent from reference in footnote *t* (Table I). [e] Assuming that $\Delta H°_s$ for *n*-pentane (liquid) in *n*-hexane is zero. [f] This is the value of $-\Delta H°_v$ for *n*-hexane. [g] M. H. Abraham, unpublished work. [h] These are values for solvent *n*-heptane. [i] Footnote *f* in Table I. [j] Reference 47. [k] Footnote *g* in Table I. [l] Reference 43. [m] Reference 46. [n] This is the value of $-\Delta H°_v$ for cyclohexane. [o] Average values from ref 40-43. [p] T. E. Burchfield and G. L. Bertrand, *J. Soln. Chem.*, **4**, 205 (1975). [q] H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 507 (1945). [r] Using a value for $\Delta G°_s$ estimated through the correlations in Table IV. [s] Footnote v in Table I. [t] Reference 48. [u] J. A. Gerster, J. A. Gordon, and R.-B. Eklund, *J. Chem. Eng. Data*, **5**, 423 (1960). [v] H. Wolff, *Z. Electrochem.*, **57**, 419 (1953). [w] Reference 45. [x] J.-Y. Lenoir, P. Renault, and H. Renon, *J. Chem. Eng. Data*, **16**, 340 (1971). [y] From data by E. A. Symons, *Can. J. Chem.*, **49**, 3940 (1971). [z] Reference 23 except for Me_4Sn in 1-octanol.[22] [aa] Footnote *t* in Table I. [ab] From data in ref 30. [ac] Footnote *u* in Table I. [ad] Footnote *v* in Table I. [ae] Reference 44. [af] Footnote *z* in Table I. [ag] From $\Delta H°_s$(liq) given by M. F. Lappert, D. S. Patil, and J. B. Pedley, *Chem. Commun.*, 830 (1975). [ah] From data in footnote *x* in Table I. [ai] From data by T. L. Flitcroft and H. A. Skinner, *Trans. Faraday Soc.*, **54**, 47 (1958).

inconsistency in the final results, $\Delta H°_h - T\Delta S°_h = 0.61$ kcal mol^{-1} whereas $\Delta G°_h = 0.54$ kcal mol^{-1} for the methylene increments. If the enthalpic and entropic contributions are scaled down, the increments are 0.44 kcal mol^{-1} in ethalpy and 0.10 kcal mol^{-1} in $-T\Delta S°$.

A related method[9] of obtaining the expected solution parameters in water is to use a given solvent, for example, methanol, to construct the rare gas lines:

$$\Delta G°_s(\text{rare gas in water}) = 0.6505\Delta G°_s(\text{rare gas in methanol}) + 3.300 \quad (11)$$

$$\Delta H°_s(\text{rare gas in water}) = 0.9162\Delta H°_s(\text{rare gas in methanol}) - 2.076 \quad (12)$$

$$-T\Delta S°_s(\text{rare gas in water}) = -1.1324T\Delta S°_s(\text{rare gas in methanol}) - 10.2814 \quad (13)$$

Values for the C_2–C_7 methylene increment to the true hydrophobic effect calculated by using the above equations are 0.55 ($\Delta G°_h$), 0.33 ($\Delta H°_h$), and 0.27 kcal mol^{-1} ($-T\Delta S°_h$). There is a very slight discrepancy between $\Delta G°_h$ and ($\Delta H°_h - T\Delta S°_h$), and if allowance is made for this and also the 0.01-kcal mol^{-1} difference in $\Delta G°_h$, the corrected values are 0.54 ($\Delta G°_h$), 0.30 ($\Delta H°_h$), and 0.24 kcal mol^{-1} ($-T\Delta S°_h$), in exact agreement with values obtained through the R_G plots. However, in view of the difficulty in the experimental determination of $\Delta H°_s$ and $\Delta S°_s$ for the higher alkanes in water, it is probably best just to conclude that the main contribution to the methylene group free energy effect of 0.54 kcal mol^{-1} comes from the hydrophobic enthalpic term (0.30–0.44 kcal mol^{-1}) and that the term in $-T\Delta S°_s$ is smaller (0.10–0.24 kcal mol^{-1}).[54]

In Table X are also listed the methylene group contributions for *n*-alkanes with respect to a number of solvent → water transfers. For these processes the enthalpic term is usually the main contributor to $\Delta G°_t$, acetone solvent being an exception. For all the gas → solvent transfers, the $\Delta G°_t$ term is enthalpy dominated, since the $T\Delta S°_t$ term actually runs counter to the free energy term. It is of some interest that the methylene increments for pure 1-octanol are almost identical with those for cyclohexane so that the use of pure 1-octanol as a "mimic" of a hydrocarbon solvent is justified for the alkane solutes. How far this extends to water-saturated 1-octanol in partition experiments is not so clear. It may be noticed, however, that the values of *l* and *d* for solvent octanol in eq 2, obtained for pure octanol in this work, are very close to those for water-saturated 1-octanol given before[9] so that pure 1-octanol and water-saturated 1-octanol give rise to quite similar $\Delta G°_s$ values.[55] Thus "partition coefficients" calculated from $\Delta G°_s$ values in pure water and pure octanol are usually quite close to those obtained in actual partition experiments for the nonpolar compounds considered. It is possible that for more polar compounds with various functional groups, this similarity will not continue, and it is unlikely that $\Delta H°_t$ values for transfer from water to octanol obtained by measurements in the two pure solvents will be identical with values determined from the temperature dependence of actual partition coefficients because the latter measurements are complicated by the temperature dependence of the solubility of water in octanol.

The observed methylene increments to the entropy changes for the processes gas → water (Table VIII) and solvent → water (Table X) are quite small, amounting to no more than −3 and −1 cal K^{-1} mol^{-1}, respectively. On these observed values, it seems unlikely that a methylene group in an *n*-alkane chain can cause any large-scale alteration in water structure corresponding to "freezing out" of numbers of water molecules; compare the molar entropy of freezing of water of −5.3 cal K^{-1} mol^{-1}. Quite recently, Berendson et al.[17] have shown that there is a linear relation between the dynamic effect of water in the hydration layer of alcohols and the entropies of solution of the liquid alcohols, $\Delta S°$(liq), whereas there was no such relation involving the corresponding enthalpies of solution, $\Delta H°$(liq). Thus a plot of Berendson et al.'s

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(54) In a preliminary communication[12] values given were calculated just from the R_{HS} plots rather than from all three methods used here.

(55) See also, S. S. Davis, *Sep. Sci.* **10**, 1 (1975).

Table VII. Analysis of ΔH°_s and $-T\Delta S^\circ_s$ in Terms of R_{HS}

solvent	no.		l	d	σy	ρ	CL, %
hexadecane	11	ΔH	−4.761	8.076	0.18	0.9989	99.9999
		$-T\Delta S$	1.485	1.168	0.23	0.9821	99.9999
decane	12	ΔH	−4.710	8.035	0.22	0.9950	99.9999
		$-T\Delta S$	1.244	1.639	0.29	0.8907	99.99
hexane	23	ΔH	−5.136	8.766	0.23	0.9979	99.9999
		$-T\Delta S$	1.891	0.478	0.25	0.9825	99.9999
OMCTS	13	ΔH	−4.622	7.752	0.29	0.9898	99.9999
		$-T\Delta S$	1.547	0.825	0.23	0.9451	99.999
cyclohexane	22	ΔH	−5.255	9.166	0.33	0.9968	99.9999
		$-T\Delta S$	1.738	0.900	0.16	0.9927	99.9999
CCl_4	16	ΔH	−5.286	9.355	0.17	0.9991	99.9999
		$-T\Delta S$	1.808	0.684	0.22	0.9866	99.9999
diethyl ether	7	ΔH	−4.827	8.472	0.12	0.9993	99.9999
		$-T\Delta S$	1.731	0.602	0.16	0.9901	99.99
toluene	15	ΔH	−5.034	9.555	0.45	0.9848	99.9999
		$-T\Delta S$	1.798	0.659	0.39	0.9097	99.999
benzene	25	ΔH	−4.969	9.113	0.27	0.9970	99.9999
		$-T\Delta S$	1.500	1.143	0.18	0.9860	99.9999
PhCl	15	ΔH	−5.191	9.206	0.22	0.9980	99.9999
		$-T\Delta S$	1.724	1.024	0.14	0.9930	99.9999
$PhNO_2$	8	ΔH	−5.207	10.121	0.15	0.9994	99.9999
		$-T\Delta S$	1.983	0.174	0.17	0.9951	99.9999
acetone	17	ΔH	−4.455	7.990	0.42	0.9936	99.9999
		$-T\Delta S$	1.546	1.246	0.38	0.9606	99.9999
PC	9	ΔH	−4.413	8.749	0.40	0.9798	99.999
		$-T\Delta S$	2.280	−0.832	0.33	0.9522	99.99
1-decanol	8	ΔH	−3.763	6.547	0.16	0.9860	99.999
		$-T\Delta S$	1.287	1.847	0.16	0.8968	99.5
1-octanol	9	ΔH	−4.640	7.937	0.42	0.9874	99.9999
		$-T\Delta S$	1.682	1.366	0.38	0.9301	99.9
1-butanol	12	ΔH	−4.655	7.519	0.44	0.9916	99.9999
		$-T\Delta S$	1.815	1.428	0.32	0.9710	99.9999
2-propanol	10	ΔH	−4.735	8.087	0.36	0.9922	99.9999
		$-T\Delta S$	1.750	1.367	0.40	0.9325	99.99
1-propanol	8	ΔH	−4.907	8.429	0.28	0.9972	99.9999
		$-T\Delta S$	1.967	1.024	0.28	0.9821	99.99
ethanol	18	ΔH	−4.777	8.139	0.15	0.9991	99.9999
		$-T\Delta S$	2.005	1.064	0.19	0.9924	99.9999
methanol	22	ΔH	−4.454	7.504	0.30	0.9966	99.9999
		$-T\Delta S$	1.769	1.773	0.25	0.9845	99.9999
water	6^a	ΔH	−4.829	5.917	0.26	0.9932	99.99
		$-T\Delta S$	3.017	3.543	0.30	0.9765	99.9
water	10^b	ΔS	−4.856	5.900	0.29	0.9850	99.9999
		$-T\Delta S$	3.052	3.579	0.40	0.9351	99.99
water	25^c	ΔH	−3.736	3.826	0.49	0.9833	99.9999
		$-T\Delta S$	3.714	2.713	0.71	0.9659	99.9999

[a] Rare gases. [b] Rare gases plus inorganic gases. [c] All solutes in Table IV for which ΔH and $-T\Delta S$ values are given.

d parameter against $T\Delta S^\circ$(liq) yields a line of slope 0.0169 and $\rho = 0.894$ whereas against ΔH°(liq) the slope is only 0.0085 and $\rho = 0.488$, for 12 alcohols. However, as has been pointed out before,[9] the standard state of the pure liquid amounts to the assumption of a different standard state for each solute. If Berendson et al.'s relationships are replotted by using ΔS° and ΔH° values for solution of the gaseous solutes as defined by eq 1, there is a much better enthalpy correlation than before: against $T\Delta S^\circ$ the line has slope of 0.0229 with $\rho = 0.828$ and against ΔH° the slope is 0.0222 with $\rho = 0.737$, for 11 alcohols. The conclusion of Berendson et al.[17] with regard to the negative entropy of solvation of hydrocarbon chains in water is still valid, namely, that a positive entropic contribution due to the solute is outweighed by a larger negative contribution due to the water molecules, but with the new standard states it seems as though the entropic effect and the enthalpic effect are of similar magnitude. The present results are therefore in reasonable agreement with the conclusions of Berendson et al.,[17] both with respect to the enthalpy/entropy contributions to the methylene hydrophobic effect and with respect to the overall negative methylene hydrophobic entropic effect. However, it is not easy to suggest the origin of a positive solute methylene contribution to the entropy of solution in water, and from the present results all that can be said is that for solution in water of hydrocarbon chains there is an overall additional negative entropic effect. If the present method of uncovering "unusual" or "hydrophobic" effects is accepted, then the extra entropic effect specific to solution in water amounts to no more than 0.10–0.24 kcal mol^{-1} in $-T\Delta S^\circ$, that is, to only −0.3 to −0.8 cal K^{-1} mol^{-1} per methylene group. Since this extra effect is only about 10% of the molar entropy of freezing of water, the general concept of freezing out of water molecules by alkane chains seems no longer necessary.[56]

Calculations of interaction terms and SPT cavity terms[22] indicate that the positive hydrophobic methylene contribution in the gas → water transfer of n-alkanes (0.30–0.44 kcal mol^{-1}, Table VIII) is due to a more endothermic methylene/water interaction then expected. The conclusion is therefore that the methylene hydrophobic effect in n-alkanes is mostly enthalpic in character and that the origin of this effect lies in the methylene/water interaction. The rather small negative hydrophobic entropy could arise either from a cavity effect in water or from reorganization of water solvent molecules, although the latter would not be expected to be very extensive.

The observed parameters for the gas → solvent or solvent → transfers can be examined in the light of suggestions[13-15,18,19] on the effect of flexibility of solute molecules. Comparison of the isomeric molecules n-butane and isobutane, or n-pentane and neopentane, suggests that in nonaqueous solvents, and perhaps

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(56) Cramer[8] has also suggested that ordering of water molecules near to a nonpolar surface cannot account for the observed entropies of solution of methane and ethane in water and nonaqueous solvents.

Table VIII. Methylene Group and Methyl Group Increment for Transfer of n-Alkanes from Hexane to Water at 298 K[a]

	methylene group			methyl group[b]		
process	ΔG°_t	ΔH°_t	$-T\Delta S^\circ_t$	ΔG°_t	ΔH°_t	$-T\Delta S^\circ_t$
hexane → water	0.92	0.66	0.26	2.01	−1.29	3.30
hexane → gas	0.74	1.33	−0.59	−1.02	1.07	−2.09
gas → water	0.18	−0.67	0.85	3.03	−2.36	5.39
gas → water, normal[c]	−0.36	−0.97	0.61	2.70	−2.43	5.13
gas → water, hydrophobic[c]	0.54	0.30	0.24	0.33	0.07	0.26
gas → water, normal[d]	−0.36	−1.11	0.75	2.70	−2.29	4.99
gas → water, hydrophobic[d]	0.54	0.44	0.10	0.33	−0.07	0.40

[a] Using values for the C_2–C_8 n-alkanes for transfers from gas → hexane and values for C_2–C_7 n-alkanes for gas → water transfers. [b] Note that all the ΔG°_t and $-T\Delta S^\circ_t$ values for the methyl group depend on the standard states adopted (1-atm gas and unit mole fraction solution), except for the calculated hydrophobic terms. [c] Obtained by using the R_G plots, eq 5–7. [d] Obtained by using the R_{HS} plots, eq 9 and 10, for ΔH° and $-T\Delta S^\circ$.

Table IX. Quantitative Assessment of the Hydrophobic Effect at 298 K[a]

solute	ΔG°_h	ΔH°_h	$-T\Delta S^\circ_h$
CH_4	0.25	−0.09	0.33
C_2H_6	0.70	0.14	0.55
C_3H_8	1.18	0.44	0.73
n-C_4H_{10}	1.70	0.67	1.03
n-C_5H_{12}	2.29	1.25	1.05
n-C_6H_{14}	2.88	1.26	1.62
n-C_7H_{16}	3.33	1.62	1.70
n-C_8H_{18}	3.93	1.14	2.80
i-C_4H_{10}	1.79	1.09	0.71
CF_4	1.01	−1.31	2.32
SF_6	1.41	−1.20	2.60
Me_4C	2.18	0.37	1.84
c-C_5H_{10}	1.39		
Me_4Sn	2.59	0.80	1.81
c-C_6H_{12}	1.79	1.44	0.35
Et_4C	3.55	1.57	2.08

[a] Values of ΔG°_h, ΔH°_h, and $-T\Delta S^\circ_h$ obtained through eq 8, where the calculated quantities have been obtained through the R_G plots in eq 5–7.

also in water, the more flexible isomer in each pair of molecules is the more soluble, with a more negative ΔG°_s value. This is largely an enthalpic effect, ΔH°_s being also more negative for the more flexible isomer. The corresponding entropic effect is quite small, the value of ΔS°_s for the more flexible isomer being only about 1 cal K^{-1} mol^{-1} more negative than for the more rigid isomer; this small entropic effect would lead to the more flexible isomer being less soluble were it not for the much larger enthalpic effect in favor of solution of the more flexible isomer. It seems, from the results to date, that entropic effects of flexible or nonrigid alkanes are comparatively unimportant in influencing the overall free energy of solution.

Hydrophobic Effect of the Methyl Group. Having calculated the methylene increment for various processes it is possible also to determine the corresponding methyl group contribution. Values for a number of gas → solvent and solvent → water transfers are in Table X, obtained from the average of values from the C_2–C_8 n-alkanes. It must be stressed that, unlike the methylene increments, these methyl group contributions to ΔG° and $-T\Delta S^\circ$ depend on the standard states adopted and that there is little point in discussing the absolute values of ΔG°_t and $-T\Delta S^\circ_t$ in Table X. For example, in the solvent → water transfers, alteration of standard states from that of unit mole fraction in each phase to one of unit molar concentration in each phase would reduce the values of ΔG°_t and $-T\Delta S^\circ_t$ by about 0.5–1.5 kcal mol^{-1}, depending on the solvent, thus making the methyl group values more in line with the methylene increments shown in Table X. The enthalpic effect of the methyl group does not depend on standard states, and for this function it can be seen that whereas a methyl group stabilizes a hydrocarbon in the sense gas phase < nonaqueous solvent < water, the corresponding order of enthalpic stability of a methylene group is gas phase < water < nonaqueous solvent. For the gas phase/hexane/water system, a breakdown of the methyl group effect into a "hydrophobic" and a "normal" effect may be made in exactly the same way as for the methylene increment; details are in Table VIII. Because of the method of calculation, the hydrophobic contributions are all independent of standard states and so may be compared to those for the methylene entity. The rather smaller methyl ΔG°_h value (0.33 kcal mol^{-1}) is now completely entropically dominated ($-T\Delta S^\circ_h \simeq 0.33$ and $\Delta H^\circ_h \simeq 0.00$) in contrast to the enthalpically dominated methylene hydrophobic effect. The calculated "normal" methyl group effects in Table VIII are very large, but again the ΔG° and $-T\Delta S^\circ$ value depend on standard states.

General Considerations. For solutes other than the alkanes, there is often a complicated interplay of enthalpic and entropic effects on the ΔG°_s or ΔG°_h value. The compounds CF_4 and SF_6 for example are very hydrophobic solutes. But now the large ΔG°_h values are entirely due to entropic effects. On the other hand, cyclohexane is less hydrophobic than n-hexane because the (un-

Table X. Methylene Group and Methyl Group Contributions in n-Alkanes at 298 K

	methylene group						methyl group[a]					
	gas → solvent[b]			solvent → water[c]			gas → solvent[b]			solvent → water[c]		
solvent	ΔG°_s	ΔH°_s	$-T\Delta S^\circ_s$	ΔG°_t	ΔH°_t	$-T\Delta S^\circ_t$	ΔG°_s	ΔH°_s	$-T\Delta S^\circ_s$	ΔG°_t	ΔH°_t	$-T\Delta S^\circ_t$
hexadecane	−0.74	−1.15	0.41	0.92	0.48	0.44	0.97	−1.18	2.15	2.06	−1.18	3.24
cyclohexane	−0.76	−1.12	0.36	0.94	0.45	0.49	1.08	−1.38	2.46	1.95	−0.98	2.93
hexane	−0.74	−1.33	0.59	0.92	0.66	0.26	1.02	−1.07	2.09	2.01	−1.29	3.30
benzene	−0.74	−1.07	0.33	0.92	0.40	0.52	1.23	−1.03	2.26	1.80	−1.33	3.13
acetone	−0.62	−0.88	0.26	0.80	0.21	0.59	1.34	−1.19	2.53	1.69	−1.17	2.86
PC	−0.48	−0.99	0.51	0.66	0.32	0.34	1.61	−0.48	2.09	1.42	−1.88	3.30
1-octanol[d]	−0.68	−1.10	0.42	0.86	0.43	0.43	1.20	−1.20	2.40	1.83	−1.16	2.99
1-butanol	−0.66	−1.19	0.53	0.84	0.52	0.32	1.33	−1.24	2.57	1.70	−1.12	2.82
ethanol	−0.61	−1.17	0.56	0.79	0.50	0.29	1.47	−1.11	2.58	1.56	−1.25	2.81
methanol	−0.56	−1.06	0.50	0.74	0.39	0.35	1.63	−1.06	2.69	1.40	−1.30	2.70
ethylene glycol	−0.35			0.53			2.09			0.94		
water[e]	0.18	−0.67	0.85				3.03	−2.36	5.39			

[a] Note that all the values of ΔG° and $-T\Delta S^\circ$ for the methyl group depend on the standard states adopted (1-atm gas and unit mole fraction solution). [b] Values calculated for the C_2–C_8 n-alkanes. [c] Using the results for the C_2–C_8 n-alkanes in nonaqueous solvents and the C_2–C_7 n-alkanes in water. [d] Values for ΔH° and $-T\Delta S^\circ$ are approximate. [e] Results for the C_2–C_7 n-alkanes.

Table XI. Enthalpies of Transfer of Solutes from *n*-Hexane and 1-Octanol to Water (in kcal mol^{-1}) at 298 K[a]

solute	1-octanol → water	*n*-hexane → water
O_2	−2.60	−2.65
CH_4	−2.37	−2.76
C_2H_6		−2.73
C_3H_8		−2.01
n-C_4H_{10}		−1.31
n-C_5H_{12}		−0.11
n-C_6H_{14}		0.04
n-C_7H_{16}		0.64
Me_4Sn	−0.86	−0.70

[a] Values from Tables IV and VI.

favorable) entropic term is rather small.

Finally, I refer to the suggestion of Wertz[16] that it is possible to calculate partition coefficients or $\Delta G°_t$ values for transfer of solutes from nonaqueous solvents to water on the assumption that the corresponding $\Delta H°_t$ values are zero. Wertz[16] applied this assumption in the calculation of values of $\Delta G°_t$ for transfer of methane, ethane, propane, and *n*-butane from 1-octanol to water. In Table XI are listed the $\Delta H°_t$ values for transfer of solutes from 1-octanol and *n*-hexane to water. It is clear that the $\Delta H°_t$ values can be so far from zero that Wertz' assumption cannot be at all generally valid. In any case, it is now possible to obtain the required $\Delta G°_t$ values either from the observed $\Delta G°_s$ values in Tables I and IV or from $\Delta G°_s$ values estimated through the correlations in Table III. The other suggestion of Wertz,[16] that all molecules lose the same fraction of their entropy on solution in water, has already been shown not to be generally valid.[57]

Registry No. He, 7440-59-7; Ne, 7440-01-9; Ar, 7440-37-1; Kr, 7439-90-9; Xe, 7440-63-3; Rn, 10043-92-2; H_2, 1333-74-0; N_2, 7727-37-9; CO, 630-08-0; O_2, 7782-44-7; CH_4, 74-82-8; C_2H_6, 74-84-0; C_3H_8, 74-98-6; n-C_4H_{10}, 106-97-8; n-C_5H_{12}, 109-66-0; n-C_6H_{14}, 110-54-3; n-C_7H_{16}, 142-82-5; n-C_8H_{18}, 111-65-9; CF_4, 75-73-0; SF_6, 2551-62-4; Me_4C, 463-82-1; Me_4Sn, 594-27-4; Et_4C, 1067-20-5; Et_4Sn, 597-64-8; Et_4Pb, 78-00-2; isobutane, 75-28-5; cyclopentane, 287-92-3; cyclohexane, 110-82-7.

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Photochromic Forms of 6-Nitrobenzospiropyran. Emission Spectroscopic and ODMR Investigations

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Abstract: The photochromic compound 6-nitrobenzopiropyran was investigated by luminescence and ODMR spectroscopic techniques at temperatures $T \leq 4.2$ K. The data are discussed with respect to a model based on a calculation of charge-transfer wave functions. Both the uncolored A form and the long suspect X form could be identified, and the properties of their triplet state were determined, i.e. phosphorescence, zero-field splitting, and the selective kinetics of population and deactivation (radiative and radiationless) of the triplet zero-field levels. By symmetry arguments, these data indicate that the triplet states of the A and the X form are of $\pi\pi^*$ nature and surprisingly belong to the point group C_{2v}. This is in excellent agreement with the calculation which showed that the nitrochromene part of the molecule can be considered as a para-disubstituted benzene subunit, the wave function of which exhibits considerable charge-transfer character. On the basis of this theory, the vibrational analysis of the phosphorescence with its strong solvent dependence as well as the zero-field splitting can be explained qualitatively and quantitatively. The results can serve as a guideline for future investigations of the detailed photochemical reactivity of 6-nitrobenzospiropyran.

Since its discovery in 1953,[1] the photochromism of spiropyrans has been extensively investigated with mainly four aims: (i) use for optical storage of data or for phototropic glasses,[2] (ii) elucidation of the excited states involved in the photochromic process and their chemical and physical properties,[2,3] (iii) modeling the role of natural chromenes in the photoregulation of biological processes in plants,[4] (iv) and use as a probe for specific investigations of bulk polymers.[5]

This paper deals with topic ii of the above enumeration, especially with the physical properties of the lowest excited triplet state T_1 of 6-nitrobenzospiropyran (6-NB). These are prerequisite data[6] to subsequent work of this laboratory on the detailed chemical kinetics of triplet photoreactions,[7] the aim of which is to show that the triplet sublevels (zero-field levels) possess individual chemical reactivities—just as is the case for the various photophysical processes involving T_1.[8,9]

Here we present the results of the investigation of the photophysical parameters of 6-NB carried out with the help of emission spectroscopic and ODMR techniques. It is shown that the various photochromic forms—under the very low temperature conditions used throughout—can be identified from the spectra, even the long-suspect intermediate form X.[10] The symmetry properties and the electronic nature of both the uncolored and the inter-

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