

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES, UNIVERSITY OF CALIFORNIA]

On Some Partial Molal Volumes of Gases in Solution

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In a recent paper on the solubility of nitrogen¹ we discussed the role of its partial molal volume, \bar{v}_2 , in the theoretical treatment, and again, in a paper on the solubility of chlorine,² we determined this quantity in perfluoroheptane, and found it to be close to the molal volume of the pure liquid. In the case of nitrogen, at temperatures above its critical point, we have no liquid volume to serve even as a first approximation, and must have recourse to direct measurement. Fortunately we have the measurements of Horiuti³ for a number of gases in a variety of solvents, but only two of these, benzene and carbon tetrachloride, can represent normal liquids, and they are so nearly alike in their internal pressure as to leave unanswered the question whether \bar{v}_2 is strongly affected by the internal pressure of the solvent. We undertook to throw light upon this question by finding the values of \bar{v}_2 for nitrogen, methane and ethane, gases of very different solubility, in three liquids of considerably different internal pressures, or "solubility parameters," δ , (*i. e.*, the square roots of their energies of vaporization per cc.), normal perfluoroheptane $\delta = 5.9$, normal hexane, 7.3 and carbon disulfide, 10.0.

Materials and Experimental Procedure.—

The nitrogen, normal hexane, benzene, normal perfluoroheptane and carbon disulfide were those used in a previous paper.¹ The methane was from the Ohio Chemical Company. Slow combustion yielded carbon dioxide equivalent to 98.4% CH₄. Fractional distillation of about 30 cc. of liquid methane gave beginning and end fractions analyzing 97.8 and 98.4%, respectively. We concluded that the amount of impurity was too small to interfere with the desired accuracy of our measurements. Ethane from Southern California Gas Company analyzed in the same way gave the figure 97.7% C₂H₆.

The apparatus and procedure were essentially the same as those of Horiuti. The volume of the bulb in the experiments with ethane was approximately 7.5 cc., but with nitrogen and methane, which are much less soluble, a 75-cc. bulb was used. The capillary stems had a capacity of ~2.7 cu. mm. per cm. A correction was made for the increase in the head of mercury resulting from the expansion.

To check our procedure against that of Horiuti, we determined the expansion of the liquid per cc. of gas absorbed, for ethane in benzene at 25°

finding 3.01×10^{-3} , which agrees well with Horiuti's value, 2.98×10^{-3} . Our results are given in Table I.

TABLE I
PARTIAL MOLAL VOLUMES OF GASES

Gas	Solvent	Temp., °C.	V = cc. gas abs.	Δv = cu. mm. vol. in- crease of solvent		Δv/V × 10 ³	Δv/V × 10 ³ mean	\bar{v}_2
				ap- par.	cor- rected			
C ₂ F ₁₀	C ₂ F ₁₀	0	9.96	34.36	34.45	3.46	3.455	76.5
			17.51	60.32	60.47	3.45		
	C ₂ F ₁₀	25	6.35	23.67	23.73	3.74		
			9.09	33.69	33.77	3.71		
			9.23	34.76	34.85	3.78		
			13.37	49.97	50.09	3.75		
C ₂ H ₆	C ₂ H ₁₄	25	11.40	35.61	35.70	3.132	3.128	69.3
			15.98	49.91	50.04	3.131		
			17.34	54.24	54.34	3.134		
			22.69	70.53	70.71	3.116		
	CS ₂	25	7.26	21.98	22.04	3.04		
			7.29	22.16	22.21	3.05		
CH ₄	C ₂ F ₁₀	25	9.06	27.37	27.92	3.08	3.06	68.4
			18.31	54.56	55.66	3.04		
	C ₂ H ₁₄	25	2.34	6.29	6.30	2.69		
			4.15	11.08	11.11	2.68		
			4.18	10.32	10.53	2.52		
			5.11	12.69	13.00	2.54		
CS ₂	25	8.70	21.11	21.58	2.48			
		5.11	12.69	13.00	2.54			
N ₂	C ₂ F ₁₀	25	6.55	18.92	19.27	2.94	2.95	66.1
			11.59	33.65	34.31	2.96		
			11.59	33.65	34.31	2.96		

TABLE II

PARTIAL MOLAL VOLUMES IN CC. AT 25°

Solvent	δ_1	N ₂	CH ₄	C ₂ H ₆
C ₂ F ₁₀	5.9	66.1	68.4	82.9
C ₂ H ₁₄	7.3	...	60.0	69.3
CCl ₄	8.6	53.0 ^a	52.4 ^a	65.9 ^a
C ₆ H ₆	9.15	52.6 ^a	52.0 ^a	66.0 ^a
CS ₂	10.0	...	56.1	67.4

^a Calculated from measurements of Horiuti.

The values of \bar{v}_2 represent the expansion that would be obtained if the molal volume of gas were dissolved in a large volume of solvent.

Table II shows the degree of correlation between the solubility parameters⁴ of the solvents and the molal volumes of the solute gases, with Horiuti's values for carbon tetrachloride and benzene added to our own. The dependence is evidently strong, but size and shape factors are doubtless also involved, as shown particularly by the values in carbon disulfide.

Summary

Partial molal volumes of nitrogen, methane and ethane have been determined in perfluoro-*n*-

(1) J. Chr. Gjaldbaek and J. H. Hildebrand, *THIS JOURNAL*, **71**, 3147 (1949).(2) J. Chr. Gjaldbaek and J. H. Hildebrand, *ibid.*, **72**, 609 (1950).(3) J. Horiuti, *Sci. Papers, Inst. phys. chem. Res., Tokyo*, **17**, 125 (1931).

(4) J. H. Hildebrand and R. L. Scott, "Solubility of Non-electrolytes," third edition, 1950, Reinhold Publ. Corp., New York, N. Y.

heptane, *n*-hexane and carbon disulfide. Combined with the figures of Horiuti for the same gases in carbon tetrachloride and benzene, they

are seen to increase strongly with decreasing internal pressures of the solvents.

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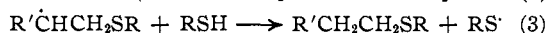
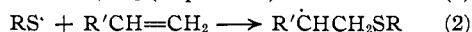
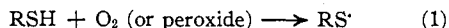
[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC CO.]

The Reaction of Mercaptans with Alkenyl Silanes

BY CHARLES A. BURKHARD

In a previous paper the peroxide catalyzed addition of trichlorosilane to vinyl- and allyl-trichlorosilanes to form α,ω -bis-trichlorosilylalkanes was discussed.¹ A continuation of the study of peroxide catalyzed addition reactions involving alkenyl silanes has shown that mercaptans react with alkenyl silanes to form thio ethers.

Kharasch, *et al.*,² have proposed that the addition of the mercapto group to an olefin proceeds by a free-radical chain-transfer type reaction.



The addition of the mercapto group to an alkenyl silane appears to proceed by the same reaction mechanism as that proposed by Kharasch for the addition of mercaptans to olefins,³ since the reaction is catalyzed by peroxide and proceeds

The presence of a silicon atom in the olefin does not appear to inhibit the addition reaction. Furthermore, it has been shown that the addition reaction proceeds normally when one or more of the following groups is also attached to the silicon atom to which the alkenyl group is attached: (1) alkyl group, (2) alkoxy group, (3) siloxane linkages and (4) a second alkenyl group.

The carbon-silicon bond is not weakened by the presence of the sulfur atom in the delta position (with respect to the silicon atom) as evidenced by the stability of these compounds when they are used in the presence of acids or alcoholic caustic. On the other hand, a halogen atom attached to either the beta or gamma carbon atom in an ethyl- or *n*-propylsilane causes a weakening of the carbon-silicon bond and in the presence of an alkali cleavage of this bond occurs.⁴

The types of compounds that can be prepared will depend on the type of mercaptan

TABLE I
NEW ALKENYL SILANES AND MERCAPTO ADDUCTS

Compound	Formula	Reagents used olefin ^d thiol	B. p., °C.	Mm.
I Allyltriethoxysilane ^a	$\text{CH}_2=\text{CHCH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$		100	50
II Allyltrimethylsilane ^b	$\text{CH}_2=\text{CHCH}_2\text{Si}(\text{CH}_3)_3$		85-86	
III Diallyldimethylsilane	$(\text{CH}_2=\text{CHCH}_2)_2\text{Si}(\text{CH}_3)_2$		68	50
IV Allylpentamethyl-disiloxane	$(\text{CH}_2=\text{CHCH}_2)_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_3$		141.5-142	
V 1,3-Diallyltetramethyl-disiloxane	$[(\text{CH}_2=\text{CHCH}_2)_2\text{Si}(\text{CH}_3)_2]_2\text{O}$		179-180	758.3
VI 3-Thia-6-sila-6,6-dimethylheptanoic acid	$(\text{CH}_3)_2\text{Si}(\text{CH}_2)_2\text{SCH}_2\text{CO}_2\text{H}$	I f	143-144	7
VII 3-Thia-7-sila-7,7-dimethyloctanoic acid	$(\text{CH}_3)_2\text{Si}(\text{CH}_2)_3\text{SCH}_2\text{CO}_2\text{H}$	II f	164-166	9
VIII 3-Thia-7,7-dimethyl-7-trimethylsiloxy-7-silaheptanoic acid	$(\text{CH}_3)_2\text{SiOSi}(\text{CH}_3)_3(\text{CH}_2)_3\text{SCH}_2\text{CO}_2\text{H}$	IV f	149-150.2	2
IX Ethyl 3-thia-7-sila-7,7-triethoxyheptanoate	$(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_3)_2\text{SCH}_2\text{CO}_2\text{C}_2\text{H}_5$	I o	200-201.5	50
X Ethyl 3-thia-7,7-dimethyl-7-silaoctanoate	$(\text{CH}_3)_2\text{Si}(\text{CH}_2)_2\text{SCH}_2\text{CO}_2\text{C}_2\text{H}_5$	II o	148-149 262-264	24
XI 1-(<i>p</i> -Tolylthio)-3-trimethylsilylpropane	$\text{CH}_3\text{C}_6\text{H}_4\text{S}(\text{CH}_2)_3\text{Si}(\text{CH}_3)_3$	II h	206-209	46
XII <i>p</i> -Tolyl-3-thia-7,7-dimethyl-7-silaoctanamide	$\text{CH}_3\text{C}_6\text{H}_4\text{NHCOCH}_2\text{S}(\text{CH}_2)_3\text{Si}(\text{CH}_3)_3$		M. p. 72.5-73	
XIII	$[-(\text{CH}_2)_2\text{Si}(\text{CH}_3)_2(\text{CH}_2)_2\text{SCH}_2\text{CO}_2(\text{CH}_3)_2\text{O}_2\text{CCH}_2\text{S}-]_x$	III		
XIV	$[-(\text{CH}_2)_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_3(\text{CH}_2)_2\text{SCH}_2\text{CO}_2(\text{CH}_3)_2\text{O}_2\text{CCH}_2\text{S}-]_x$	V		

exclusively by addition of the sulfur-hydrogen bond to the olefinic linkage forming a thio ether. The formation of the thioether is evidenced by the following facts: (1) elemental analyses indicate that no loss of sulfur has occurred during the reaction and (2) no mercapto group is detectable in the purified reaction products (reaction with I_2/KI solution).

(1) Burkhard and Krieble, *THIS JOURNAL*, **69**, 2687 (1947).

(2) Kharasch, Read and Mayo, *Chem. & Ind.*, **57**, 752 (1938).

(3) For a review of the addition reaction of the mercapto group to olefins see Mayo and Walling, *Chem. Revs.*, **27**, 387 (1940).

and alkenyl silane that are used, *e. g.*, thiols, thioglycolic acid and its esters have been used to prepare thio ethers, thia acids and thia esters. When dimercaptans and dialkenylsilanes are allowed to react, viscous oils result. These viscous oils are similar to those reported by Marvel and Chambers⁵ in which dithiols and dienes were allowed to react to form polyalkylene sulfides.

(4) Sommer, Dorfman, Goldberg and Whitmore, *THIS JOURNAL*, **68**, 488 (1946).

(5) Marvel and Chambers, *ibid.*, **70**, 993 (1948).