XIX.—*The Parachor and Chemical Constitution. Part XVI. Silicon Compounds.*

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Up to the present the only data from which the atomic parachor of silicon could be calculated are the observations of Ramsay and Shields (J., 1893, **63**, 1089) and of Mills and Robinson (J., 1927, 1823) on the surface tension and density of silicon tetrachloride. These give very different values for the parachor of silicon (Table I, 1*a* and 1*b*). We have therefore prepared a number of other silicon compounds and measured their parachors, with the results shown in Table I. It will be seen that the constant for silicon is about 28 units and that the data of Ramsay and Shields for silicon tetrachloride probably contain a serious error.

TABLE I.

Atomic Parachor of Silicon.

	Substance.	[*P*].	Σ[*P*].	Si.
1*a*	Silicon tetrachloride	229·2	217·2	12·0
1*b*	,, ,,	242·2	217·2	25·0
2	Methyl orthosilicate	330·9	304·4	26·5
3	Ethyl orthosilicate	487·6	460·4	27·2
4	Tetraethylsilicane	412·1	380·4	31·7
5	Tetrapropylsilicane	565·3	536·4	28·9
6	Tetraphenylsilicane	787·5	760·0	27·5
			Mean (excluding 1*a*)	27·8

EXPERIMENTAL.

Surface tensions were determined by the method of maximum bubble pressure (Sugden, J., 1922, **121**, 858; 1924, **125**, 27), and densities with a U-shaped pyknometer (J., 1924, **125**, 1171). The tables below are set out in the same way as in earlier papers of this series and need no further description.

Methyl orthosilicate, $C_4H_{12}O_4Si$, $M = 152{\cdot}4$, was prepared from silicon tetrachloride and pure dry methyl alcohol, and was purified by fractional distillation. The specimen used boiled at 121—122° (corr.)/759 mm. Densities determined: $D_{4^\circ}^{23^\circ}$ 1·032, $D_{4^\circ}^{37^\circ}$ 1·010, $D_{4^\circ}^{47{\cdot}5^\circ}$ 0·993, $D_{4^\circ}^{60{\cdot}5^\circ}$ 0·973, whence $D_{4^\circ}^{t^\circ} = 1{\cdot}067 - 0{\cdot}00155t$.

t	18°	32°	48·5°	61°	
γ	24·98	23·71	21·64	20·44	
D	1·039	1·017	0·991	0·972	
Parachor	328·0	330·6	331·6	333·3	Mean 330·9

Ethyl orthosilicate, $C_8H_{20}O_4Si$, $M = 208{\cdot}5$. A commercial specimen was purified by repeated fractionation. The fraction used boiled at 165·3—165·8° (corr.)/756 mm. Densities determined: $D_{4^\circ}^{17^\circ}$ 0·933, $D_{4^\circ}^{39{\cdot}5^\circ}$ 0·904, $D_{4^\circ}^{51{\cdot}5^\circ}$ 0·887, $D_{4^\circ}^{64^\circ}$ 0·870, whence $D_{4^\circ}^{t^\circ} = 0{\cdot}957 - 0{\cdot}00135t$.

t	16·5°	32°	43·5°	60·5°	
γ	22·21	20·65	19·44	17·95	
D	0·934	0·913	0·898	0·874	
Parachor	484·8	486·9	487·7	491·1	Mean 487·6

Tetraethylsilicane, $C_8H_{20}Si$, $M = 144{\cdot}5$. The preparation of this substance from magnesium ethyl bromide and silicon tetrafluoride is described by Jaeger and Dijkstra (*K. Akad. Wetensch. Amsterdam*, 1924, **27**, 398). When the more easily handled silicon tetrachloride is used, the yield is much smaller and becomes very small when the method is applied to the preparation of tetrapropylsilicane. By replacing part of the solvent ether with benzene, thus obtaining a higher reaction temperature, and using a large excess of Grignard reagent, we have been able to use the method for preparing both these substances.

To 128 g. of magnesium in 690 c.c. of dry ether, 10 g. of ethyl bromide and a crystal of iodine were added. When a vigorous reaction set in, the remainder of the ethyl bromide (10 mols.; 440 g. in all), diluted with 200 c.c. of benzene, was added slowly. Finally a further 500 c.c. of benzene warmed to 40° were added and the Grignard solution was decanted from excess of magnesium. To this solution, 68 g. (1 mol.) of silicon tetrachloride were added, and the mixture was heated on the water-bath for 12—15 hours.

After decomposition with dilute acid and removal of the solvent from the benzene-ether layer, 45 g. of crude product were obtained. This contained a considerable amount of silicols, which were removed by repeated shaking with concentrated sulphuric acid. The insoluble residue (20 g.) was then fractionated, and was nearly pure. The fraction used for measurement boiled at 153° (corr.)/759 mm. and had $D_{4^\circ}^{20^\circ}$ 0·7660; Jaeger and Dijkstra give b. p. 155°/760 mm. and $D_{4^\circ}^{20^\circ}$ 0·7673. Densities determined: $D_{4^\circ}^{12^\circ}$ 0·7563, $D_{4^\circ}^{54^\circ}$ 0·7396, $D_{4^\circ}^{66^\circ}$ 0·7305, $D_{4^\circ}^{96^\circ}$ 0·7402, $D_{4^\circ}^{122\cdot5^\circ}$ 0·6857, whence $D_{4^\circ}^{t^\circ} = 0\cdot7818 - 0\cdot000791t$.

t	12°	40°	62·5°	78°	125·5°	
γ	23·69	21·17	19·15	17·86	13·68	
$D-d$	0·7722	0·7500	0·7321	0·7196	0·6014	
Parachor	412·9	413·2	412·8	412·9	408·6	Mean 412·1

Tetrapropylsilicane, $C_{12}H_{28}Si$, $M = 200\cdot6$, was prepared in a similar manner and was purified by repeated treatment with concentrated sulphuric acid, followed by fractional distillation. The specimen used boiled at 213—215° (corr.)/751 mm. Densities determined: $D_{4^\circ}^{24\cdot5^\circ}$ 0·7809, $D_{4^\circ}^{40\cdot5^\circ}$ 0·7696, $D_{4^\circ}^{59\cdot5^\circ}$ 0·7560, $D_{4^\circ}^{75^\circ}$ 0·7444, $D_{4^\circ}^{101^\circ}$ 0·7254, whence $D_{4^\circ}^{t^\circ} = 0\cdot7990 - 0\cdot000727t$.

t	14°	38·5°	64°	85·5°	
γ	24·65	22·22	20·22	18·46	
D	0·7888	0·7710	0·7522	0·7366	
Parachor	566·7	564·8	565·5	564·2	Mean 565·3

Tetraphenylsilicane, $C_{24}H_{20}Si$, $M = 336\cdot6$. We are indebted to Prof. F. Challenger for a pure specimen of this substance melting at 234° (corr.). Densities determined: $D_{4^\circ}^{251\cdot5^\circ}$ 0·937, $D_{4^\circ}^{263^\circ}$ 0·927, $D_{4^\circ}^{275^\circ}$ 0·917, whence $D_{4^\circ}^{t^\circ} = 0\cdot983 - 0\cdot000883(t - 200)$.

t	245°	256°	267°	279·5°	
γ	23·70	22·78	21·79	20·90	
D	0·943	0·934	0·924	0·913	
Parachor	787·5	787·3	787·0	788·1	Mean 787·5

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