

of this work and the permission to publish the results.

WESTVACO CHEMICAL DIVISION  
FOOD MACHINERY AND CHEMICAL CORP.  
SOUTH CHARLESTON, WEST VIRGINIA

### The Si-C Bond Energy in Alkylsilanes

By STANLEY TANNENBAUM  
RECEIVED OCTOBER 17, 1953

There is considerable discrepancy in the reported values for the Si-C bond energy. Pauling<sup>1</sup> gives a value of 57.6 kcal./mole for crystalline carborundum, whereas Gilman and Dunn<sup>2</sup> calculate a value of 75.0 kcal./mole using newer heats of atomization for carbon and silicon. Thompson<sup>3</sup> found an average value of 64 kcal./mole for the Si-C bond in polydimethylsiloxanes. In order to add to the information available, it was considered worthwhile to calculate the Si-C bond energy in some alkylsilanes from heats of combustion recently obtained at this Laboratory.<sup>4</sup>

Table I lists the heats of formation for the alkylsilanes and the energies calculated for the Si-C bond<sup>5</sup> using the elemental heats of atomization and other required bond energies given by Gilman and Dunn<sup>2</sup> and by Thompson.<sup>3</sup> Except for vinylsilane, the values in the last two columns of Table I agree very well. The heats of formation differ slightly from those originally reported by Tannenbaum, *et al.*<sup>4</sup> Corrections were made for the newer value of the heat of formation of amorphous SiO<sub>2</sub> (-208.14 kcal./mole) formed in the combustion process as calculated by Thompson from the data of Humphrey and King.<sup>6</sup> The heats of vaporization of triethylsilane and dimethyldi-*n*-propylsilane, not previously measured, were estimated from Trouton's rule.

There appears to be a definite dependence of Si-C bond energy on the nature of the alkyl group joined to the silicon. The maximum estimated uncertainty in the measurement of the heat of combustion was -1.5 to +0.5%. This could result in a maximum error in the heats of formation of from 12 to 30 kcal./mole depending on the heat of combustion of the alkylsilane.<sup>4</sup> However, either the data are considerably more accurate than the uncertainty indicates, or the same relative error was involved in each determination, for there is little scatter within the methyl and ethyl series. It therefore appears that the trend observed in Table I is too large to be dismissed as within the experimental error.

Although no simple propylsilanes were investigated, a value of 57 kcal./mole for the Si-propyl

(1) L. Pauling, "The Nature of the Chemical Bond," 2nd Edition, Cornell University Press, Ithaca, N. Y., 1949, p. 53.

(2) H. Gilman and G. E. Dunn, *Chem. Revs.*, **52**, 77 (1953).

(3) R. Thompson, *J. Chem. Soc.*, 1908 (1953).

(4) S. Tannenbaum, S. Kaye and G. F. Lewenz, *THIS JOURNAL*, **75**, 3753 (1953).

(5) A recent article by M. L. Huggins, *ibid.*, **75**, 4125 (1953), lists values for bond energies based on a heat of atomization of C = 137 kcal./mole. Calculations of the Si-C bond energy using these data result in values about 10 kcal./mole less than those in Table I; however, the same type of dependence on alkyl group is found.

(6) G. L. Humphrey and E. G. King, *ibid.*, **74**, 2041 (1952).

TABLE I  
HEATS OF FORMATION AND SI-C BOND ENERGY OF ALKYL  
SILANES

Compound	$\Delta H_{form}$ , kcal./mole		Si-C bond energy, kcal./mole	
	Liquid	Gas	Calcd. from values Gilman and Dunn <sup>a</sup>	Calcd. from values of Thomp- son <sup>b</sup>
(CH <sub>3</sub> ) <sub>2</sub> SiH <sub>2</sub>	-47	-42	76	72
(CH <sub>3</sub> ) <sub>3</sub> SiH	-66	-60	76	74
(CH <sub>3</sub> ) <sub>4</sub> Si	-75	-69	74	72
			Av. 75	Av. 73
C <sub>2</sub> H <sub>5</sub> SiH <sub>3</sub>	-26	-21	64	61
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> SiH <sub>2</sub>	-43	-36	66	65
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> SiH	-47	-39	62	63
(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> Si	-47	-37	59	60
			Av. 62	Av. 62
<i>i</i> -C <sub>4</sub> H <sub>9</sub> SiH <sub>3</sub>	-31	-24	52	56
<i>n</i> -C <sub>4</sub> H <sub>9</sub> SiH <sub>3</sub>	-32	-14	52	56
CH <sub>2</sub> =CHSiH <sub>3</sub>	+ 1	+ 6	71	63
(CH <sub>3</sub> ) <sub>2</sub> Si( <i>n</i> -C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub>	-50	-41	60	61

<sup>a</sup> The C=C value was calculated from  $\Delta H_{form}$  C<sub>2</sub>H<sub>4</sub> (g) = -12.57 kcal./mole, C-H energy = 98.1 kcal./mole, and heat of atomization of C = 170 kcal./mole. <sup>b</sup> The Si-H value was calculated from  $\Delta H_{form}$  SiH<sub>4</sub> (g) = -14.87 kcal./mole and heat of atomization of Si = 88.0 kcal./mole.

bond was obtained from a plot of the average Si-C bond energy *vs.* type of alkyl group. Using this value along with the value of 74 kcal./mole for Si-methyl, the average Si-C bond energy in dimethyldi-*n*-propylsilane would be 65 kcal./mole compared to a value of 61 kcal./mole actually found.

These results are similar to those obtained in studies of the bond dissociation energies of tetraalkylsilanes. The activation energy for the thermal decomposition of tetramethylsilane was found to be 79 kcal./mole,<sup>8</sup> whereas the values for tetraethylsilane and tetrapropylsilane were 50.5 and 46.0 kcal./mole, respectively.<sup>9</sup>

(7) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," Circular No. 500, Natl. Bur. Standards, Feb. 1, 1952.

(8) D. F. Helm and E. Mack, *THIS JOURNAL*, **59**, 60 (1937).

(9) C. E. Waring, *Trans. Faraday Soc.*, **36**, 1142 (1940).

LEWIS FLIGHT PROPULSION LABORATORY  
NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS  
CLEVELAND 11, OHIO

### The Solubility of Phosphine in Aqueous Solutions<sup>1</sup>

By RALPH E. WESTON, JR.  
RECEIVED OCTOBER 27, 1953

In the course of recent work<sup>2</sup> it became necessary to determine the solubility of phosphine in water and aqueous solutions. Because of the low solubility, the solubility coefficient was determined by measuring directly the concentration of gas in a saturated solution, rather than by the usual procedure of measuring the pressure decrease upon

(1) Research carried out under the auspices of the U. S. Atomic Energy Commission.

(2) R. E. Weston, Jr., and J. Bigeleisen, *THIS JOURNAL*, to be published.

addition of solvent to a vessel containing the solute gas.

### Experimental

A known amount of phosphine<sup>3</sup> was condensed into a conical solubility vessel; this was equipped with a special stopcock, the hollow plug of which could be opened to either the vessel or an external ground joint. The vessel had previously been filled with a suitable measured amount of water or solution, which was degassed by the usual vacuum techniques. The solution was thawed and the vessel was placed in a shaking device in a thermostat.<sup>4</sup>

After equilibrium between the gas and liquid phases had been reached, the hollow stopcock was filled with solution, while the solubility vessel was still in the thermostat. The solution in the stopcock plug was then transferred to a vacuum line consisting of an extraction bulb containing a magnetic stirrer, a trap at  $-78^\circ$  to remove water vapor, and a gas buret with a small freeze-out tip at  $-196^\circ$ . Phosphine was extracted from the solution by repeated cycles of freezing, thawing and stirring, and the amount of extracted gas was measured in the gas buret.

The results may be expressed in terms of the Ostwald solubility coefficient,  $\beta = \text{concn. of solute in solution phase} / \text{concn. of solute in gas phase}$ . Then  $\beta = n_s V_g / V_s [n_g - (n_s V' / V_s)]$  where  $n_s$  is the number of moles of gas extracted from the solution in the stopcock plug with volume  $V_s$ ,  $n_g$  is the number of moles of gas originally added to the solubility vessel with gas volume  $V_g$ , and  $V'$  is the total volume of solution in the solubility vessel. The values of  $n_s$  and  $n_g$  can be computed from the known data and a suitable equation of state for the gas; for phosphine at pressures below one atmosphere, the perfect gas law is accurate.

### Results and Discussion

The experimental results are presented in Table I and Fig. 1. In the latter, a least-mean-squares plot of  $\log \beta$  against  $1/T$  was used to obtain a value of  $-2950 \pm 100$  cal./mole for the enthalpy of solution. This may be compared with an extrapolated enthalpy of vaporization of 2800 cal./mole at  $312^\circ\text{K}$ ,<sup>5</sup> the mid-point of the temperature range covered.

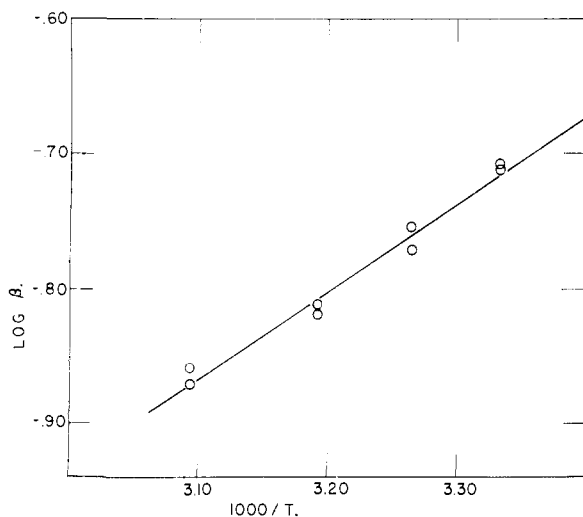


Fig. 1.—Effect of temperature on solubility.

The experiments at  $297.5^\circ$  were actually carried out using an earlier modification of the apparatus

(3) For method of preparation, cf. "Inorganic Syntheses," W. C. Fernelius, editor, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, Vol. 2, p. 141.

(4) Cf. ref. 2 for information on temperature control and rate of attainment of equilibrium.

(5) C. C. Stephenson and W. F. Giauque, *J. Chem. Phys.*, **5**, 149 (1937).

TABLE I  
SOLUBILITY OF PHOSPHINE IN WATER AND AQUEOUS SOLUTIONS

Solution	T, °K.	Press., mm. <sup>a</sup>	$\beta$
Distilled water	297.5 <sup>b</sup>	118	0.206
Distilled water	297.5 <sup>b</sup>	147	.195
Distilled water	297.5 <sup>b</sup>	322	.209
Distilled water	297.5 <sup>b</sup>	582	.201
Distilled water	297.5 <sup>b</sup>	650	.195
Mean value = $0.201 \pm 0.005$			
Distilled water	300.0	250	0.196
Distilled water		352	.194
Distilled water	306.2	276	.176
Distilled water		339	.170
Distilled water	313.3	256	.155
Distilled water		317	.152
Distilled water	323.2	294	.139
Distilled water		359	.135
0.275 M NaCl	297.5 <sup>b</sup>	322	0.192
0.550 M NaCl	297.5 <sup>b</sup>	320	.176
0.825 M NaCl	297.5 <sup>b</sup>	324	.169
1.100 M NaCl	297.5 <sup>b</sup>	328	.151
1 N NaOH	297.5 <sup>b</sup>	323	.115
0.2 M H <sub>2</sub> SO <sub>4</sub>	297.5 <sup>b</sup>	326	.202
2.0 M H <sub>2</sub> SO <sub>4</sub>	297.5 <sup>b</sup>	331	.183

<sup>a</sup> Calculated phosphine pressure at equilibrium. <sup>b</sup> See text.

in which the equilibration temperature was constant from run to run, but was not accurately known. The value of  $297.5^\circ$  was determined from the enthalpy of solution and the mean experimental value of  $\beta$  at the unknown temperature. Regardless of this uncertainty, the data show that  $\beta$  is independent of pressure, so that Henry's law is obeyed below one atmosphere. The data obtained with sodium chloride solutions fit the Setchnekov equation<sup>6</sup>  $\log (S^\circ/S) = k_s C_s$ , where  $S^\circ$  is the solubility in pure solvent,  $S$  is that in a solution with salt concentration  $C_s$ , and  $k_s$  is a constant which depends on the particular salt. For sodium chloride,  $k_s = 0.097$  liter/mole.

The effect of acid and base on the solubility does not differ enough from the effect of inert electrolyte to be ascribed to acidic or basic properties of phosphine. This fact is in agreement with estimates of the acid and base strengths based on other methods.<sup>2</sup>

The only other value reported in the literature for the solubility of phosphine in water is  $\beta = 0.26$  at  $17^\circ$ ,<sup>7</sup> compared with a value of 0.228 extrapolated from our data. The difference is understandable, since the literature value was obtained in the course of other work, using relatively crude apparatus.

I wish to acknowledge helpful discussions with Dr. Jacob Bigeleisen concerning this work, the assistance of Mr. Clayton Weaver during some preliminary experiments, and the construction of the special stopcock by Mr. Irvin Meyer.

DEPARTMENT OF CHEMISTRY  
BROOKHAVEN NATIONAL LABORATORY  
UPTON, LONG ISLAND, N. Y.

(6) Cf. for example, M. Randall and C. F. Failey, *Chem. Revs.*, **4**, 271 (1927).

(7) A. Stock, W. Bottcher and W. Langer, *Ber.*, **42**, 2855 (1909).