## Experimental

The current–voltage curves were determined manually by means of a Fisher Elecdropode after removing dissolved air in the usual way with tank nitrogen. All solutions were made up in 50% isopropanol by volume. For the ammonium chloride and lithium chloride solutions an electrolysis cell of the type described by Lingane and Laitinen[5] was used with a saturated calomel reference electrode. In these experiments the *m* and *t* values of the dropping electrode were, respectively, 1.931 mg./sec. and 4.10 seconds with the capillary dipping into distilled water at 25° and an open electrical circuit.

For the tetramethylammonium hydroxide solutions a cylindrical cell with a mercury pool anode was used. The *m* and *t* values of the dropping electrode in these experiments were, respectively, 3.296 mg./sec. and 2.23 seconds. The potential of the mercury anode in 0.2 *N* tetramethylammonium hydroxide was −0.250 volt (*vs.* saturated calomel electrode). In all of the above cases the temperature was 25°. In the experiments in 0.01 *M* tetramethylammonium hydroxide, 0.1 *M* tetramethylammonium bromide solution the potential was −0.150 volt and the temperature was 28°.

The acetophenone, benzalacetone and benzylacetone were purified by distillation before using. The sample of acetophenone pinacol used melted at 124–5°. 4,5-Diphenyloctanedione-2,7 and 3,5-diphenylcyclohexen-2-one were prepared according to directions given by Harries[6] and Kohler,[7] respectively.

## Summary

1. Benzalacetone has no effect on the total diffusion current of acetophenone but affects the shape of the acetophenone wave.

2. The relative height of the first wave of acetophenone decreases with increasing alkalinity. In ammonium chloride and lithium chloride solutions, only one wave is observed.

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(5) J. J. Lingane and H. A. Laitinen, *Ind. Eng. Chem., Anal. Ed.*, **11**, 504 (1939).

(6) C. Harries and G. Eschenbach, *Ber.*, **29**, 383 (1896).

(7) E. P. Kohler, *Am. Chem. J.*, **37**, 386 (1907).

URBANA, ILLINOIS RECEIVED JUNE 13, 1941

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

# The Heat Capacity and Entropy, Heats of Fusion and Vaporization and the Vapor Pressure of Silicon Tetramethyl

BY J. G. ASTON, R. M. KENNEDY AND G. H. MESSERLY

A preliminary value[1] for the entropy of gaseous silicon tetramethyl has shown that the potential hindering internal rotation of the methyl groups is about 1280 cal. This value was based on a heat of vaporization obtained from the vapor pressure equation and approximate state data. This paper presents a final value obtained using the measured heat of vaporization, and the complete thermal data down to 11.8°K. on which it is based.

**Preparation and Purification of Silicon Tetramethyl.**—The silicon tetramethyl was prepared from a Grignard reagent according to the procedure of Krause,[2] modified by the use of *n*-butyl ether as a solvent. The silicon tetrachloride and methyl iodide were purified by fractional distillation before use.

The silicon tetrachloride was added to the methylmagnesium iodide in *n*-butyl ether. After completion of the reaction, the solution was refluxed at 125° under a condenser kept at 30° until no more condensate formed in the carbon dioxide-snow trap attached to the outlet of the reflux condenser. The condensate was purified by distilling it into a solution of two moles of methylmagnesium iodide in one liter of *n*-butyl ether, stirring for five hours at room temperature and removing the product in the same manner. The gas was passed through two concentrated sulfuric acid traps, a potassium hydroxide tube and a phosphorus pentoxide drying tube before introduction into the laboratory low-temperature column. A middle cut of about 44 cc., boiling range 0.1°, was taken and put into gold calorimeter C in the usual manner.

The melting range of this sample (freezing point 171.78° K.) indicated 0.10 mole per cent. of solid-insoluble liquid-soluble impurity. However, the heat capacities of the liquid showed a peak 7° below the melting point of methyl iodide (207°K.). Qualitative examination of the sample showed the presence of an iodide; and gas density measurements showed that 20.1 mole per cent. of methyl iodide[3] was present. The failure to detect this in the melting point examination could be due only to the fact that the minimum boiling mixture (b. p. 26.1°) obtained in the fractionation was very close to the eutectic composition.

Thus 171.78°K. is the eutectic temperature of this binary system.

The methyl iodide was removed by formation of the methiodide of pyridine. A 100% excess of purified pyridine (based on the methyl iodide) was introduced with the sample into a glass bulb which was sealed and heated to 80°. The methylpyridinium iodide was separated by filtration and the silicon tetramethyl by distillation. The distillate was dried by passage over potassium hydroxide

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(1) Aston and Kennedy, THIS JOURNAL, **62**, 2567 (1940).

(2) Krause and v. Grosse, "Die Chemie der metall-organischen Verbindungen," Gebr. Borntraeger, Berlin, 1937, p. 258.

(3) In computing the number of moles per cc. the mixed gas was assumed to obey the modified Berthelot equation with the same critical constants that are assumed for pure silicon tetramethyl—see subsequent paragraphs.

and phosphorus pentoxide and fractionated. The middle cut of about 32 cc. contained no iodide. After removal of the last traces of air, this sample was weighed and put into the calorimeter.

Silicon tetramethyl was found to exist in two crystalline forms. The amount of solid-insoluble liquid-soluble impurity found from the melting point range of either crystalline variety was 0.1 mole per cent.

**The Heat Capacity Measurements.**—The apparatus, method, temperature scale and accuracy were as already described.[4,5] The heat capacity measurements on both forms uncorrected for premelting are listed in Table I and plotted in Fig. 1. The temperature rises can be estimated from the intervals between points of a series, only premelting heat capacities could be obtained on the α-form. One defined calorie was taken equal to 4.1833 international joules. Table II lists the molal heat capacity corrected for premelting at round values of the temperature for the stable modification of the solid (β-form) and the liquid.

Table I

The Heat Capacity of Silicon Tetramethyl

Mol. wt. 88.197; 0.23051 mole in calorimeter; 0°C. = 273.16°K.

| Temp., °K. | $C_p$, cal./deg./mole |
|---|---|
| Series V (β-form) | |
| 12.29 | 0.873 |
| 14.39 | 1.467 |
| 16.43 | 2.033 |
| 18.26 | 2.477 |
| 20.04 | 3.114 |
| 21.78 | 3.692 |
| 24.18 | 4.211 |
| 27.88 | 5.392 |
| 32.84 | 6.848 |
| 37.12 | 7.976 |
| 41.27 | 9.015 |
| 46.21 | 10.295 |
| 51.14 | 11.810 |
| 56.29 | 12.863 |
| 61.54 | 14.258 |
| Series I (β-form) | |
| 57.69 | 13.279 |
| 64.05 | 14.989 |
| 69.16 | 16.069 |
| 74.01 | 17.136 |
| 79.00 | 18.247 |
| 84.39 | 19.292 |
| 89.80 | 20.207 |
| 95.05 | 21.214 |
| 100.44 | 22.19 |
| 106.13 | 23.22 |
| 111.91 | 24.08 |
| 117.36 | 24.82 |
| 122.43 | 25.31 |
| 127.69 | 26.49 |
| 133.15 | 27.32 |
| 139.16 | 28.19 |
| 145.22 | 29.09 |
| 151.73 | 30.14 |
| 158.13 | 31.29 |
| 164.17 | 32.23 |
| Series II (liquid) | |
| 178.41 | 39.30 |
| 183.12 | 39.57 |
| Series III (liquid) | |
| 205.95 | 40.97 |
| Series IV (liquid) | |
| 188.90 | 40.08 |
| 194.50 | 40.25 |
| 198.84 | 40.47 |
| 209.35 | 41.00 |
| 214.22 | 41.30 |
| 219.82 | 41.66 |
| 225.51 | 41.92 |
| 230.83 | 42.22 |
| 236.41 | 42.71 |
| 242.55 | 42.81 |
| 250.50 | 43.50 |
| 256.33 | 43.76 |
| 262.83 | 44.24 |
| 269.77 | 44.72 |
| 276.17 | 45.32 |
| 282.51 | 45.86 |
| 288.40 | 47.00 |
| 293.53 | 48.38 |
| Series VI (liquid) | |
| 176.85 | 39.11 |
| Series VII (β-form) | |
| 168.65 | 34.71 |
| 171.40 | 40.65 |
| 172.84 | 73.65 |
| Series VIII (α-form) | |
| 167.62 | 37.01 |
| 168.47 | 40.76 |
| 169.18 | 47.59 |

Table II

The Molal Heat Capacity of Silicon Tetramethyl

| Solid (β-form) | | Liquid | |
|---|---|---|---|
| $T$, °K. | $C_p$, cal./°K. | $T$, °K. | $C_p$, cal./°K. |
| 11 | 0.53 | 180 | 39.32 |
| 13 | 1.00 | 190 | 39.93 |
| 15 | 1.60 | 200 | 40.55 |
| 17 | 2.15 | 210 | 41.02 |
| 20 | 3.05 | 220 | 41.59 |
| 25 | 4.50 | 230 | 42.18 |
| 30 | 5.95 | 240 | 42.79 |
| 35 | 7.35 | 250 | 43.40 |
| 40 | 8.80 | 260 | 44.00 |
| 50 | 11.35 | 270 | 44.75 |
| 60 | 13.90 | 280 | 45.78 |
| 70 | 16.25 | 290 | 47.30 |
| 80 | 18.41 | | |
| 90 | 20.35 | | |
| 100 | 22.13 | | |
| 110 | 23.75 | | |
| 120 | 25.30 | | |
| 130 | 26.80 | | |
| 140 | 28.33 | | |
| 150 | 29.89 | | |
| 160 | 31.30 | | |
| 170 | 32.80 | | |

Corrections to the heat capacities for vaporization into the filling line were made using the density of the liquid given by Krause.[2]

**The Melting Point of Silicon Tetramethyl.**—The two crystalline forms of silicon tetramethyl differed in melting point by 3.08°. The melting point of each was obtained in the usual manner.[5] Tables III and IV summarize the melting point data.

Table III

Melting Point of Silicon Tetramethyl (β-form), 0°C. = 273.16°K.

| Melted, % | Total time, Hr. | Min. | $T$, °K. Res. Th. | $T$, °K. Thermocouple S-4 | $T$, °K. Thermocouple S-7 |
|---|---|---|---|---|---|
| 9.2 | 2 | 15 | 173.877 | 173.857 | 173.894 |
| 18.3 | 4 | 35 | 173.955 | 173.918 | 173.955 |
| 30.5 | 6 | 35 | 173.995 | 173.958 | 173.997 |
| 57.7 | 10 | 5 | 174.023 | 174.015 | 174.054 |
| 84.7 | 12 | 15 | 174.075 | 174.022 | 174.075 |

M. p. lowering from 50 to 100% melted = 0.039°K. (S-7). M. p. corrected to the pure state 174.12±0.05°K. Mole per cent. impurity = 0.11.

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[4] Aston and Messerly, This Journal, 58, 2354 (1936).

[5] Messerly and Aston, *ibid.*, 62, 886 (1940).

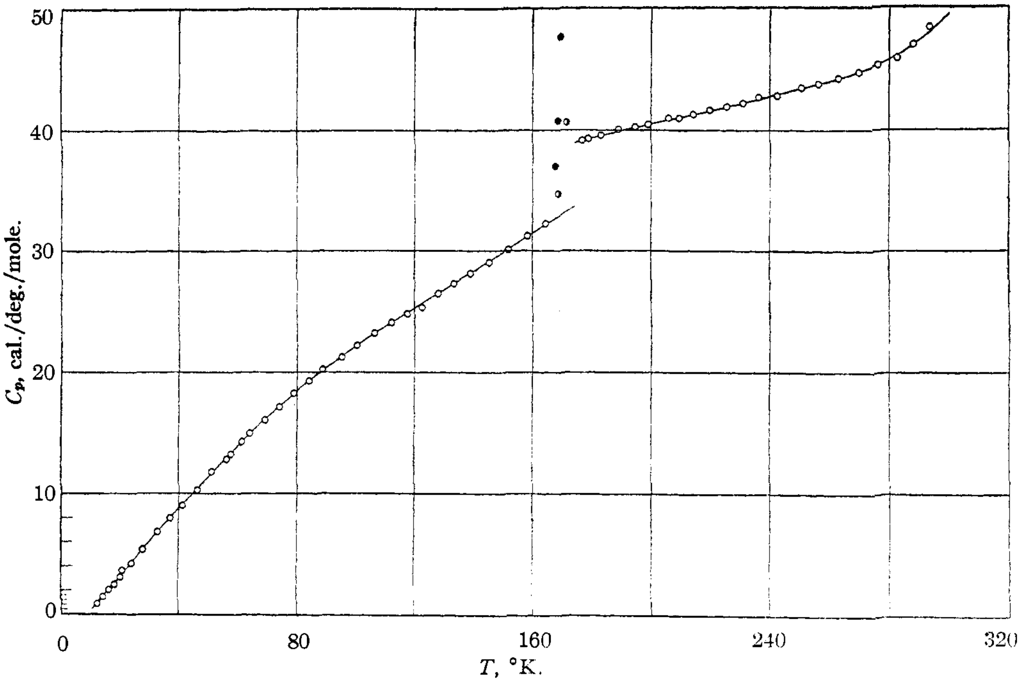

Fig. 1.—The molal heat capacity of silicon tetramethyl: ○, solid $\beta$-form and liquid; ●, $\alpha$-form premelting; ◑, $\beta$-form premelting.

TABLE IV

MELTING POINT OF SILICON TETRAMETHYL ($\alpha$-FORM), 0°C. = 273.16°K.

| Melted, % | Total Hr. | time Min. | $T$, °K. Res. Th. | $T$, °K. S-4 | $T$, °K. S-7 |
|---|---|---|---|---|---|
| 9.1 | 1 | 20 | 170.759 | 170.751 | 170.772 |
| 18.6 | 3 | 25 | 170.834 | 170.828 | 170.856 |
| 27.9 | 6 | 5 | 170.862 | 170.864 | 170.889 |
| 35.1 | 9 | 5 | 170.900 | 170.895 | 170.910 |
| 46.0 | 10 | 50 | 170.913 | 170.913 | 170.930 |
| 65.8 | 11 | 25 | 170.911 | 170.913 | 170.933 |
| 93.0 | 13 | 55 | 170.949 | 170.964 | 170.983 |

M. p. lowering from 50 to 100% melted = 0.053°K. (S-7). M. p. corrected to pure state 171.04 ± 0.05°K. Mole per cent. impurity = 0.13.

The metastable form (designated $\alpha$) could not be preserved more than 8° below its melting point. The heat of fusion of each form was determined. The equilibrium in the transition of the $\alpha$-form to the $\beta$-form (stable) is above the melting point of either form as is evident from the following considerations.

The calculation of the difference in heat content and entropy of the $\alpha$- and $\beta$-forms at 171.04° K. is summarized in Table V. From these values $\Delta F$ is found to be − 29.28 cal. Using the relation $\partial \Delta F/\partial T = -\Delta S$ it is found that $\Delta F$ becomes zero at 199.2 ± 1.0°K. Thus the transition point of the $\beta$ to the $\alpha$ is above the melting point of either and is a metastable transition. Therefore it was not possible to obtain a third law check using the entropy difference between the forms. Since the heats of fusion were constant, it can be assumed that 100% of either form was present in any fusion. The particular form obtained on crystallization was unpredictable.

TABLE V

ENTROPY AND HEAT CONTENT DIFFERENCES BETWEEN $\alpha$- AND $\beta$-SILICON TETRAMETHYL

| | $\Delta S$ | $\Delta H$ |
|---|---|---|
| Liquid from 174.12 to 171.04°K. (graphical) | − 0.69 | − 122.86 |
| Crystallization of $\alpha$ (see Table VII) | − 8.34 | −1426.80 |
| | − 9.03 | −1549.66 |
| Crystallization of $\beta$ (see Table VII) | − 9.46 | −1648.00 |
| $\beta$ from 174.12 to 171.04°K. | − 0.61 | − 108.82 |
| | −10.07 | −1756.82 |
| $H_\beta - H_\alpha$ at 171.04°K. | −207.16 | |
| $S_\beta - S_\alpha$ at 171.04°K. | − 1.04 | |

If the $\alpha$-form was obtained it was not cooled below 164°K. preparatory to measuring the heat of fusion because below this temperature it invariably changed to the $\beta$-form.

No other values for the melting point of silicon tetramethyl could be found in the literature. The eutectic with methyl iodide presumably involved the $\beta$-form.

**The Vapor Pressures, Heat of Fusion, and Heat of Vaporization.**—The methods have been described before.[4–6] The results are given as usual[4,5,6] in Tables VI, VII, and VIII. The vapor pressures can be represented by equation (1).

$$\log P_{\text{mm.}} = -2346.9849/T - 12.239609 \log T + 0.00662430T + 39.038565 \quad (1)$$

From this equation the normal boiling point was found to be 299.80 ± 0.05°K. (26.64°C.). No other values for these physical properties could be found in the literature except that of Krause[2] for the boiling point, 26–27°. In Table VIII is given a value for the heat of vaporization at the normal boiling point calculated from equation (1) and the modified Berthelot equation. Since the critical constants are unknown for silicon tetramethyl, they were estimated by analogy with isopentane (see footnote 17, ref. 4). The agreement with the measured value is not entirely satisfactory but is sufficient justification for the use of the modified Berthelot equation with these constants for the correction of the entropy and for calculating the heat of vaporization at a lower temperature. In Table VIII a value of the heat of vaporization, calculated from equation (1) using the modified Berthelot equation, at 227.00° K. is also given. This is used in the next paragraph.

Table VI

The Vapor Pressure of Silicon Tetramethyl

0°C. = 273.16°K.; boiling point, 299.80°K.; *g* for State College = 980.124 (I. C. T.)

| $T$ obsd., °K. | $P$ obsd. Int. mm. Hg. | $P$ obsd.[a] − $P$ calcd., mm. | $T$ calcd. − $T$ obsd., °K. |
|---|---|---|---|
| 208.94 | 6.24 | +0.02 | +0.043 |
| 217.18 | 11.71 | − .01 | − .014 |
| 236.17 | 41.50 | .00 | .000 |
| 242.85 | 61.28 | + .01 | + .003 |
| 250.05 | 90.79 | + .02 | + .004 |
| 256.08 | 123.68 | + .03 | + .005 |
| 263.73 | 178.77 | + .02 | + .002 |
| 269.19 | 229.12 | − .01 | − .001 |
| 274.57 | 289.35 | .00 | + .000 |
| 281.99 | 392.31 | − .01 | − .001 |
| 287.97 | 494.99 | .00 | + .000 |
| 292.62 | 588.54 | − .01 | − .001 |
| | 1/3 Sample distilled off | | |
| 282.95 | 407.57 | + .03 | + .005 |
| 288.41 | 503.41 | + .16 | + .008 |
| 293.65 | 611.29 | + .31 | + .014 |

[a] $\log P_{\text{mm.}} = -2346.9849/T - 12.239609 \log T + 0.00662430T + 39.038565$.

Table VII

The Heats of Fusion of Silicon Tetramethyl

Mol. wt. 88.197; 0.23051 mole; stable β-form, melting point, 174.12 ± 0.05°K.

| Temp. interval, °K. | Heat input, cal./mole | $\int C_p dT$, cal./mole | $\Delta H$ fusion, cal./mole |
|---|---|---|---|
| 169.443–178.515 | 2207.1 | 564.9 | 1642.2 |
| 167.414–176.103 | 2174.7 | 525.5 | 1649.2 |
| 167.158–177.298 | 2269.5 | 619.0 | 1650.5 |
| | | Average | 1648.0 ± 3.5 |
| Unstable α-form, melting point = 171.04 ± 0.05°K. | | | |
| 167.881–174.438 | 1834.2 | 407.7 | 1426.5 |
| 168.515–173.748 | 1751.6 | 325.4 | 1426.2 |
| 167.688–173.783 | 1803.9 | 376.0 | 1427.9 |
| | | Average | 1426.8 ± 0.7 |

Table VIII

The Heat of Vaporization of Silicon Tetramethyl at the Normal Boiling Point

Mol. wt. 88.197; boiling point 299.80°K.

| Moles vaporized | Mean temp. of vap., °K. | Total input, cal./mole | $\int C_p dT$, cal./mole | $\Delta H$ at 299.80°K. cal./mole |
|---|---|---|---|---|
| 0.05495 | 293.63 | 6382.3 | 496.5 | 5766.7 |
| .04800 | 293.72 | 6343.7 | 414.3 | 5808.6 |
| .04732 | 293.81 | 6410.6 | 520.3 | 5771.2 |
| .04757 | 293.86 | 6394.8 | 482.8 | 5793.8 |
| | | | Average | 5785.1 ± 16.0 |
| Calculated from equation (1) and critical data: $T_c = 458$°K., $P_c = 33$ atm. estimated by analogy with isopentane. (Berthelot correction = 301.5 cal.) | | | | 5876.8 |
| Calculated from equation (1) and same critical data at 227°K. (Berthelot correction = 27.9 cal.) | | | | 6925.4 |

**The Entropy from Thermal Data and its Comparison with the Entropy from Molecular Data.**—The calculation of the entropy from thermal data is summarized in Table IX. Only the data on the β-form (corrected for premelting) were used. The correction to the ideal gas state was made using the modified Berthelot equation and the critical constants discussed above. The essential correctness of this procedure is shown by the agreement between the measured heats of vaporization in Table VIII and those calculated from equation (1) and the modified Berthelot equation using the same critical constants. An actual determination of the density of the gas[7] at 296.9°K. and 0.3029 atm. gave a value for the second virial coefficient, $B$, of −1.208 ± 0.01 liters/mole compared to a value

$$B = (9/128)(PV/P_c)(T_c/T)(1 - 6T_c^2/T^2) = -1.047$$

calculated using the modified Berthelot equation with the same critical constants. This discrepancy is in general agreement with the error in the heat of vaporization calculated from the vapor

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(6) Aston, Siller and Messerly, This Journal, **59**, 1743 (1937).

(7) *In an apparatus to be described in a forthcoming publication.*

TABLE IX

THE MOLAL ENTROPY OF SILICON TETRAMETHYL FROM THERMAL DATA

Mol. wt. 88.197; 0°C. = 273.16°K.

| | E. u. | |
|---|---|---|
| 0 to 12.59°K., Debye extrapolation (6 degrees of freedom, $\theta$ = 122.0). | 0.342 | |
| 12.59 to 174.12°K., graphical | 33.572 | |
| Fusion, 1648.0/174.12 | 9.465 | |
| 174.12 to 227°K., graphical | 10.813 | |
| Entropy liquid at 227°K. | 54.19 ± 0.05 | 54.19 ± 0.05 |
| Vaporization 6925.4/227 | | 30.51 |
| Entropy real gas, at 0.03062 atm. | | 84.68 |
| Correction to ideal gas state[a] | | 0.013 |
| Entropy ideal gas, 0.03062 atm. | | 84.69 |
| $\Delta S$ from 0.03062 to 1 atm. | | −6.93 |
| Entropy ideal gas at 227°K., 1 atm. | | 77.78 ± 0.10 |
| 227 to 299.80°K., graphical | 12.376 | |
| Vaporization, 5785.1/299.80 | 19.297 | |
| Entropy real gas at N. B. P. | 85.86 ± 0.07 | |
| Correction to ideal gas state[a] | 0.18 | |
| Entropy ideal gas at N. B. P. | 86.04 ± 0.15 | |
| Entropy ideal gas at 298.16°K. | 85.79 ± 0.15 | |
| Entropy of the liquid at 298.16°K. | 66.27 ± 0.15 | |

[a] $S_{\text{ideal}} - S_{\text{real}} = 27RT_c^3P/32T^3P_c$; $P_c$ = 33 atm., $T_c$ = 458°K.

TABLE X

THE ENTROPY OF SILICON TETRAMETHYL IN THE IDEAL GAS STATE FROM MOLECULAR AND SPECTROSCOPIC DATA

| | 227°K., e. u. | 299.80°K., e. u. |
|---|---|---|
| Translational and rotational (free) | 72.34 | 75.66 |
| Vibrational ($^3\omega_{7,8,9.}$) | 0.23 ± 0.08 | 0.63 ± 0.1 |
| Vibrational ($^8\delta$ = 950) | 0.28 ± 0.08 | 0.94 ± 0.1 |
| Vibrational (other modes) | 7.55 | 10.43 |
| Total | 80.40 ± 0.16 | 87.66 ± 0.2 |
| Calorimetric | 77.78 ± 0.10 | 86.04 ± 0.15 |
| $(S_f - S) \times 4$ (experimental) | 2.62 ± 0.3 | 1.62 ± 0.3 |
| $(S_f - S) \times 4$ ($V$ = 1300 ± 200, $I_{me} = 5.3 \times 10^{-40}$) | 2.64 | 1.78 |

pressure data using the modified Berthelot equation.

Table X contains a summary of the calculation of the entropy from molecular data at 227.00°K. and the normal boiling point, and its comparison with the calorimetric value to obtain the potential hindering internal rotation. This differs from Table I of the previous communication[1] only by the use of revised values for the constants involved in the theoretical calculation (the Avogadro number, $N = 6.0227 \times 10^{23}$; $h = 6.62365 \times 10^{-27}$ erg. sec.; $k = 1.38052 \times 10^{-16}$ erg./deg. and $R$ = 1.98688 cal./deg.)[8] and the more accurate calorimetric value. As seen, the value of 1300 ± 200 cal. for the restricting potential hindering internal rotation of the methyl groups is practically unchanged. In its calculation, three equal minima were assumed.

The calorimetric entropy used to obtain the potential at 227.00°K. is probably as reliable as the calorimetric value at the normal boiling point because the Berthelot correction is small and the precision in the manometry of the vapor pressure meaurements was of the order of 0.01 mm. A more accurate value of the potential can be obtained at this temperature because of the lower contribution of the vibrational frequencies.

## Discussion

The potential of 1300 ± 200 cal. for the hindering potential is so much lower than that of tetramethylmethane[9] (5000 cal.) that a force law involving a high power of the distance between the centers of interaction is indicated. Such a law is suggestive of a repulsive type of interaction. This leads to the conclusion that the equilibrium configuration is that with the hydrogen atoms farthest apart.

A preliminary comparison[10] of the "calorimetric" and spectroscopic entropies of cyclopentane and its methyl and ethyl derivatives indicates that the symmetry number is unity (instead of ten) in the first case and that there are several geometric isomers in the other two cases. These facts point to a non-planar cyclopentane ring. Such a condition could only be stable if hydrogen repulsions balanced the necessary bond distortions.

**Acknowledgments.**—We wish to thank Dr. S. C. Schumann and Mr. Malcolm Sagenkahn for making the liquid hydrogen. The National Research Council, through its generous Grants-in-Aid for equipping the Cryogenic Laboratory, made this research possible.

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[8] Birge, Aug., 1939. Private communication through Prof. H. S. Taylor. These values are slightly different from those used in previous papers from the laboratory, that on dimethyl ether excepted.

[9] Aston, *Chem. Rev.*, **27**, 67 (1940).

[10] Aston, Schumann, Fink and Doty, THIS JOURNAL, **63**, 2029 (1941).

## Summary

1. Silicon tetramethyl with 0.1 mole per cent. impurity has been prepared.

2. The normal boiling point of silicon tetramethyl is 299.80 ± 0.05°K. (26.64°C.). The vapor pressures of the liquid have been measured from 208 to 293°K. and can be represented by the equation: $\log P_{\text{mm.}} = -2346.9849/T - 12.239609 \log T + 0.00662430T + 39.038565$.

3. There are two crystalline forms of silicon tetramethyl. The stable variety ($\beta$-form) melts at 174.12 ± 0.05°K. (−99.04°C.). The ($\alpha$-form), unstable with respect to the $\beta$-form at all temperatures below the melting point of the $\beta$-form, has a melting point of 171.04 ± 0.05°K. (−102.12° C.) and cannot be preserved more than 8° below its melting point. The equilibrium for the transition between the two forms is above the melting point of either. By thermodynamic calculation from the thermal data this temperature has been found to be 199.2 ± 1.0°K. (−74.0°C.).

4. Silicon tetramethyl forms a minimum boiling mixture with methyl iodide boiling at 26.1 ± 0.1°C. (1 atm.) and containing 20.1 mole per cent. of methyl iodide.

5. The eutectic (quadruple) point for the system silicon tetramethyl–methyl iodide is at 171.78 ± 0.05°K. (−101.38°C.) and presumably involves the $\beta$-form of the former.

6. The heat capacities of both forms of the solid and of the liquid silicon tetramethyl have been determined over the range 11.5 to 295.7°K.

7. The heat of fusion of the unstable $\alpha$-form of silicon tetramethyl is 1426.8 ± 0.7 cal./mole while that of the stable $\beta$-form is 1648.0 ± 3.5 cal./mole.

8. The heat of vaporization of liquid silicon tetramethyl at the normal boiling point has been measured calorimetrically and found to be $\Delta H_{299.8} = 5785 \pm 16.0$ cal./mole.

9. The second virial coefficient for silicon tetramethyl is − 1.208 ± 0.01 liters per mole at 296.9°K. as found from a direct determination of the density.

10. The molal entropy of the ideal gas calculated from the experimental data at the normal boiling point and 1 atmosphere is 86.04 ± 0.15 cal./deg. mole. At 227°K. and 1 atm. it is 77.78 ± 0.10 cal./deg. mole.

11. To bring the values of the entropy calculated from molecular data into agreement with the values from the calorimetric data requires the assumption of three equal potential energy maxima of 1300 ± 200 cal. hindering internal rotation of the methyl groups. These are shown probably to be due to repulsive forces.

12. The entropies of the ideal gas and the liquid at 298.16°K. are 85.79 ± 0.15 and 66.27 ± 0.15 cal./deg. mole, respectively.

STATE COLLEGE, PENNA. RECEIVED MAY 19, 1941

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

# Thermodynamic Properties of the Crystalline Forms of Silica

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Although a rather extensive array of thermodynamic data on silica has existed for some time, a complete analysis of the relative stability of quartz, tridymite, and cristobalite has never been made. Indeed it was not possible, because the heat capacity of tridymite above 300°K. has not been determined previously. Since tridymite is the stable form in the intermediate temperature range (1140 to 1743°K.), data on this substance are very important. By combining our measurements with those of others, the heat content, $H_T - H_0$, was obtained throughout the temperature range 0 to 2000°K. The integral of this function divided by $T^2$ gives the free energy, $(H_0 - F_T)/T$, throughout the same range. Differences in the $H_0$ values for the various forms are determined from the temperatures at which two modifications are in equilibrium. Thus a rather complete analysis has been made which allows, among other things, the calculation of the trend of transition temperatures with pressure.

Each of the three principal modifications of crystalline silica shows one or more reversible transitions. These are associated with only slight changes of the structure, as compared to the relatively complete rearrangement necessary to go from one principal form to another. Our results in Fig. 1 show clearly the existence of one second-