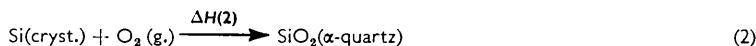### 524. Heats of Formation and Bond Energies. Part XII.* Silicon Tetrachloride.
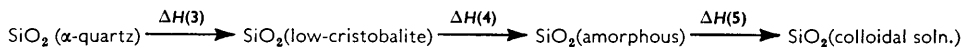
By A. E. Beezer and C. T. Mortimer.

The heat of hydrolysis, $\Delta H = -97 \cdot 81 \pm 0 \cdot 36$ kcal./mole, of liquid silicon tetrachloride in an excess of aqueous hydrofluoric acid to give an aqueous solution of fluorosilicic, hydrofluoric, and hydrochloric acids (reaction 6) has been measured. The value has been used to calculate $\Delta H_f°(SiCl_4, \text{liq.}) = -170 \cdot 2 \pm 0 \cdot 8$ kcal./mole. The mean bond dissociation energy, $\bar{D}(Si-Cl) = 97 \cdot 2 \pm 0 \cdot 7$ kcal./mole, is derived, together with the heat of formation of the radical, $\Delta H_f°(SiCl_3, \text{g.}) = -86 \cdot 1 \pm 4 \cdot 8$ kcal./mole.
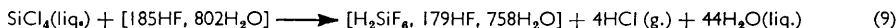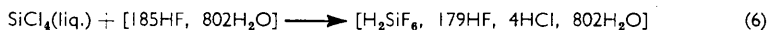
THE currently accepted value for the heat of formation of silicon tetrachloride is based on measurements of the heats of the reactions:

$$SiCl_4(\text{liq.}) + 2H_2O(\text{liq.}) \xrightarrow{\Delta H(1)} SiO_2(\text{colloidal soln.}) + 4HCl(\text{aq.}) \qquad (1)$$

$$Si(\text{cryst.}) + O_2(\text{g.}) \xrightarrow{\Delta H(2)} SiO_2(\alpha\text{-quartz}) \qquad (2)$$

and on the heats of the transformations:

$$SiO_2(\alpha\text{-quartz}) \xrightarrow{\Delta H(3)} SiO_2(\text{low-cristobalite}) \xrightarrow{\Delta H(4)} SiO_2(\text{amorphous}) \xrightarrow{\Delta H(5)} SiO_2(\text{colloidal soln.})$$

The heat of hydrolysis, $\Delta H(1) = -70 \cdot 1 \pm 0 \cdot 15$ kcal./mole, was measured by Roth and Schwartz,[1] and confirmed by Chernick (reported by Flitcorft and Skinner [2]). The heat of oxidation of silicon to α-quartz, $\Delta H(2)$, was measured by two independent methods as $-217 \cdot 75 \pm 0 \cdot 32$ kcal./mole [3] and $-217 \cdot 5 \pm 0 \cdot 5$ kcal./mole,[4] the mean value being $-217 \cdot 63 \pm 0 \cdot 32$ kcal./mole. $\Delta H(3)$ and $\Delta H(4)$ were measured by Coughlin [5] and by Humphrey and King [6] as $+0 \cdot 35 \pm 0 \cdot 05$ and $+1 \cdot 19 \pm 0 \cdot 05$ kcal./mole, respectively. The heat of transformation of amorphous silica to a colloidal solution is less certain, as the final state is not well-defined. However, Thiessen and Koerner [7] measured the heats of hydration of amorphous silica to a number of distinct hydrates, including $SiO_2,2H_2O$, $2SiO_2,3H_2O$, and SiO_2,H_2O. The heats lie in the range $-1 \cdot 2$ to $-1 \cdot 5$ kcal./mole SiO_2. It seems likely, therefore, that $-1 \cdot 5$ kcal./mole is a minimum value for $\Delta H(5)$. Taking these values for $\Delta H(1)$ to $\Delta H(5)$, and the heats of formation: H_2O (liq.) $-68 \cdot 3149 \pm 0 \cdot 0096$ kcal./mole,[8] and HCl (aq.) $-40 \cdot 02$ kcal./mole,[9] the heat of formation $\Delta H_f°(SiCl_4, \text{liq.})$ is calculated to be $-170 \cdot 9 \pm 0 \cdot 7$ kcal./mole. A more direct determination, using the heat of reaction, $\Delta H(6)$, of silicon tetrachloride with aqueous hydrofluoric acid (reaction 6), which is well-defined thermochemically, is reported in this Paper.

$$SiCl_4(\text{liq.}) + [185HF, 802H_2O] \longrightarrow [H_2SiF_6, 179HF, 4HCl, 802H_2O] \qquad (6)$$

$$[H_2SiF_6, 179HF, 758H_2O] + 4[HCl, 11H_2O] \longrightarrow [H_2SiF_6, 179HF, 4HCl, 802H_2O] \qquad (7)$$

$$HCl(\text{g.}) + 11H_2O(\text{liq.}) \longrightarrow [HCl, 11H_2O] \qquad (8)$$

$$SiCl_4(\text{liq.}) + [185HF, 802H_2O] \longrightarrow [H_2SiF_6, 179HF, 758H_2O] + 4HCl(\text{g.}) + 44H_2O(\text{liq.}) \qquad (9)$$

* Part XI, *J.*, 1964, 1965.
[1] Roth and Schwartz, *Z. phys. Chem.*, 1928, **134**, 456.
[2] Flitcroft and Skinner, *J.*, 1956, 3355.
[3] Wise, Margrave, Feder, and Hubbard, *J. Phys. Chem.*, 1962, **66**, 381.
[4] Good, *J. Phys. Chem.*, 1962, **66**, 380.
[5] Coughlin, Bureau of Mines Bulletin 542, Washington, D.C., 1954, reported by Feder, Hubbard, Wise, and Margrave, *J. Phys. Chem.*, 1963, **67**, 1148.
[6] Humphrey and King, *J. Amer. Chem. Soc.*, 1952, **74**, 2041.
[7] Thiessen and Koerner, *Z. anorg. Chem.*, 1931, **197**, 307.
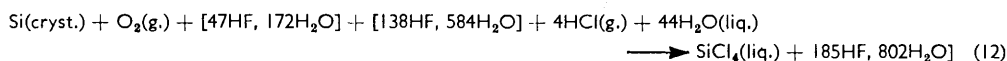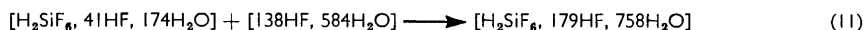[8] Wagman, Kilpatrick, Taylor, Pitzer, and Rossini, *J. Res. Nat. Bur. Stand.*, 1945, **34**, 143.
[9] Nat. Bur. Stand. (U.S.) Circ., No. 500, Washington, D.C., 1952.

The heat, $\Delta H(7)$, of mixing an aqueous solution of hydrochloric acid with an aqueous solution of fluorosilicic acid and hydrofluoric acid (reaction 7) has also been measured. These data, together with the well-established heat of solution, $\Delta H(8) = 16 \cdot 72 \pm 0 \cdot 01$ kcal./mole [9] (reaction 8), make it possible to calculate the heat of reaction (9), from the relationship

$$\Delta H(9) = \Delta H(6) - \Delta H(7) - 4\Delta H(8)$$

Good [4] measured the heat, $\Delta H(10) = -250 \cdot 3 \pm 0 \cdot 3$ kcal./mole, of reaction (10), so that, with the additional heat, $\Delta H(11)$, of the dilution reaction (11), it is possible to calculate $\Delta H(12)$ from the relationship

$$\Delta H(12) = \Delta H(10) + \Delta H(11) - \Delta H(9)$$

$$\text{Si(cryst.)} + O_2(g.) + [47HF, 172H_2O] \longrightarrow [H_2SiF_6, 41HF, 174H_2O] \qquad (10)$$

$$[H_2SiF_6, 41HF, 174H_2O] + [138HF, 584H_2O] \longrightarrow [H_2SiF_6, 179HF, 758H_2O] \qquad (11)$$

$$\text{Si(cryst.)} + O_2(g.) + [47HF, 172H_2O] + [138HF, 584H_2O] + 4HCl(g.) + 44H_2O(liq.)$$
$$\longrightarrow SiCl_4(liq.) + 185HF, 802H_2O] \qquad (12)$$

The heat of formation of silicon tetrachloride can then be calculated from the expression

$$\Delta H_f^\circ(SiCl_4, liq.) = \Delta H(12) + 4\Delta H_f^\circ(HCl, g.) - 2\Delta H_f^\circ(H_2O, liq.) + \Sigma\Delta H_s$$

where

$$\Sigma\Delta H_s = 47\Delta H_s[HF \text{ in } 3 \cdot 66H_2O] + 138\Delta H_s[HF, \text{ in } 4 \cdot 24H_2O] - 185[HF, \text{ in } 4 \cdot 33H_2O].$$

The heats of formation, H_2O (liq.) $-68 \cdot 3149 \pm 0 \cdot 0096$,[8] and HCl (g.) $-22 \cdot 061 \pm 0 \cdot 01$,[9] and the heats of solution, HF (g.) in $3 \cdot 66H_2O$ $-11 \cdot 246$, HF (g.) in $4 \cdot 24H_2O$ $-11 \cdot 289$, and HF (g.) in $4 \cdot 33H_2O$ $-11 \cdot 293$ kcal./mole [9] are also required. It is noteworthy that the calculated heat of formation of silicon tetrachloride depends only on the heats of formation of liquid water and of gaseous hydrogen chloride, on the heats of solution of hydrogen chloride and hydrogen fluoride in water, and on the heats of reactions (6), (7), (10), and (11).

The heats of reactions (6) and (7) have been measured in a calorimeter fitted with an adiabatic jacket, and, since the construction differs in some ways from that of others which have been described previously for use with hydrofluoric acid solutions,[10] some details of the reaction vessel are given.

EXPERIMENTAL

Compounds.—Silicon tetrachloride (B.D.H., redistilled, b. p. $57 \cdot 5^\circ/743$ mm.) was distilled a number of times through a 36 in. Fenske column in an atmosphere of oxygen-free nitrogen. It was transferred, in an atmosphere of pure nitrogen, to small weighed glass phials, the outside of which were coated with Flucalub-H (a suspension of Teflon in Freon). Hydrofluoric acid (40%) and hydrochloric acid (36%; B.D.H. AnalaR) were diluted to the required concentrations before use.

Calorimeter.—The reaction vessel, shown in the Figure, was a cylindrical can (A) (diam. $7 \cdot 5$ cm., height $12 \cdot 0$ cm.) fitted with a PTFE washer (B) and closed by a flanged lid (C). The lid was provided with three chimneys (internal diam., $1 \cdot 9$, $1 \cdot 5$, and $1 \cdot 3$ cm.) in which PTFE rings (D) were set, in order to close the system and prevent the escape of reactants. A stirrer shaft (E) supported by two stainless steel ballraces (F) passed through the PTFE rings in the largest chimney. A PTFE rod, which passed through the rings in the intermediate-sized chimney, held an inverted phial (G), filled with a weighed quantity of silicon tetrachloride, which could be broken by pressing it on a spike in the base of the vessel. The can also contained a resistance heater (H) ($101 \cdot 00 \pm 0 \cdot 05$ ohms) made from manganin wire round non-inductively on a mica sheet and encased in a thin oil-filled sheath. Leads of negligible resistance passed

[10] Torgeson and Sahama, *J. Amer. Chem. Soc.*, 1948, **70**, 2156; King, *J. Amer. Chem. Soc.*, 1951, **73**, 656; Coughlin, " Experimental Thermochemistry," vol. 2, ed. Skinner, Interscience, New York, 1962, p. **304**.

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through a tube, which was supported by the PTFE rings in the smallest chimney. Except where indicated otherwise, rhodium-plated copper was used throughout in the construction of these parts.

The vessel was immersed in water, to 1·5 cm. below the top of the chimneys, contained in a calorimeter can, which was provided with a stirrer and a metal lid. The shaft of this stirrer had a wheel (I) attached below the lid. A pin, mounted eccentrically on this wheel, passed through the lid. The wheel was connected by a rubber drive to a similar wheel (J) attached to the shaft (E) of the stirrer in the reaction vessel. The pin engaged a horizontal bar fixed to the underside of a third wheel (K) which was connected to a ballrace let into a hollow lid, forming part of an adiabatic jacket surrounding the calorimeter can. The can and jacket were separated by an air space of 1·5 cm. The adiabatic jacket, manufactured by A. Gallenkamp and Co. Ltd, for use with a combustion bomb, is described in detail elsewhere.[11]

The resistance heater was connected in series with a standard resistance of 1·0003 ohms, at 23°, and with a current supply. This supply consisted of three banks, each of four, 40 amp. hr., 12v lead accumulators joined in series. The banks were connected in parallel to give a potential of 48v. The resistance heater was also connected by heavy copper leads (16 s.w.g., total length 4 yd., resistance 0·0298 ohm) to two standard resistances of 100·004 and 10,000·4 ohms, joined in series. The circuit was similar to that described by Skinner, Sturtevant, and Sunner.[12] The current flowing through, and the potential across, the resistance heater were determined from the potentials across the standard 1 ohm and 100 ohm resistances, measured with a Pye precision vernier potentiometer capable of reading 0·00001v, in conjunction with a cadmium cell (Pye and Co. Ltd.), having an e.m.f. of 1·01848v at 23°. Corrections were applied to these measured potentials for (a) the current flowing through the circuit containing the two standard resistances of 100 and 10,000 ohms, and (b) the potential drop along the leads from these resistances to the resistance heater.
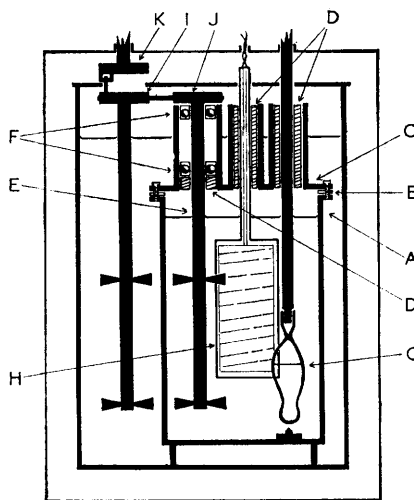
The energy equivalent, E, of the calorimeter was determined by observing the change in resistance, ΔR, of a platinum resistance thermometer immersed in the water in the calorimeter can, when a measured current was passed through the resistance heater, at a measured potential for a known time. This time, usually about 300 sec., was measured by a Millisecond Stop-clock, Type TSA4 (Venner Electronics, Ltd.), to an accuracy of better than ±0·01 sec.

Initially, the vessel was charged with water, and the energy equivalent of the system was determined with the resistance heater placed (a) in the reaction vessel, and (b) in the calorimeter can. The mean values of the two energy equivalents differed by only 0·015%. In subsequent determinations of the energy equivalent, when the vessel was charged with hydrofluoric acid, the resistance heater was placed in the calorimeter can for convenience. The vessel was charged with the same quantities of products which were present after reactions (6) and (7) had occurred $E = 26·038$ kcal./ohm (standard deviation of mean, $\bar{s}E$, +0·013 kcal./ohm, i.e., ±0·05%).

Since the temperatures of the water in the calorimeter can and in the surrounding jacket were always the same, no corrections for heat exchange between the two were necessary, and no account had to be taken of the much slower rate of temperature rise in the determination of the energy equivalent, as compared with that accompanying the hydrolysis of silicon tetrachloride.

The coating of Teflon on the outside of the glass phials prevented reaction between the hydrofluoric acid and the phial, before it was broken. Independent measurements showed that, after the phial was broken, the rate at which it dissolved in the hydrofluoric acid solution

[11] *Lab. Practice*, 1959, **8**, 119.
[12] Skinner, Sturtevant, and Sunner, " Experimental Thermochemistry," vol. 2, ed. Skinner, Interscience, New York, 1962, p. 179.

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was constant and slow.   Correction for this heat effect was made simply by interpolating the rate of heating during the post-reaction period to the time at which the ampoule was broken.

Units.—Heat quantities are given in units of the thermochemical calorie, 1 cal. = 4·1840 abs. J.   The atomic weights used are those recommended by the International Union in 1961.[13] All heats of formation and of reaction quoted from other sources have been recalculated in terms of these atomic weights.   Reactions were carried out so that the final temperature was 25°.   Weights used were calibrated against N.P.L. standards.

Results.—Details of the measurements of the heat of hydrolysis of silicon tetrachloride, $\Delta H(6)$, are shown in the Table.   The heat of mixing of hydrochloric acid solution and an

Heat of hydrolysis of silicon tetrachloride (M, 169·898).

Wt. of SiCl$_4$ (grams)	3·30250	4·79024	4·09586	5·10645	4·66000
ΔR (ohm)	0·07270	0·10555	0·09050	0·11335	0·10350
$-\Delta H$ (kcal./mole)	97·38	97·75	98·20	98·25	97·48

Mean $\Delta H(6)$ = −97·81 ± 0·36 kcal./mole (standard deviation of mean ±0·18%).

aqueous solution of fluorosilicic acid in hydrofluoric acid, $\Delta H(7)$, was measured as +0·80 ± 0·04 kcal./mole.   The errors, $\bar{s}\Delta H(6)$ and $\bar{s}\Delta H(7)$, associated with the heats of these reactions, are twice the standard deviations of the mean values.   The design of the calorimeter made it difficult to measure the heat of the dilution reaction (11).   However, since the initial concentration of fluorosilicic acid in this reaction is already very low, the heat of dilution is likely to be very small and is neglected.

DISCUSSION

Calculations using the values of $\Delta H(6)$ and $\Delta H(7)$ and other thermochemical data given above yield $\Delta H_f°(\text{SiCl}_4, \text{liq.}) = -170\cdot2 \pm 0\cdot8$ kcal./mole.   This value is close to that calculated from the heat of hydrolysis in aqueous solution, $-170\cdot9 \pm 0\cdot7$ kcal./mole. Accepting the value $\Delta H_{\text{vap.}} = 7\cdot0$ kcal./mole[9] for the heat of vaporisation of silicon tetrachloride, the heat of formation, $\Delta H_f°(\text{SiCl}_4, \text{g.}) = -163\cdot2 \pm 0\cdot8$ kcal./mole is obtained.

The mean bond dissociation energy, $\overline{D}(\text{Si–Cl}) = 97\cdot2 \pm 0\cdot7$ kcal./mole, can be calculated from the expression

$$\overline{D}(\text{Si–Cl}) = \tfrac{1}{4}\Delta H_f°(\text{Si, g.}) + \Delta H_f°(\text{Cl, g.}) - \tfrac{1}{4}\Delta H_f° (\text{SiCl}_4, \text{g.})$$

This value is based on the heat of formation of gaseous silicon tetrachloride given above, and the values $\Delta H_f°$ (Cl, g.) = 28·94 kcal./g.-atom,[14] and $\Delta H_f°$ (Si, g.) = 110 ± 2 kcal./g.-atom.   Measurements of the vapour pressure of silicon and the dissociation pressure of silicon carbide[15] yielded values of 108·4 ± 3 and 112·6 ± 3 kcal./g.-atom, respectively, for the heat of formation of gaseous silicon.   The latter value also depends on a value for the heat of formation of silicon carbide of −13 ± 1 kcal./mole, which is in some doubt. However, until the discrepancy between the two values for the heat of formation of gaseous silicon is resolved, it is reasonable to take a mean value of 110 ± 2 kcal./g.-atom.

Steele, Nichols, and Stone[16] obtained the value $D(\text{Cl}_3\text{Si–Cl}) = 106 \pm 4$ kcal./mole, from electron-impact data, for the dissociation energy of the first silicon–chlorine bond. From the expression

$$\Delta H_f°(\text{SiCl}_3, \text{g.}) = D(\text{Cl}_3\text{Si–Cl}) + \Delta H_f°(\text{SiCl}_4, \text{g.}) - \Delta H_f° (\text{Cl, g.})$$

and the data given previously, the value $\Delta H_f°(\text{SiCl}_3, \text{g.}) = -86\cdot1 \pm 4\cdot8$ kcal./mole is calculated.

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[13] *J.*, 1961, 5564.
[14] Cottrell, " The Strengths of Chemical Bonds," 2nd edn., Butterworths, London, 1958.
[15] Davis, Anthrop, and Searcy. *J. Chem. Phys.*, 1961, **34**, 659.
[16] Steele, Nichols, and Stone, *J. Amer. Chem. Soc.*, 1962, **84**, 4441.