233. *The Heats of Formation of Germanium Tetrabromide and Germanium Tetraiodide.*

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The heats of solution of germanium tetrabromide and tetraiodide, and of germanium dioxide in 1·2N-sodium hydroxide solution have been measured. From these results the heats of formation of the two tetrahalides have been deduced. The bond energies and stabilisation energies of the Ge–Br and the Ge–I link in these compounds are also given.

Of the germanium tetrahalides, the chloride is the only one for which reliable thermochemical data are available. Roth and Schwartz (*Z. physikal. Chem.*, 1928, **134**, 456) determined the heat of formation from the heat of hydrolysis in water to give germanium dioxide (colloidal) and hydrochloric acid. Since only one of their experiments was successful owing to separation of solid germanium dioxide, and since the heat of formation of a colloidal solution of germanium dioxide is probably less accurately known than that of solid GeO_2, a modified procedure has been used in these measurements. The heats of solution of germanium tetrabromide and tetraiodide in 1·2N-sodium hydroxide to give sodium germanate and sodium halide were measured, and combined with the heat of solution of GeO_2 in the same solvent.

Experimental

Commercial germanium tetrabromide was fractionally crystallised in a sealed vessel, and then had m. p. 26° (Dennis and Hance, *J. Amer. Chem. Soc.*, 1922, **44**, 299, give 26·1°). Germanium tetraiodide, prepared by the method of " Inorganic Syntheses," Vol. II, p. 112, and twice recrystallised from chloroform, had m. p. 146°. A pure specimen of germanium dioxide from Messrs. Johnson Matthey was used without further purification.

The calorimetric measurements were made with a modified form of the adiabatic calorimeter described by Cottrell and Wolfenden (*J.*, 1948, 1019). The solvent was placed in the cylindrical silver calorimeter, and the sample was contained in a small glass tube mounted on a silver frame inside the calorimeter. The open end of the glass tube was ground flat, and a mica lid was fastened to the end of the tube by a thin film of oil, and when the calorimeter rotated, this lid was dislodged by a glass-coated weight. Experiments made with thin glass lids, and greases of various kinds, showed that a much heavier weight was required to dislodge the lid. This was unsatisfactory as it gave rise to large and irregular heats of stirring. The glass tube, sealed as described with a mica lid, showed no gain in weight during 12 hours, when filled with calcium chloride and kept in an atmosphere saturated with water vapour. The calorimeter was calibrated by means of the heat of solution of solid potassium chloride in water, the following value being assumed :

$$\mathrm{KCl(solid)} + 200\mathrm{H_2O} = \mathrm{KCl,200H_2O};\ \Delta H = 4{\cdot}201\ \text{kcal. at } 25^\circ$$

(" Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, 1948.) The heat of hydrolysis of germanium tetraiodide was also measured with a twin calorimeter of high sensitivity, electrical calibration being used. The sample was contained in a sealed glass bulb which was broken at the beginning of the experiment. A description of this calorimeter will be published later.

The heat of the reaction Ge(solid) + O_2 = GeO_2(solid) has been measured by Becher and Roth (*Z. physikal. Chem.*, 1932, *A*, **161**, 69; 128·1 kcal.) and by Hahn and Juza (*Z. anorg. Chem.*, 1940, **244**, 111; 128·6 kcal.). The value given in the " Selected Tables of Thermodynamic Properties," *viz.*, 128·3 kcal., was accordingly adopted. The heats of formation of sodium hydroxide, iodide, and bromide in solution were also taken from the same source (the difference between the heats of formation of the halides in water and in 1·2N-sodium hydroxide solution being assumed to be small), and also the heats of vaporisation, sublimation, or dissociation of germanium (78·44 kcal./g.-atom) and germanium tetrabromide, bromine, and iodine. The heat of sublimation of germanium tetraiodide was assumed to be the same as for tin tetraiodide, which has very similar m. p. and b. p.

The results are given in the following table, from which we have

$$\mathrm{Ge(solid)} + 2\mathrm{Br_2(liquid)} = \mathrm{GeBr_4(liquid)};\ \text{mean } \Delta H = -\ 78{\cdot}5\ \text{kcal./mole}$$

$$\mathrm{Ge(solid)} + 2\mathrm{I_2(solid)} = \mathrm{GeI_4(solid)};\ \text{mean } \Delta H = -\ 30{\cdot}5\ \text{kcal./mole}$$

Whence bond energy of Ge–Br link = 63·5 kcal./mole, and of Ge–I link = $48{\cdot}_1$ kcal./mole.

Wt. of Ge compd., g.	Wt. of 1·2N-NaOH, aq., g.	Δt	Final temp.	$-\ \Delta H$, kcal./mole
Heat of hydrolysis of germanium tetrabromide (liquid).				
0·2948	52·10	0·905°	27·4°	92·0
0·2358	52·12	0·721	27·3	91·6
0·2008	52·10	0·611	27·2	91·4
Heat of hydrolysis of germanium tetraiodide (solid).				
0·1990	52·20	0·3486	27·1	78·0
0·06870 *	*ca.* 305	—	25·0	77·3
* Second measurement made with twin calorimeter.				
Heat of solution of germanium dioxide in 1·2N-sodium hydroxide solution.				
0·0778	52·12	0·0936	26·7	9·50

Discussion.—If the bond energy of a pure covalent bond A–B is defined as the arithmetic mean of the bond energies of A_2 and B_2, then one-quarter of the heats of formation of the gaseous germanium (or silicon) tetrahalides from solid germanium or silicon and gaseous halogen is equal to the stabilisation energies of the M–halogen bond due to such factors as ionic character and possibly double-bond character (Pauling, " Nature of the Chemical Bond," 2nd edn., p. 61). The heats of formation of gaseous germanium tetrabromide and tetraiodide together with those for other gaseous tetrahalides are given below. The additional thermodynamical data are from " Selected Values, etc." (see above), except the heat of sublimation of silicon tetraiodide which is an estimated one (Brewer, in " The Chemistry and Metallurgy of Miscellaneous Materials," edited by Quill).

Heats of formation (kcal./mole) of gaseous compounds from solid metals and gaseous halogens.

$SiCl_4$	145·7	$SiBr_4$	100·7	SiI_4	$47{\cdot}_7$
$GeCl_4$	122	$GeBr_4$	83·3	GeI_4	$42{\cdot}_0$

It is noteworthy that the stabilisation energies are less for germanium halides than for silicon halides, indicating that the simple interpretation of these bonds in terms of ionic and covalent character is incomplete, since on this basis alone the converse might be expected.

A similar situation is found in the observed bond contractions (sum of covalent radii minus actual bond distance) for silicon–halogen and germanium–halogen links, which are usually greater in the former than in the latter. This is clearly shown in accurate microwave measurements (Sheridan and Gordy, *J. Chem. Physics*, **1951**, **19**, 965).

We thank the Department of Scientific and Industrial Research for a Maintenance Grant (D. F. E.).

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[*Received, December,* 13*th* 1951.]