stirring blades on the end, but also had a hole near the bottom which permitted bubbling inert gas through the solution in the calorimeter. The water in the calorimeter was deaerated before each run. Three runs gave for $\Delta H$, $-9.37$, $-9.46$ and $-9.34$ kcal./mole. With the aid of the Debye–Hückel equation, these heats were extrapolated to infinite dilution to give $-9.63$, $-9.72$ and $-9.57$ kcal./mole. We shall take $\Delta H^\circ = -9.64 \pm 0.10$ kcal./mole for reaction (4).

By adding together the heats for reactions (1), (−2), (3) and (4), we obtain for (5), $\Delta H^\circ = -25.1 \pm 2.0$ kcal./mole. By adding $\Delta H^\circ = -1.0$ kcal./mole[6] for reaction (6), we obtain $\Delta H^\circ = -26.1 \pm 2.0$ kcal./mole for reaction (7).

The two experimentally independent methods have given essentially the same value for the heat of reaction (7), and we shall take $\Delta H^\circ = -26.0 \pm 1.0$ kcal./mole.

Pugh,[7] Laubengayer and Morton,[8] Schwarz and Huf[9] and Winkler[10] measured the solubility of $GeO_2$ at various temperatures. From the temperature coefficient of the solubility, we can obtain an approximate value for the heat of solution of the soluble form of $GeO_2$. It appears that the two low temperature measurements of Schwarz and Huf give solubilities which are too high. For the process $H_2O + GeO_2(ppt.) = H_2GeO_3(aq)$ we calculate $\Delta H^\circ = +3.3 \pm 1.0$ kcal./mole. Pugh gave the solubility of $GeO_2$ in water as 4.47 g. per liter at 25°, while Laubengayer and Morton reported 4.53 g. Taking an average of 4.50 g. per liter, we find $\Delta F^\circ = +1.86$ kcal./mole for the solution of $GeO_2$. Combining this with the above heat yields $\Delta S^\circ = +4.7 \pm 3.4$ e.u. By estimating $S^\circ = 13$ e.u. for $GeO_2$ (using Latimer's tables[11]) we calculate the entropy of $H_2GeO_3(aq)$ to be $34.5 \pm 4.0$ e.u.

For the oxidation of $GeI_2$ to $GeO_2$ by triiodide

$$2H_2O + GeI_2(s) + I_3^- = GeO_2(s) + 4H^+ + 5I^-$$

we calculate $\Delta H^\circ = -29.3 \pm 1.4$ kcal./mole.

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[6] National Bureau of Standards, Selected Values of Chemical Thermodynamic Properties, Washington, D. C., 1947, *et seq.*

[7] W. Pugh, *J. Chem. Soc.*, 1537 (1929).

[8] A. W. Laubengayer and D. S. Morton, This Journal, **54**, 2318 (1932).

[9] R. Schwarz and E. Huf, *Z. anorg. Chem.*, **203**, 195 (1931).

[10] C. Winkler, *J. prakt. Chem.*, [2] **34**, 213 (1886).

[11] W. M. Latimer, This Journal, **73**, 1480 (1951).

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[Contribution from the Department of Chemistry and Chemical Engineering, and Radiation Laboratory, University of California]

# The Vapor Pressure of Germanic Iodide. The Entropies of Germanic Halides. The Disproportionation of Germanous Iodide

By William L. Jolly[1] and Wendell M. Latimer

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Germanic iodide sublimes readily at temperatures in the neighborhood of 100°, and in this research the vapor pressure has been measured over a range of 55°. These data have been employed to calculate $\Delta F^\circ$ and $\Delta H^\circ$ for the sublimation. Since there are no values for the entropy of $GeI_4(g)$, the method of Hildebrand has been employed to estimate the vibrational frequencies and hence calculate the entropy. The vapor pressure of $GeI_4(g)$ over mixtures of Ge and $GeI_2$ has been measured over a range of 100°. These data have been employed to calculate $\Delta F^\circ$ and $\Delta H^\circ$ for the disproportionation of $GeI_2$.

**The Vapor Pressure of $GeI_4(s)$.**—A saturated vapor flow-method was employed. Germanic iodide crystals were placed in a horizontal glass tube which was heated to a constant temperature while a steady stream of argon was passed through the tube. By assuming that the gas was saturated with $GeI_4$ vapor in passing through the tube, the amount of $GeI_4$ which condensed out on the cooler portions of the tubing was taken as a measure of the vapor pressure.

**Experimental Procedure.**—Germanic iodide was prepared by the method of Foster and Williston.[2] The product was purified by recrystallization from chloroform followed by air drying at 80°.

Two methods for heating the tube containing the $GeI_4$ were used. In two low temperature experiments the tubing was heated by a vapor-jacket similar to that used in Abderhalden driers. The vapors of boiling benzene and of boiling water were used to maintain the temperatures 79.8 and 99.8°, respectively. Higher temperatures were maintained by heating the tubing in a horizontal tube furnace. A "Celectray" electronic controller (C. J. Tagliabue Mfg. Co.) was used in conjunction with a chromel–alumel thermocouple to keep the temperature of the furnace constant to ±3°. The thermocouple was calibrated at the boiling point of water and the melting points of ice, tin and cadmium. A sheath of nickel foil was wrapped around the tubing where the $GeI_4$ was contained.

Linde argon was freed of oxygen and water by passing the gas consecutively through hot copper turnings and magnesium perchlorate. The total volume of gas passed in a run was determined by collecting the gas over water at the end of the flow system. (It was necessary to correct for the vapor pressure of water.) The runs were timed with an

Table I

The Vapor Pressure of $GeI_4(s)$

| Run | $T$, °K. | Time, min. | Flow rate, mole A/min. | Total pressure in tube, atm. | Calcd. vapor pressure of $GeI_4$, atm. |
|---|---|---|---|---|---|
| A | 393 | 106 | $0.746 \times 10^{-3}$ | 0.999 | $8.2 \times 10^{-4}$ |
| B | 393 | 206 | $0.387 \times 10^{-3}$ | 1.007 | $8.4 \times 10^{-4}$ |
| C | 393 | 47 | $1.69 \times 10^{-3}$ | 1.008 | $7.1 \times 10^{-4}$ |
| | 393 | | 0 (extrap.) | | $8.7 \times 10^{-4}$ |
| D | 408 | 75 | $0.527 \times 10^{-3}$ | 1.010 | $1.79 \times 10^{-3}$ |
| E | 379 | 203 | $.774 \times 10^{-3}$ | 1.000 | $2.9 \times 10^{-4}$ |
| F | 373.0 | 215 | $.735 \times 10^{-3}$ | 1.002 | $2.20 \times 10^{-4}$ |
| G | 353.0 | 380 | $.634 \times 10^{-3}$ | 0.999 | $4.7 \times 10^{-5}$ |

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[1] Taken from a thesis presented by William L. Jolly for partial satisfaction of the requirements of the Ph.D. degree, University of California, 1952.

[2] L. S. Foster and A. F. Williston, *Inorg. Syntheses*, **2**, 112 (1946).

electric timer; runs were started by suddenly bringing the temperature up to the desired point and ended by suddenly removing the heat.

Quantitative condensation of the volatilized $GeI_4$ was found to occur in the cool, narrow tubing immediately outside the hot zone. This narrow tubing was cracked off after each run and the sublimed $GeI_4$ was dissolved. The iodide was titrated to $ICl_2^-$ with a standard permanganate solution. Details of the run are given in Table I.

Runs A, B and C were carried out at the same temperature, but with different flow rates. It can be seen that relatively good vapor saturation is attained if the flow rate is kept below about $0.7 \times 10^{-3}$ mole argon/minute. The error due to incomplete saturation in the remaining runs is probably less than 10% in the vapor pressure.

**Interpretation of Data.**—A very satisfactory representation of vapor pressure data is given by an equation of the form

$$\Delta F^\circ = \Delta H_0^\circ - \Delta C_p^\circ T \ln T + IT$$

where $\Delta H_0^\circ$ and $I$ are empirical constants. In this case $\Delta C_p^\circ$ is the difference in heat capacity between the gas and solid. In the second part of this paper we calculate $C_p^\circ = 25.1$ for $GeI_4(g)$ at 25°; by Kopp's rule we estimate $C_p^\circ = 33$ for the solid. Taking $\Delta C_p^\circ$ to be $-8$, we have plotted the "sigma function," $\Delta F^\circ/T + \Delta C_p^\circ \ln T$, *versus* $1/T$. The slope of the straight line drawn through the points is $\Delta H_0^\circ = 22{,}500$ cal./mole. The intercept on the $1/T = 0$ axis is $I = -90.8$. Hence the free energy of sublimation of $GeI_4$ can be represented within experimental error by the equation

$$\Delta F^\circ = 22{,}500 + 8\,T \ln T - 90.8T$$

The heat and entropy of sublimation can similarly be represented by

$$\Delta H^\circ = 22{,}500 - 8T$$
$$\Delta S^\circ = 82.8 - 8 \ln T$$

At 298°K., these functions have the values: $\Delta F_{298}^\circ = 9.0$ kcal./mole, $\Delta H_{298}^\circ = 20.1$ kcal./mole, $\Delta S_{298}^\circ = 37$ e.u.

**The Heat Capacities and Entropies of Germanium Tetrahalides.**—Sufficient experimental data exist for germanium tetrafluoride, germanium tetrachloride and germanium tetrabromide to calculate their entropies on the basis of molecular constants. Both the vibrational energies[3–5] and the interatomic distances[6–8] are known. It was necessary to estimate the vibration frequencies for $GeI_4$. Hildebrand[9] has shown that when $\nu_1$ and $\nu_2$ (for various tetrahalides) are plotted against interatomic distance, smooth curves are obtained, which are roughly straight lines. The points on each curve are characterized by the same halogen and mode of vibration; each point on a given curve represents a tetrahalide with a different central atom. An extension of this idea was used in estimating the frequencies for germanium tetraiodide. Figure 1 shows a plot of all four vibrational frequencies of $GeF_4$, $GeCl_4$ and $GeBr_4$ against the Ge–X distance. It is apparent that the points for a given mode of vibration form a smooth curve, approximating a straight line. (A similar set of curves is obtained for the silicon tetrahalides.)

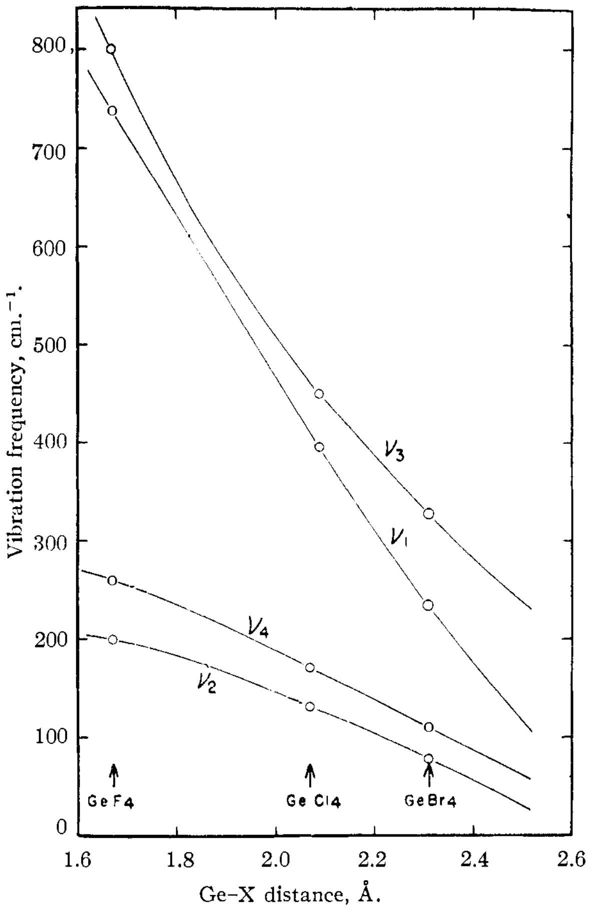

Fig. 1.—Vibration frequency for germanium tetrahalides.

Lister and Sutton[8] give 2.50 Å. for the Ge–I distance in germanium tetraiodide; by extrapolation we find $\nu_1 = 116 \pm 15$, $\nu_2 = 30 \pm 10$, $\nu_3 = 238 \pm 20$, $\nu_4 = 62 \pm 10$ cm.$^{-1}$. Using tables of Einstein functions[10] and the standard thermodynamic equations, the heat capacities at constant pressure and standard entropies of the germanium tetrahalides were calculated. The results are shown in Table II.

TABLE II

HEAT CAPACITIES AND ENTROPIES OF $GeX_4(g)$ AT 298.16°K.

| | $C_p^\circ$, cal./deg. mole | $S^\circ$, cal./deg. mole |
|---|---|---|
| $GeF_4$ | 19.57 | 72.51 |
| $GeCl_4$ | 22.97 | 83.05 |
| $GeBr_4$ | 24.34 | 94.77 |
| $GeI_4$ | 25.1 | 107.9 |

**The Disproportionation of Germanous Iodide.**—Brewer and Dennis[11,12] have observed that when germanous iodide is heated, it decomposes into germanic iodide and germanium metal. In this investigation, the vapor pressure of $GeI_4(g)$ over mixtures of Ge(s) and $GeI_2(s)$ was measured over the temperature range 544–643°K.

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[3] For $GeF_4$: P. J. H. Woltz and A. H. Nielsen, *J. Chem. Phys.*, **20**, 307 (1952).

[4] For $GeCl_4$: J. T. Neu and W. D. Gwinn, THIS JOURNAL, **70**, 3463 (1948).

[5] For $GeBr_4$: G. Herzberg, "Infra-Red and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945.

[6] For $GeF_4$: A. D. Caunt, H. Mackle and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 943 (1951).

[7] For $GeCl_4$: L. Pauling and L. O. Brockway, THIS JOURNAL, **57**, 2684 (1935).

[8] For $GeBr_4$: M. W. Lister and L. E. Sutton, *Trans. Faraday Soc.*, **37**, 393 (1941) and M. Rouault, *Ann. phys.*, **14**, 78 (1940).

[9] J. H. Hildebrand, *J. Chem. Phys.*, **15**, 727 (1947).

[10] H. L. Johnston, L. Savedoff and J. Belzer, "Contributions to the Thermodynamic Functions by a Planck–Einstein Oscillator in One Degree of Freedom," Office of Naval Research, July, 1949.

[11] F. M. Brewer, *J. Phys. Chem.*, **31**, 1817 (1927).

[12] F. M. Brewer and L. M. Dennis, *ibid.*, **31**, 1537 (1927).

**Experimental Procedure and Results.**—The preparation of germanous iodide has been described in another publication by the authors.[13]

A saturated vapor flow method, with an apparatus similar to that for measuring the vapor pressure of solid $GeI_4$ was used. $GeI_2$ crystals were placed in a glass tube through which dry argon was passed. The tube was heated by a tube furnace (same method of control as in the $GeI_4$ vapor pressure experiments) and the volume of gas passed through the tube was measured by collecting it over water.

When the tube was heated to about 270° reaction commenced and clouds of $GeI_4$ dust began emerging from the furnace. Some of the $GeI_4$ (approximately 50%) condensed in the cool, narrow tubing leading from the reaction chamber, but the remainder passed right into the container used for collecting the argon at the end of the line. Additional coiled glass tubing was put into the line beyond the furnace in an attempt to condense out the $GeI_4$, but even with more than a meter of tubing for condensation, some of the $GeI_4$ particles were swept through the line. Thus it was impossible to accurately determine the amount of $GeI_4$ formed by collecting that which condensed out in the cooler tubing. However, two runs were carried out using this method; the results are given in Table III. In these two runs, the condensed $GeI_4$ was dissolved out of the tubing and titrated with permanganate.

In addition to $GeI_4$ being evolved due to the disproportionation of $GeI_2$, some $GeI_2$ sublimed and quantitatively condensed out. At the end of the runs, this $GeI_2$ could be easily separated from the condensed $GeI_4$, because the $GeI_2$ condensed out in a much hotter zone (almost within the furnace) than did the $GeI_4$. This sublimed $GeI_2$ was also dissolved and titrated with permanganate. Thus these measurements yielded both the vapor pressure of $GeI_2$ and the pressure of $GeI_4$ due to disproportionation.

TABLE III

VAPOR PRESSURES OVER Ge + $GeI_2$

| Run | $T$, °K. | Pressure of $GeI_4$, atm. | Pressure of $GeI_2$, atm. |
|---|---|---|---|
| C' | 557 | $4.1 \times 10^{-4}$ | $1.3 \times 10^{-4}$ |
| D' | 557 | $9.6 \times 10^{-4}$ | $1.6 \times 10^{-4}$ |

It was then decided to modify the flow-method technique. The $GeI_2$ was put in a metal boat and the boat was weighed before and after each run. Then there was no concern over where or how the $GeI_4$ condensed out—the extent of reaction was determined by the change in the weight of the boat, after correcting for the sublimation of $GeI_2$.

For the first five runs, a platinum boat weighing about 4 g. was used. It was noticed after a few runs that the boat was being alloyed by the metallic germanium, and since this alloying might cause erroneous results (because of the formation of non-standard metallic germanium), the remaining runs were carried out using a molybdenum boat weighing about 3 g.

About 2–3 g. of $GeI_2$ was used in each series of runs; volatile impurities were eliminated by making preliminary blank runs. Between runs, the mixture of $GeI_2$ and Ge in the boat was stirred slightly so that the metal particles (which formed mainly on the top surface) would not keep equilibrium from being rapidly established. After four or five runs, so much disproportionation had occurred that, for fear of the metal particles preventing equilibrium, a fresh batch of $GeI_2$ was put in the boat.

In runs 10 and 11 the sublimed $GeI_2$ was separated from the $GeI_4$, dissolved and titrated with permanganate. The vapor pressures for $GeI_2$ calculated from these runs are: at 594°K., $p = 5.1 \times 10^{-4}$ atm.; at 618°K., $p = 20.7 \times 10^{-4}$ atm. Using these data and the data in Table III, we calculate $\Delta F° = 30{,}000 - 36T$ as a rough free energy equation for the sublimation of $GeI_2$. In all the following runs except runs 10 and 11, the amount of sublimed $GeI_2$ was calculated from this equation. The weight of sublimed $GeI_2$ was always about 10% of the total loss in weight, so very little inaccuracy resulted from use of the crude equation.

The experimental data and calculated pressures are presented in Table IV. It can be seen that the trends in calculated pressure with various flow rates are rather small compared to the experimental error. It is difficult to say whether the higher calculated pressures at lower flow rates are due to better equilibria or to convection in the reaction chamber, hence equal weight will be assigned to all the data.

TABLE IV

THE DISPROPORTIONATION OF GERMANOUS IODIDE

| Run | $T$, °K. | Moles of argon | Flow rate, ml./min. | Loss in weight of boat, g. | Weight of sublimed, $GeI_2$ | Moles $GeI_4$ formed $\times 10^5$ | Total pressure, atm. | Pressure of $GeI_4$, atm. $\times 10^3$ |
|---|---|---|---|---|---|---|---|---|
| 2 | 569 | 0.0805 | 16.9 | 0.0961 | 0.0058 | 15.6 | 0.996 | 1.93 |
| 3 | 569 | .0812 | 41.7 | .0540 | .0058 | 8.3 | 1.000 | 1.02 |
| 4 | 569 | .0819 | 54 | .0629 | .0058 | 9.8 | 1.003 | 1.20 |
| 6 | 569 | .0808 | 16.3 | .0592 | .0058 | 9.2 | 1.000 | 1.14 |
| 7 | 594 | .0211 | 6.9 | .0593 | .0048 | 9.4 | 0.995 | 4.4 |
| 8 | 594 | .0211 | 13.8 | .0507 | .0048 | 7.9 | .995 | 3.7 |
| 10 | 594 | .0210 | 21.0 | .0551 | .0036 | 8.9 | .988 | 4.2 |
| 9 | 544 | .236 | 26.8 | .0415 | .0052 | 6.3 | .989 | 0.26 |
| 12 | 544 | .239 | 17.9 | .0762 | .0052 | 12.2 | .993 | 0.51 |
| 11 | 618 | .0210 | 11.2 | .1647 | .0186 | 25.2 | .987 | 11.8 |
| 13 | 643 | .0208 | 12.7 | .3300 | .0329 | 51.2 | .992 | 24.4 |
| 14 | 643 | .0208 | 14.0 | .3569 | .0329 | 55.9 | .992 | 26.7 |

TABLE V

VALUES OF $\Delta H_0^\circ$ FOR THE DISPROPORTIONATION OF $GeI_2$(s)

| Run | $T$, °K. | $\Delta F°$ | $\Delta H_0^\circ$ |
|---|---|---|---|
| 2 | 569 | 7060 | 32,050 |
| 3 | 569 | 7780 | 32,770 |
| 4 | 569 | 7600 | 32,590 |
| 6 | 569 | 7660 | 32,650 |
| 7 | 594 | 6400 | 32,280 |
| 8 | 594 | 6610 | 32,490 |
| 10 | 594 | 6460 | 32,340 |
| 9 | 544 | 8920 | 33,000 |
| 12 | 544 | 8190 | 32,270 |
| 11 | 618 | 5450 | 32,180 |
| 13 | 643 | 4740 | 32,350 |
| 14 | 643 | 4630 | 32,240 |
| C' | 557 | 8630 | 33,170 |
| D' | 557 | 7690 | 32,230 |

The entropy of Ge(s) is 10.1 cal./deg. at 298°K.[14] We have calculated $S_{298}^\circ = 107.9$ for $GeI_4$(g), and by Latimer's tables[15] $S_{298}^\circ = 38.5$ for $GeI_2$(s). Hence $\Delta S_{298}^\circ = 41.0$ cal./deg. for

$$2GeI_2(s) = Ge(s) + GeI_4(g)$$

For $GeI_4$(g), $C_{p_{298}}^\circ = 25.1$ and for Ge(s), $C_{p_{298}}^\circ = 6.2$. Using Kopp's rule, we calculate $C_{p_{298}}^\circ = 19.5$ for $GeI_2$(s). Therefore as a rough approximation we shall take $\Delta C_p^\circ = -8$ for the above reaction from 298 to 643°K. Then $\Delta S° = -8 - I - 8 \ln T$ and $I = -94.6$. For each run in Tables III and IV, it is now possible to calculate $\Delta H_0^\circ$ using the equation

$$\Delta H_0^\circ = \Delta F° - 8T \ln T + 94.6T$$

The calculated values of $\Delta H_0^\circ$ are given in Table V. It can be seen that over the experimental range of 100° there is no significant trend in $\Delta H_0^\circ$. We shall use the average value $\Delta H_0^\circ = 32{,}500$ cal./mole. Hence

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(13) W. L. Jolly and W. M. Latimer, THIS JOURNAL, **74**, 5752 (1952).

(14) K. K. Kelley, U. S. Bureau of Mines Bulletin 477, 1950.

(15) W. M. Latimer, THIS JOURNAL, **73**, 1480 (1951).

$$\Delta H^\circ = 32{,}500 - 8T$$
$$\Delta F^\circ = 32{,}500 + 8\,T\ln T - 94.6T$$
$$\Delta S^\circ = 86.6 - 8\ln T$$

and $\Delta H^\circ_{298} = 30{,}100$ cal./mole, $\Delta F^\circ_{298} = 17{,}900$ cal./mole, $\Delta S^\circ_{298} = 41.0$ cal./deg.-mole.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, AND RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA, BERKELEY]

# The Equilibrium $Ge(s) + GeO_2(s) = 2GeO(g)$. The Heat of Formation of Germanic Oxide

BY WILLIAM L. JOLLY[1] AND WENDELL M. LATIMER

RECEIVED JULY 7, 1952

The vapor pressure of GeO(g) over germanium and germanic oxide has been measured over the range 758–859°K. and the results have been compared with similar data obtained by Bues and v. Wartenberg. Vapor pressure data for GeO(s) obtained by the latter investigators have been discussed. The heat of formation of $GeO_2(s)$ has been determined calorimetrically to be $\Delta H_f^\circ = -129.2 \pm 2.0$ kcal./mole.

**The Equilibrium** $Ge(s) + GeO_2(s) = 2GeO(g)$.—Bues and v. Wartenberg[2] have reported vapor pressures of GeO(g) over both $Ge + GeO_2$ and GeO in the neighborhood of 1000°K. Some inconsistencies in their data have been noticed and will be discussed here. For the reaction GeO(s) = GeO(g), Bues and v. Wartenberg give the equation

$$4.57 \log P_{\text{atm}} = -63{,}000/T + 57.9$$

and for the reaction $^1/_2Ge(s) + {}^1/_2GeO_2(s) = GeO(g)$, they give the equation

$$4.57 \log P_{\text{atm}} = -54{,}800/T + 42.0$$

These data give for the reaction $^1/_2Ge(s) + {}^1/_2GeO_2(s) = GeO(s)$ at 1000°K., $\Delta H^\circ = -8.2$ kcal./mole, $\Delta F^\circ = +7.7$ kcal./mole and $\Delta S^\circ = -15.9$ e.u. Such a large entropy change is difficult to imagine for such a proportionation; one would expect the entropy change to be very close to zero or slightly positive.

If we admit the existence of solid GeO, then it appears that Bues and v. Wartenberg have erred in drawing a straight line through their log $P$ *vs.* $1/T$ plot for GeO. In general, it is more satisfactory to estimate entropies and heat capacities when interpreting vapor pressure data. We have estimated $\Delta C_p^\circ = -3$ cal./deg. mole and $\Delta S^\circ_{298} = 42$ e.u. for both sublimations. From the equation $\Delta H_0^\circ = \Delta F^\circ - 6.9T\log T + 62T$, we have calculated values of $\Delta H^\circ$ for the two sets of data of Bues and v. Wartenberg. For the reaction $^1/_2Ge(s) + {}^1/_2GeO_2(s) = GeO(g)$, the average $\Delta H_0^\circ = 54.1$ kcal./mole. For the reaction GeO(s) = GeO(g), the calculated values of $\Delta H_0^\circ$ ranged from 46.8 to 49.0 kcal./mole.

Using a Knudsen effusion cell, we have measured the vapor pressure of what we thought to be GeO(s) over the temperature range 758–859°K. In Table I we have listed our experimental results and the calculated values of $\Delta H_0^\circ$.

TABLE I

OBSERVED VAPOR PRESSURES AND CALCULATED VALUES OF $\Delta H_0^\circ$[3]

| $T$, °K. | Pressure, atm. | $\Delta H_0^\circ$, cal./mole |
|---|---|---|
| 770 | $1.3 \times 10^{-6}$ | 53,160 |
| 788 | $1.8 \times 10^{-6}$ | 53,790 |
| 816 | $2.6 \times 10^{-6}$ | 55,030 |
| 835 | $1.06 \times 10^{-5}$ | 53,940 |
| 758 | $6.7 \times 10^{-8}$ | 56,790 |
| 816 | $1.5 \times 10^{-6}$ | 55,930 |
| 790 | $3.7 \times 10^{-7}$ | 56,440 |
| 859 | $7.7 \times 10^{-6}$ | 55,960 |

The average $\Delta H_0^\circ$, 55.1 kcal./mole, is in fair agreement with the value calculated from Bues and v. Wartenberg's data for the reaction $^1/_2Ge(s) + {}^1/_2GeO_2(s) = GeO(g)$. We therefore feel that our solid phase was a mixture of germanium and germanium dioxide. By averaging the two values of $\Delta H_0^\circ$, we calculate the equations for the sublimation of GeO from a mixture of Ge and $GeO_2$

$$\Delta F^\circ = 54{,}600 + 6.9T\log T - 62T \text{ (cal./mole)}$$
$$\Delta H^\circ = 54{,}600 - 3T \text{ (cal./mole)}$$
$$\Delta S^\circ = 59 - 6.9\log T \text{ (cal./deg. mole)}$$

At 298°K., $\Delta H^\circ = 53.7 \pm 1.0$ kcal./mole. It is possible to calculate the heat of this reaction from independent data. Brewer and Mastick[4] have shown that linear Birge–Sponer extrapolations of vibrational levels give the correct dissociation energies for CO, SiO, SnO and PbO. Hence we feel confident in using the value $\Delta H^\circ = 159$ kcal./mole for the dissociation of GeO(g) (calculated by Herzberg[5] using a linear Birge–Sponer extrapolation). In Table II we have presented the latter heat, the heat of sublimation of germanium,[6] the dissociation energy of oxygen[7] and the heat of formation of $GeO_2(s)$.[8] From these data we calculate $\Delta H^\circ_{298} = 50$ kcal./mole for $^1/_2$

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[1] Taken from a thesis presented by William L. Jolly for partial satisfaction of the requirements of the Ph.D. degree, University of California, 1952.

[2] W. Bues and H. v. Wartenberg, *Z. anorg. allgem. Chem.*, **266**, 281 (1951).

[3] For experimental details, the reader is referred to University of California Radiation Laboratory Report 1638, "Some Problems in the Chemistry of Germanium," January, 1952.

[4] L. Brewer and D. Mastick, *J. Chem. Phys.*, **19**, 834 (1951).

[5] G. Herzberg, "Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1950.

[6] A. W. Searcy, University of California Radiation Laboratory Report 1403 (1951).

[7] National Bureau of Standards Selected Values of Chemical Thermodynamic Constants, Washington, D. C., 1947, *et seq.*

[8] *Cf.* the second part of this paper.