eter number 3, the construction and operation of which have been described.[9]

For the heat capacity measurements the calorimeter was filled with 94.163 g. (0.5024 mole) of β-Ga_2O_3. The heat capacities obtained, after correction for the effects of the impurities present, are tabulated in Table I. The heat capacities follow the law $C_p = aT^3$ up to 38°K., with a equal to 2.02×10^{-5} cal. deg.$^{-4}$ mole^{-1}. These data are expressed in terms of the defined thermochemical calorie equal to 4.1833 international joules.

TABLE II

THERMODYNAMIC FUNCTIONS FOR GALLIUM OXIDE (β-Ga_2O_3)

Temp., °C.	C_p, cal./deg./mole	S^0 cal./deg./mole	$H^0 - H_0^0$	$-(F^0 - H_0^0)/T$
16	0.083	0.028	0.331	0.007
25	0.317	.105	1.975	.026
50	2.311	.826	30.829	.209
75	5.049	2.279	122.72	.643
100	7.812	4.117	284.06	1.276
125	10.40	6.142	512.16	2.044
150	12.74	8.248	801.86	2.902
175	14.84	10.37	1147.2	3.818
200	16.60	12.47	1540.9	4.770
225	18.14	14.52	1975.5	5.740
250	19.58	16.51	2447.3	6.718
275	20.88	18.44	2953.4	7.696
298.16	21.95	20.23	3468.1	8.597
300	22.03	20.30	3490.1	8.669

Thermodynamic functions derived from the smooth heat capacity curve by graphical integration, are listed in Table II at convenient temperatures.

The molal entropy at 298.16°K. is 20.23 ± 0.1 e.u., of which only 0.03 e.u. was obtained by extrapolation below 16°K.

Discussion

No irregularity was observed in the heat capacity curve for β-Ga_2O_3. The correction for impurities was applied in the form of a multiplying factor, with the assumption that the impurities existed in the oxide in a state such that their heat capacities were those of the pure compounds in their standard states. This correction made the largest contribution at the lowest temperatures, (0.5% from 40–300°K., and 0.5 to 7.5% from 40–15°K.).

It was noted that prior to the application of the correction, the data did not follow an aT^3 law below 25°K.

Acknowledgment.—We wish to thank Dr. J. W. Newsome, of the Aluminum Corporation of America Research Laboratories, for so kindly furnishing a spectrographic and chemical analysis of the gallium oxide sample used in this research.

COLUMBUS, OHIO

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

The Vapor Pressure of Germanium[1]

BY ALAN W. SEARCY[2]

RECEIVED JANUARY 11, 1952

The vapor pressure of liquid germanium has been determined over a 370° range by the Knudsen effusion method. The data lead to the equation $\Delta F = 87{,}490 + 2.00\,T \ln T - 45.5T$ for vaporization of liquid germanium. The vapor pressure results combined with estimated heat capacity and heat content data yield 84.0 ± 1.5 kcal. for the heat of sublimation of germanium at 298.15°K. Germanium vapor is demonstrated to react with a heated platinum collector plate.

Recently germanium has been shown to form compounds with many of the transition metals.[3,4] The author and co-workers plan to measure germanium partial pressures over some of these compounds. The present paper reports a determination of the vapor pressure of germanium itself.

Experimental

The vapor pressure of a substance inside a container whose temperature is known can be determined from the weight of the material passing through a small knife-edged orifice in the container into a vacuum in a measured time interval. The pressure is calculated from the Knudsen effusion equation

$$P = W(T/M)^{1/2}/44.38\,at.$$

Where P is the pressure in atmospheres, W is the weight of material of molecular weight M effusing in time t through the orifice of area a square centimeters at a temperature T°K. In the present research, germanium was effused from either a 0.336- or a 0.175-cm. diameter hole in the lid of a small graphite crucible. Spectrographic analysis of the germanium showed no evidence of significant impurity. Nevertheless, a preliminary degassing run was made to drive off any impurities sufficiently volatile to affect the pressure measurements. X-Ray diffraction analysis of germanium heated to 2125°K. in a graphite container showed no evidence of carbon contamination.

For a vapor pressure determination the germanium was heated in a graphite crucible which was nested inside tantalum and molybdenum radiation shields. Concentric holes through a set of tantalum plates above the hole in the graphite crucible collimated the beam of germanium atoms effused from the crucible.

The weight of germanium effused in each experiment was determined from the gain in weight of a platinum collector plate suspended on a water-cooled stand approximately 6 cm. above the effusion hole. About 10% of the effusing germanium was collected on this plate. The sticking coefficient on the collector (fraction of the molecules striking the collector which collided inelastically) was determined to be 1.01 ± 0.10 by comparing the approximate weight loss of the crucible with the weight gain of the collector during three of the determinations. A number of blank runs made with the same shields and temperatures used for germanium pressure determinations established that about 9% of the weight gain of the collector during a determination resulted from a collection of germanium which had struck hot radia-

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(1) Presented at the Meeting of the American Chemical Society in Cleveland, April, 1951. Work supported by the Atomic Energy Commission.

(2) Department of Chemistry, Purdue University, Lafayette, Indiana.

(3) H. J. Wallbaum, *Naturwissenschaften*, **32**, 76 (1944).

(4) A. W. Searcy, R. J. Peavler and H. J. Yearian, THIS JOURNAL, **74**, 566 (1952).

tion shields and revaporized. Corrections were made for this effect.

The effusion holes were calculated to expand less than one per cent. in area during a heating. No correction was applied for expansion.

Further details of apparatus and techniques are given in a previous publication.[5] The experimental results are summarized in Table I. Column two of the table lists the total weight of germanium effused, not the weight collected. These weights have been corrected for the weights collected in the blank runs.

TABLE I

THE VAPOR PRESSURE OF GERMANIUM

Temperature, °K.	Weight, g.	Duration of experiment, min.	Pressure atm.
1510[a]	0.0145	209	1.35×10^{-6}
1527[a]	.0131	129	1.97×10^{-6}
1607[a]	.0445	152	5.84×10^{-6}
1615[a]	.0328	109	6.01×10^{-6}
1627[b]	.0211	195	7.98×10^{-6}
1645[a]	.0599	105	1.15×10^{-5}
1649[b]	.0351	183	1.42×10^{-5}
1673[a]	.0979	112	1.77×10^{-5}
1695[b]	.0517	163	2.39×10^{-5}
1746[b]	.0941	134	5.37×10^{-5}
1795[b]	.144	127	1.10×10^{-4}
1828[b]	.187	96	1.53×10^{-4}
1882[b]	.293	71	3.47×10^{-4}

[a] Diameter of the hole was 0.336 cm. [b] Diameter of the hole was 0.175 cm.

Close agreement in pressure values calculated from data obtained using the two different hole sizes demonstrates that the results are independent of the sticking coefficient of the germanium vapor inside the crucible.

Discussion

For a vaporization in which the difference in heat capacities of the gaseous and condensed phases is nearly constant, the equations $\Delta F/T = \Delta H_0/T - a \ln T + I$ and $\Delta H = \Delta H_0 + aT$ can be applied. ΔF is the free energy of vaporization, ΔH is the heat of vaporization, T is the absolute temperature, R is the gas constant, P is the vapor pressure, ΔH_0 is a constant of integration, a is the difference in heat capacity between the gaseous and condensed phases and I is a constant of integration related to the entropy of vaporization.[6]

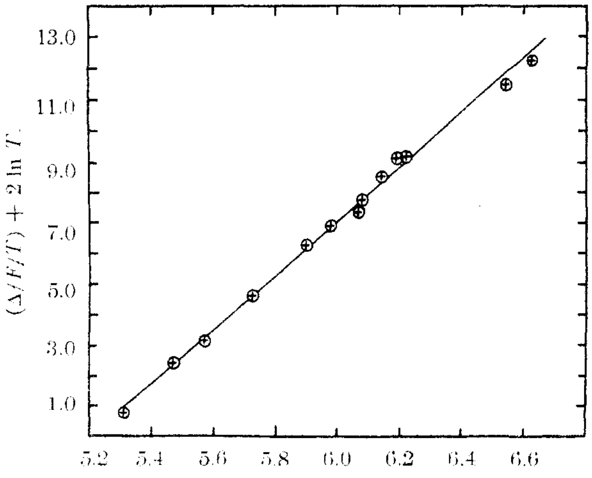

Fig. 1.—Free energy plot for vaporization of germanium.

The difference in heat capacities between gaseous and liquid germanium is estimated to be -2 cal. mole^{-1} deg.$^{-1}$. In Fig. 1, $-R \ln P + a \ln T$ has been plotted against $1/T$. The slope of the straight line obtained is ΔH_0 and the intercept on the $1/T$ axis is I. The circles of the plot were drawn to indicate an estimated error of 10% in individual pressure measurements. A least squares treatment of the data yielded $\Delta H_0 = 87{,}490$ cal. and $I = -45.47$ cal. We can therefore write $\Delta F = 87{,}490 + 2.0\ T \ln T - 45.5\ T$, and $\Delta H = 87{,}490 - 2\ T$ for vaporization of liquid germanium.

Only an approximate value of the heat of sublimation of germanium at 298.15°K. can be calculated from the vapor pressure data here reported because no high temperature heat capacity data for solid or liquid germanium are available.

We shall adopt the values estimated by Kelley[7]

$$C_p = 5.90 + 1.13 \times 10^{-3} \text{ cal. mole}^{-1} \text{ deg.}^{-1}$$

for crystalline germanium and $C_p = 7.5$ cal. mole^{-1} deg.$^{-1}$ for liquid germanium.

From the slopes of the liquidus curves in the two binary germanium systems for which satisfactory data were available, Kelley[8] calculated the heat of fusion to be 8.3 kcal. mole^{-1}. The author has attempted to obtain a value of the heat of fusion from these and similar systems in which the liquid phase was treated first as a perfect solution and next as a regular[9] solution. Except in the two systems utilized by Kelley,[8] the data were available only from small drawings of the phase diagrams so that the values for the heat of fusion obtained from individual systems were subject to error in reading the data. A perfect solution approximation applied to ten germanium systems (arsenic,[10] antimony,[10] bismuth,[10] tin,[11] zinc,[12] copper,[13] silver,[14] gallium,[15] indium,[15] thallium[15]) gave an average value of 8.3 ± 1.6 kcal. mole^{-1} for the heat of fusion. A regular solution approximation applied to the same systems, except for the germanium-arsenic and germanium-copper systems which show compound formation, yielded 4.9 ± 3.4 kcal. mole^{-1}.

Hildebrand and Scott warn against using the regular solution approximation for metal systems when compound formation is shown.[16] It is significant that two of the systems which show no solid compounds (germanium–bismuth and germanium–thallium) have solubility parameters[9] which differ so much that the liquid metals would be expected to have miscibility gaps. That these gaps do not exist is probably due to a tendency toward compound formation between the metals of the two systems.

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(5) L. Brewer and A. W. Searcy, THIS JOURNAL, **73**, 5308 (1951).

(6) K. K. Kelley, U. S. Bureau of Mines Bull. 383, 1935, p. 3.

(7) K. K. Kelley, U. S. Bureau of Mines Bull. 476, 1949, pp. 206, 208.

(8) K. K. Kelley, U. S. Bureau of Mines Bull. 393, 1936, p. 48.

(9) J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," Reinhold Publishing Corp., New York, N. Y., 1950.

(10) H. Stohr and W. Klemm, *Z. anorg. Chem.*, **244**, 205 (1940).

(11) K. Ruttewit and G. Masing, *Z. Metallkunde*, **32**, 52 (1940).

(12) E. Gebhardt, *ibid.*, **34**, 255 (1942).

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(14) T. R. Briggs, R. O. McDuffie and L. H. Willisford, *J. Phys. Chem.*, **33**, 1080 (1929).

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(16) Reference 9, page 333.

The regular solution approximation corrects for the decrease in mutual solubility of solution components due to their differences in internal pressures but does not correct for the increase in mutual solubility due to any tendency toward compound formation. The poor agreement in values of the heat of fusion for germanium calculated by use of the regular solution approximation, as well as the miscibility of two systems which by the regular solution approximation should be immiscible, suggests that internal pressure and compound formation effects are opposing each other strongly in most germanium–metal systems. The perfect solution value for the heat of fusion, therefore, was adopted as the more satisfactory.[17]

In Table II is a summary of the calculations of ΔH^0_{298} for sublimation of germanium. The value $\Delta H^0_{298} = 83.95 \pm 0.60$ kcal. was obtained from averaging the values of ΔH^0_{298} for the individual pressure measurements.

TABLE II

CALCULATED OF ΔH^0_{298} FOR SUBLIMATION OF GERMANIUM

T, °K.	$-(\Delta F - \Delta H_{298})/T$, cal. mole^{-1} deg.$^{-1}$	$\Delta F/T$, cal. mole^{-1} deg.$^{-1}$	ΔH^0_{298}, kcal. mole^{-1}
1510	29.12	26.86	84.53
1527	29.06	26.10	84.28
1607	28.76	23.95	84.70
1615	28.73	23.89	84.98
1627	28.69	23.32	84.62
1645	28.63	22.60	84.27
1649	28.61	22.18	83.75
1673	28.54	21.74	84.10
1695	28.46	21.15	84.09
1746	28.30	19.54	83.52
1795	28.15	18.11	83.04
1828	28.05	17.45	83.17
1882	27.92	15.83	82.34

The actual uncertainty in ΔH^0_{298} is greater than 0.60 kcal. because the values calculated for ΔH^0_{298} vary with the temperature at which the pressure measurements were made. The value of the boiling point obtained by extrapolation of the equation for the free energy of vaporization of liquid germanium is 2960°K. compared with 2980°K. quoted by Brewer[18] from the "Metals Handbook" of 1939. This close agreement suggests that vapor pressures obtained in the present work are probably not subject to a significant temperature dependent error and that, therefore, the estimated heat content and entropy data are probably responsible for the variation in ΔH^0_{298} values. The heat of sublimation of germanium at 298°K. may be written as 84.0 ± 1.5 kcal. mole^{-1}.

Reaction at the Collector.—X-Ray diffraction pictures of some of the germanium films on the platinum collector plates showed lines of an unknown phase, or phases, instead of the expected lines of germanium. These lines could have been those of a metastable germanium phase but a more probable explanation was that the germanium reacted with the collector plates, since the plates were usually heated to 700°K. or higher. To test this hypothesis a quartz collector was used for one run. The film formed on the collector flaked off at a touch, unlike the very adherent films on platinum, and X-ray diffraction analysis of the flakes identified them as the normal germanium phase. A surface picture of a film collected at a lower temperature on platinum also showed only the X-ray diffraction lines of germanium. Platinum has been reported to melt when heated with germanium,[19] but apparently the existence of solid platinum–germanium phases has not yet been investigated. It appears that at least one compound of platinum and germanium exists.

Acknowledgments.—I am indebted to Professor Leo Brewer for a helpful discussion of the data. The X-ray diffraction analyses were made by Mrs. Carol H. Dauben and Mr. Allan Zalken.

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[17] ADDED IN PROOF.—F. E. Wittig, *Z. Metalkunde*, **43**, 158 (1952), reports 7.13 kcal. for the heat of fusion.

[18] L. Brewer, "National Nuclear Energy Series," Vol. 19B, paper 3, McGraw-Hill Book Co., Inc., New York, N. Y., 1950.

[19] M. Hansen, "Der Aufbau der Zweistofflegierungen," Julius Springer, Berlin, 1936.