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September 1951

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THE VAPOR PRESSURE OF GERMANIUM

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September 1951

Abstract

The vapor pressure of liquid germanium has been determined over a 370° range by the Knudsen effusion method. The data lead to the equation $\Delta F = 88,400 + 2.00 T \ln T - 46.0 T$ for vaporization of liquid germanium. Estimated heat data leads to a value of 85.2 ± 1.5 kcal for the heat of sublimation of germanium at 298.15°K. Germanium vapor is demonstrated to react with a platinum plate heated to about 700°K.

Recently germanium has been demonstrated to form compounds with many of the transition elements (1,2). Nothing has yet been reported about these compounds except their compositions and some of their structures.

We plan to determine heats and free energies of formation for several of these germanide compounds by an indirect method. To take an example, the partial pressure of germanium above an equilibrium mixture of Re and ReGe_2 could be fairly readily determined at a series of temperatures by the Knudsen effusion method. The partial pressures so obtained would enable one to calculate the heat and free energy of formation of ReGe_2 provided the vapor pressure of germanium is known as a function of temperature. This relationship has not

previously been established, although Brewer (3) has calculated the variation of pressure from the normal boiling point (4) and heat capacity and entropy data. Unfortunately, the heat capacities and entropies that he was forced to use are not very accurately known. The present research was initiated in order to provide more accurate pressure data by direct measurement over a range of temperatures.

Experimental

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

$$P = W(T/M)^{1/2}/44.38 \text{ atm}$$

Where P is the pressure in atmospheres, W is the weight of material of molecular weight M effusing in t seconds through the orifice of area a square centimeters at 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 1.5 cm diameter by 2 cm high graphite crucible. The crucible was nested inside a series of tantalum and molybdenum radiation shields and supported on a tantalum plate above a series of molybdenum shields. A series of tantalum plates above the crucible cut by a set of conical holes concentric with the hole in the graphite lid completed the radiation shielding and collimated the beam of germanium atoms effusing from the crucible. Only tantalum was allowed next to the graphite crucible, because molybdenum and graphite react

readily at the temperatures used. X-ray diffraction analysis showed no evidence for reaction of the graphite with its germanium charge even when heated to 2125°K.

The weight of germanium effused in a given run was determined from the gain in weight of a platinum collector plate suspended on a water-cooled stand about 6 cm above the effusion hole. The geometry of the system was such that about 10% of the effusing germanium was collected. The sticking coefficient on the collector (fraction of the molecules striking the collector which were retained on the collector) was determined to be 1.01 ± 0.10 by comparing the weight loss of the crucible with the weight gain of the collector for three of the runs. 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 run resulted from a collection of germanium which had struck hot radiation shields and revaporized.

Further details of the apparatus and techniques used in this research are available in a previous publication (5). The experimental results are summarized in Table I. Column two of the table lists the total weight of germanium effusing, not the weight collected. These weights have been corrected for the weights collected in the blank runs. At the starred temperatures the smaller orifice was used. The results using the different orifice sizes are in agreement.

Discussion

We know that $\Delta F/T = -R \ln P = \Delta H_0/T - a \ln T + I$ and $\Delta H = \Delta H_0 + aT$ Where ΔF is the free energy of vaporization of liquid germanium, ΔH is the heat of vaporization, T is the absolute temperature, R is the gas

Table I

Temp. (°K)	Weight (gm.)	Duration of Run (minutes)	Pressure (atm.)
1510	.0145	209	1.35×10^{-6}
1527	.0131	129	1.97×10^{-6}
1607	.0445	152	5.84×10^{-6}
1615	.0328	109	6.01×10^{-6}
*1627	.0211	195	7.98×10^{-6}
1645	.0599	105	1.15×10^{-5}
*1649	.0351	183	1.42×10^{-5}
1673	.0979	112	1.77×10^{-5}
*1695	.0517	163	2.39×10^{-5}
*1746	.0941	134	5.37×10^{-5}
*1795	.144	127	1.10×10^{-4}
*1828	.187	96	1.53×10^{-4}
*1882	.293	71	3.47×10^{-4}

constant, P is the pressure of germanium, ΔH_0 is a constant of integration which is approximately the heat of vaporization of liquid germanium at absolute zero, the parameter a , is the difference in heat capacity between gaseous and liquid germanium (assumed constant), and I is a constant of integration related to the entropy of vaporization (6). Estimating the difference in heat capacity to be $-2 \text{ cal. mol.}^{-1} \text{ deg.}^{-1}$ we can now determine ΔH_0 and I by plotting $-R \ln P + a \ln T$ against $1/T$. This has been done in Figure I. The slope of the plot is ΔH_0 and the intercept on the $-R \ln P + a \ln T$ axis is I . The circles of the plot were drawn to express an estimated absolute error of 10% in individual pressure measurements. We obtain, for vaporization of liquid germanium $\Delta F = 88,400 + 2.00 T \ln T - 46.0 T$.

We would like to calculate the heat of sublimation for germanium at 298.15°K from our data. Unfortunately, there is no satisfactory high temperature heat capacity data for solid or liquid germanium. Furthermore, the heat of fusion calculated by Kelley (7) from phase diagrams is abnormally high and may be in error. A consideration of a number of phase diagrams published since 1936 using the regular solution approximation suggests that the heat of fusion may be 4-5 kcal rather than the 8.3 kcal given by Kelley.

If we calculate the heat of sublimation for germanium at 298.15°K using the heat capacities for solid germanium estimated by Kelley (8), Kelley's heat of fusion (7), National Bureau of Standards data for gaseous germanium (9), and each separate vapor pressure measurement in turn, the heats of sublimation calculated deviate only a few hundred calories from each other when compared over a short temperature range. But there is a trend in values with temperature amounting

to about 1.5 kcal. If the value 4.3 kcal is used for the heat of fusion, the trend in ΔH_{298} values calculated is more than cut in half. The average of the ΔH_{298} values thus obtained using each vapor pressure determination in turn is about 85.2 kcal. The estimated uncertainty in this value is 1.5 kcal. Fortunately the value is relatively insensitive to the heat of fusion chosen. Kelley's heat of fusion value of 8.3 instead of 4.3 would make the heat of sublimation about 83.9 instead of 85.2. But better heat data will allow the heat of sublimation to be more exactly fixed from the vapor pressure results reported here.

Reaction at the Collector

X-ray diffraction analysis 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 confirm this hypothesis a quartz collector was used for one run. The film formed 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 on platinum held at a lower temperature also showed only the X-ray diffraction lines of germanium. Platinum has been reported to melt when heated with germanium (10), but apparently the existence of solid platinum-germanium

phases has not yet been investigated.

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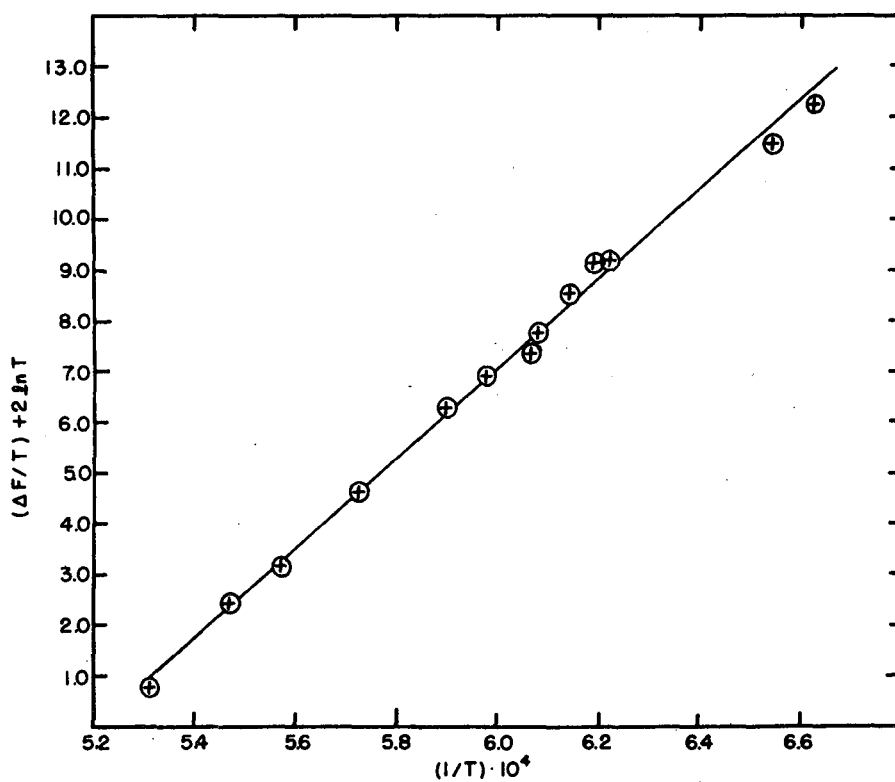


FIG. 1 - FREE ENERGY PLOT FOR LIQUID GERMANIUM

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Fig. 1