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TORSION-EFFUSION STUDY OF THE VAPOR PRESSURE AND HEAT OF SUBLIMATION OF GALLIUM

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ABSTRACT

The vapor pressure of gallium was measured by the torsion-effusion method between 1174 and 1603°K. The pressure, in atmospheres, is given by the expression: $\log P = 5.5458 - (13\,743/T)$ in that temperature range. The heat of sublimation of gallium is calculated by the third-law method to be 65.4 kcal. A second-law determination is in reasonable agreement.

INTRODUCTION

Harteck[1] in 1928 and Speiser and Johnston[2] in 1952 measured the vapor pressure of gallium by the Knudsen effusion method with quartz effusion cells. However, more recently a mass-spectrometric study[3] showed that gallium reacted with quartz, giving a considerable concentration of $Ga_2O(g)$ above 865°C. This evidence suggested that the reported gallium vapor pressures might be too high. To clarify the situation, Cochran and Foster[4] investigated the apparent vapor pressures of gallium in alumina Knudsen cells with and without added silica or magnesia. Apparent pressures obtained with silica added agreed well with the pressures of Speiser and Johnston, but pressures measured when only gallium was present were four- to fivefold lower. Cochran and Foster concluded that the previous studies in quartz cells were in error because the reaction $2\,Ga(\ell) + SiO_2(c) = SiO(g) + Ga_2O(g)$ yielded higher weight losses than did the direct vaporization of gallium.

At the time that the paper of Cochran and Foster appeared, we were engaged in a redetermination of the vapor pressure of gallium by the torsion-effusion method[5-8] with use of a graphite cell. A mass spectrometer study by Drowart and Honig[9] had demonstrated that atomic gallium is the only major vapor species when gallium is heated in graphite. Nonetheless, the pressures measured in our research are in good agreement with the average of the data of Harteck and of Speiser and Johnston and thus are four to five times the pressures reported by Cochran and Foster.

EXPERIMENTAL

Figure 1 shows a schematic diagram of the torsion-effusion apparatus. The vacuum chamber is a cylinder about 14 in. in diameter and about 18 in. long. In the center a 3-in. diameter cylinder of 20-mil tantalum sheet forms the heating element. Several layers of tantalum radiation shields are wrapped around this element. A glass tube of approximately 4-in. diameter and 3-ft length forms the upper part of the apparatus. Above this tube a goniometer acts as the anchor point for the suspension system by means of a 1/4-in. aluminum rod which enters the top of the glass tube through an O-ring seal. A 2-mil annealed tungsten wire 11 in. long hangs from the aluminum rod. To the lower end of the tungsten wire, a second 1/4-in. aluminum rod is attached. A 1/2-in. diameter circular mirror is glued to this rod directly in front of a window which has an optically flat surface. An aluminum disk attached to the rod serves as a damper when a permanent magnet is placed near it. A 0.1-in. diameter tantalum rod is joined to the aluminum one, and the graphite torsion cell is rigidly attached to the bottom of this rod. During a run the cell hangs free in the center of the heating element.

The exterior cell dimensions were 1-1/2 x 1/2 x 1/2 in. Two sets of orifices, one set of 6.3 mm^2 cross-sectional area and the other of 1 mm^2 area, were used.

Angular deflections resulting from the force of the effusing vapors were determined by returning the suspension system to its original (null) position. Measurements were made by sighting through a telescope on the mirror that reflects a scale placed outside the vacuum system just below the telescope. After returning the suspension assembly to its original position, deflection angles were read from the goniometer. With this

arrangement, it was possible to measure angles to the nearest 0.01 deg. A vacuum of better than 10^{-5} mm Hg was maintained by means of an oil diffusion pump and a liquid nitrogen trap.

A 30-kva transformer supplied the power at a maximum of 10V. Temperature measurements were made by means of a calibrated 20-mil Pt-Pt + 10% Rh thermocouple. The thermocouple bead was inserted in a small hole in the bottom of a "dummy" graphite cell located 1/2 in. below the effusion cell. The freezing points of gold, silver, copper, and aluminum measured in the dummy cell in the furnace were used as standard points in the calibration of the thermocouple.

In order to verify the assumption that the temperature of the dummy cell was the same as that of the effusion cell for a given power setting, the dummy cell was moved up and down over a distance of 3 in. in the middle portion of the heating element. The temperature remained constant to within 3°. This experiment was repeated at different power inputs and the results were all identical. The thermocouple leads were led through a Kovar seal to the outside and were protected with alumina tubes. A mixture of ice and distilled water formed the cold junction and the emf was measured by a potentiometer. The output of the thermocouple was fed to a strip chart recorder. Measurements were made only after the temperature had reached a constant value.

The gallium used was 99.97% pure material obtained from the Aluminum Company of America.

As a test of the apparatus, the vapor pressure of tin was redetermined. The results are described in the discussion section.

RESULTS

Pressures were calculated from the equation

$$P = 2\,D\phi/(q_1 a_1 f_1 + q_2 a_2 f_2) \qquad (1)$$

P = vapor pressure, atmosphere

D = torsion constant of the wire, dyn-cm

ϕ = angle of deflection, radians

q_1, q_2 = perpendicular distances from the center of the effusion hole to the axis of rotation, cm

a_1, a_2 = areas of effusion holes, cm^2

f_1, f_2 = correction factors for finite orifice lengths[10, 11]

Constants for the two sets of cells used and for the torsion wire are summarized in Table I. A 2-mil tungsten wire with D = 3.416 was used for all runs. Figure 2 shows the agreement between pressures calculated with the two orifices. Data collected below 1200°K are clearly seen from Fig. 2 to be unreliable because the force of effusing vapor is too low for accurate measurement and these data were not used in subsequent calculations.

The heat of sublimation ΔH_s was determined by using both the second- and third-law methods.[12] Apparent pressures less than 10^{-6} atm were not used in making these calculations because background torsional effects obscured the lower pressure readings. An experimental investigation by Schulz has shown that Eq. (1) can be used up to pressures for which the ratio of mean-free-path to orifice diameter becomes unity. From the diameters of the orifices and the van der Waals radius for gallium,[13] this pressure is calculated to be about 10^{-2} atm. The highest pressure measured in this work was 8×10^{-4} atm.

Second-law calculation by the least-square method gave $\Delta H_{s,298}$ = 63.5 kcal/mole. Third-law calculations based on free-energy functions selected by Hultgren[14] are given in Table II. The average value calculated for the heat of sublimation of gallium at 298°K from data collected with 2.5 mm diameter orifices is 65.39 kcal/mole and with 1.0 mm orifices is 65.50 kcal. The overall average $\Delta H_{s,298}$ is 65.44 ± 0.23 kcal/mole. Least-square solution for the experimental data gave the following expression for the vapor pressure of gallium, in atmospheres, between 1174 and 1603°K:

$$\log P = 5.458 - 13\,743/T \quad .$$

DISCUSSION

Recent studies by Cochran and Foster[4] appeared to demonstrate conclusively that any studies of the vapor pressure of gallium that were carried out in the presence of silica are in error because of extensive reaction to yield volatile oxides. But the vapor pressures measured for gallium in the present investigation are higher by about a factor of four, than the vapor pressures reported by Cochran and Foster, and the heats of sublimation calculated from the data of the present research are in excellent agreement with the heat reported by Hultgren et al.[14] from analysis of the results of the two studies made with silica effusion cells.

The possibility of errors that could make the apparent pressures of the present investigation higher than the true pressures by a factor of four will be discussed, and then evidence for the possibility of error in the work of Cochran and Foster will be examined.

The factors that might cause systematically high apparent pressures in the present investigation are contribution to the vapor of products

of reaction of gallium with the graphite effusion cell, faulty temperature calibration, faulty pressure calibration, and leakage of vapor through the cell wall. Strong evidence can be adduced that none of these factors caused the observed discrepancy.

The possibility that gaseous products of some reaction of gallium with the graphite of the effusion cell were formed in significant concentration is disproved by the mass spectrometer study by Drowart and Honig of the effusion of gallium from a graphite cell.[9] No ions other than Ga^+, Ga_2O^+, and Ga_2^+ were observed. The GaO^+ and Ga_2^+ intensities rapidly decayed to negligible levels, indicating that these ions were produced from oxides that were introduced with the initial sample, but that were soon removed by heating.

The possibility of a temperature error in this work of more than 5° at most appears excluded by the calibration of the readings of the dummy cell against the melting points of four metals measured in the actual furnace in which the vapor pressure measurements were made. Furthermore, the furnace was demonstrated to have a uniform hot zone over the region in which the dummy cell and torsion effusion cell were placed. A temperature error of 90° would be required to introduce an error of a factor of four in the pressure measurements at the midpoint of the experimental range.

Evidence that the apparatus was calibrated correctly is provided by agreement to within 10% of the vapor pressure plot obtained for tin with this apparatus and the "best" vapor pressure curve for tin as selected by Hultgren et al.[14] From nineteen separate measurements of the vapor pressure of tin with two different wires that had torsion constants which differed by a factor of 18, the heat of sublimation of tin at 298°K is

calculated to be 72.4 kcal compared to 72.2 kcal calculated by Hultgren et al. from previous work and compared to 71.8 kcal which was obtained by Schulz in an extensive study of the reliability and limitations of the torsion-effusion method for vapor pressure determinations.[15]

To test the reliability of their apparatus and techniques, Cochran and Foster also studied the vapor pressure of tin. Their three pressure measurements lie considerably lower than the pressures calculated by Stull and Sinke[16] or Hultgren et al. from evaluation of the data in the literature. We calculate from the Cochran and Foster data a heat of sublimation of tin at 298°K of 74.9 ± 1.1 kcal/mole.

Cochran and Foster commented that the vapor pressure data accepted by Stull and Sinke as the most reliable are probably in error because of unrecognized leakage through walls of the graphite crucibles that were used for the pressure studies.

There certainly is evidence that the quantity of metal that escapes from a graphite cell may sometimes be comparable to the quantity that escapes through an orifice of the dimensions normally employed in effusion studies.[17] However, in the torsion-effusion method, if the cell side walls are uniform in thickness, the escape of molecules by leakage through the walls will contribute no net torque to the assembly. As part of his investigation Schulz heated tin in cells in which no orifices were drilled and found that no measurable torque was produced by any leakage that may have taken place.[15]

While the present investigation of gallium did not include measurement of the torque produced when a sample was heated in a cell that had no orifices, the study did include measurement of the pressure with sets of orifices that had areas that differed by more than a factor of six. The

calculated pressures agree within the small random scatter in data. If leakage contributed significantly to the torque, this excellent agreement between the pressures calculated with these two sets of orifices would not have been obtained.

The heat of sublimation for tin calculated from the data of Cochran and Foster is thus 2.7 to 3.2 kcal higher than the heats calculated from the best available studies. Similarly the heat of sublimation of silver calculated from three pressure measurements by Cochran and Foster is 0.9 kcal higher than the selected value of Hultgren et al.[14]

Gallium is more volatile than tin and less volatile than silver. The heat of sublimation for gallium calculated from the Cochran and Foster data can be expected to be subject to a systematic error in pressure determination that would contribute an error in the derived heat of sublimation of 2 ± 1 kcal.

A systematic error in the measurements of Cochran and Foster would not invalidate their conclusion that in the presence of silica the weight loss is increased by a factor of four or five because of volatile oxide formation. Remaining to be explained, therefore, is the question of how the studies of Harteck[1] and of Speiser and Johnston[2] which were both conducted in silica cells, could agree with the results of the present investigation in graphite.

The probable answer to this question is that the surface area at which the heterogeneous reaction between the gallium and silica could occur in silica Knudsen cells is much smaller than the surface provided for reaction by the coarse silica powder added to the cells in the experiments of Cochran and Foster. As a result, although some reaction must

have occurred in the silica cells, the extent of reaction may well have been considerably less than was measured in the experiments of Cochran and Foster.

This hypothesis is substantiated by the results of the mass spectrometer study of gallium vaporization from a silica cell. The observed intensity ratio Ga^+/Ga_2O^+ was about 10/1 at 1140 to 1300°K.[3] From the assumptions normally applied to calculate pressures from ion intensities and usually claimed to be correct to within a factor of two,[18] these intensities would yield a Ga/Ga_2O pressure ratio of 22/1. The heat of sublimation calculated for gallium by a third-law method from weight losses measured at 1300°K and with the assumption that the total weight loss was of elemental gallium would be low only by about 0.3 kcal because of neglect of Ga_2O and SiO effusion.

We conclude that the heat of sublimation of gallium obtained by the third-law method in the present investigation, 65.4 kcal/mole is probably correct to within ± 1 kcal.

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Table I. Torsion cell constants.

Cell	Orifice diameters (cm)		Mount arms (cm)		Orifice correction factors		Orifice length-to-radius ratio	
	d_1	d_2	q_1	q_2	f_1	f_2	$(\ell/r)_1$	$(\ell/r)_2$
1	0.2563	0.2436	1.2626	1.1216	0.840	0.827	0.539	0.589
2	0.1016	0.1001	1.1242	1.1221	0.7726	0.7359	1.05	0.985

Table II. Third law heats of sublimation of gallium (ℓ).

A. Cell 1

T °K	-Rℓn P cal/deg	ΔH°_{298} cal	T °K	-Rℓn P cal/deg	ΔH°_{298} cal
1204	27.308	65 452	1326	22.414	65 392
1204	27.286	65 425	1326	22.429	65 412
1211	27.244	65 749	1333	22.281	65 552
1213	26.784	65 296	1336	22.089	65 429
1213	26.869	65 399	1340	21.909	65 388
1221	26.559	65 438	1350	21.594	65 430
1227	26.217	65 330	1352	21.569	65 488
1229	26.088	65 275	1355	21.152	65 070
1234	25.859	65 243	1360	21.269	65 451
1234	25.652	64 987	1366	21.139	65 563
1238	25.652	65 192	1367	20.812	65 154
1241	25.544	65 217	1370	20.964	65 507
1243	25.544	65 318	1374	20.707	65 335
1249	25.280	65 232	1382	20.381	65 248
1250	25.205	65 245	1384	20.572	65 602
1250	25.205	65 245	1386	20.406	65 462
1257	24.948	65 281	1390	20.203	65 374
1261	24.721	65 195	1398	19.848	65 236
1262	24.721	65 252	1403	19.831	65 442
1266	24.548	65 233	1405	19.836	65 536
1270	24.491	65 359	1410	19.453	65 224
1270	24.385	65 225	1416	19.408	65 422
1275	24.239	65 280	1416	19.473	65 514
1281	24.056	65 330	1419	19.195	65 258
1289	23.741	65 330	1426	19.134	65 482
1290	23.703	65 337	1429	18.934	65 334
1294	23.501	65 271	1435	19.037	65 740
1295	23.565	65 396	1440	18.710	65 493
1303	23.256	65 395	1446	18.724	65 770
1304	23.101	65 234	1448	18.404	65 393
1305	23.065	65 242	1455	18.225	65 437
1314	22.836	65 379	1459	18.416	65 900
1316	22.755	65 368	1465	18.223	65 887
1318	22.957	65 729	1466	17.879	65 417

Table II. (cont.)

B. Cell 2

T °K	-R ln P cal/deg	ΔH°_{298} cal	T °K	-R ln P cal/deg	ΔH°_{298} cal
1380	20.260	64 991	1491	17.361	65 716
1391	20.192	65 396	1495	17.041	65 403
1394	19.858	65 073	1498	17.253	65 852
1411	19.546	65 391	1506	16.787	65 493
1416	19.213	65 146	1508	17.044	65 961
1421	19.073	65 143	1513	16.579	65 471
1427	19.093	65 459	1519	16.299	65 287
1432	19.010	65 564	1529	16.246	65 620
1437	18.624	65 233	1530	16.047	65 363
1448	18.219	65 125	1544	15.730	65 446
1453	18.192	65 305	1556	15.433	65 486
1466	17.823	65 335	1561	15.411	65 654
1469	18.210	66 023	1566	15.263	65 626
1471	17.861	65 593	1567	15.350	65 794
1473	17.611	65 325	1575	15.034	65 622
1477	17.711	65 638	1585	14.824	65 690
1482	17.908	66 146	1588	14.770	65 729
1485	17.321	65 393	1603	14.310	65 588

FIGURE LEGENDS

Figure 1. Schematic diagram of torsion apparatus.

Figure 2. Vapor pressure of gallium (ℓ).

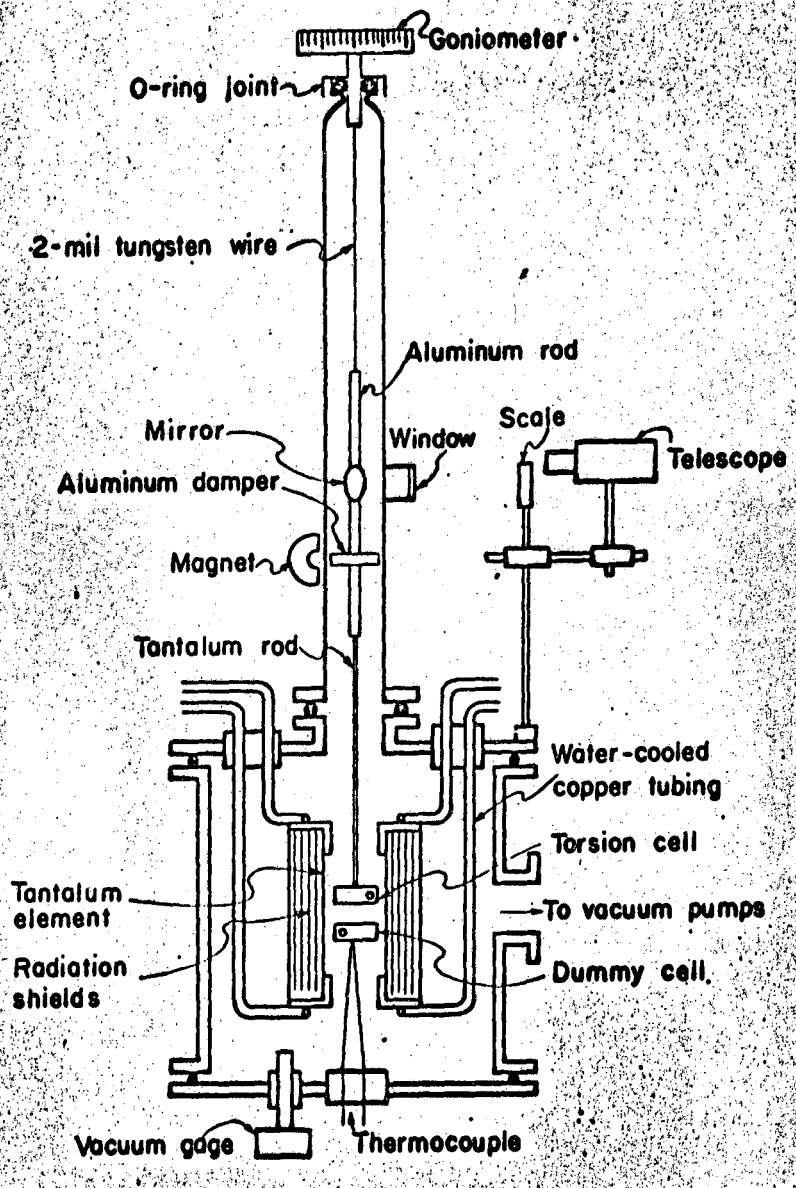
Goniometer
O-ring joint
2-mil tungsten wire
Aluminum rod
Mirror
Window
Scale
Telescope
Aluminum damper
Magnet
Tantalum rod
Water-cooled
copper tubing
Torsion cell
Tantalum
element
To vacuum pumps
Radiation
shields
Dummy cell
Vacuum gage
Thermocouple
MU-29967

Figure 1

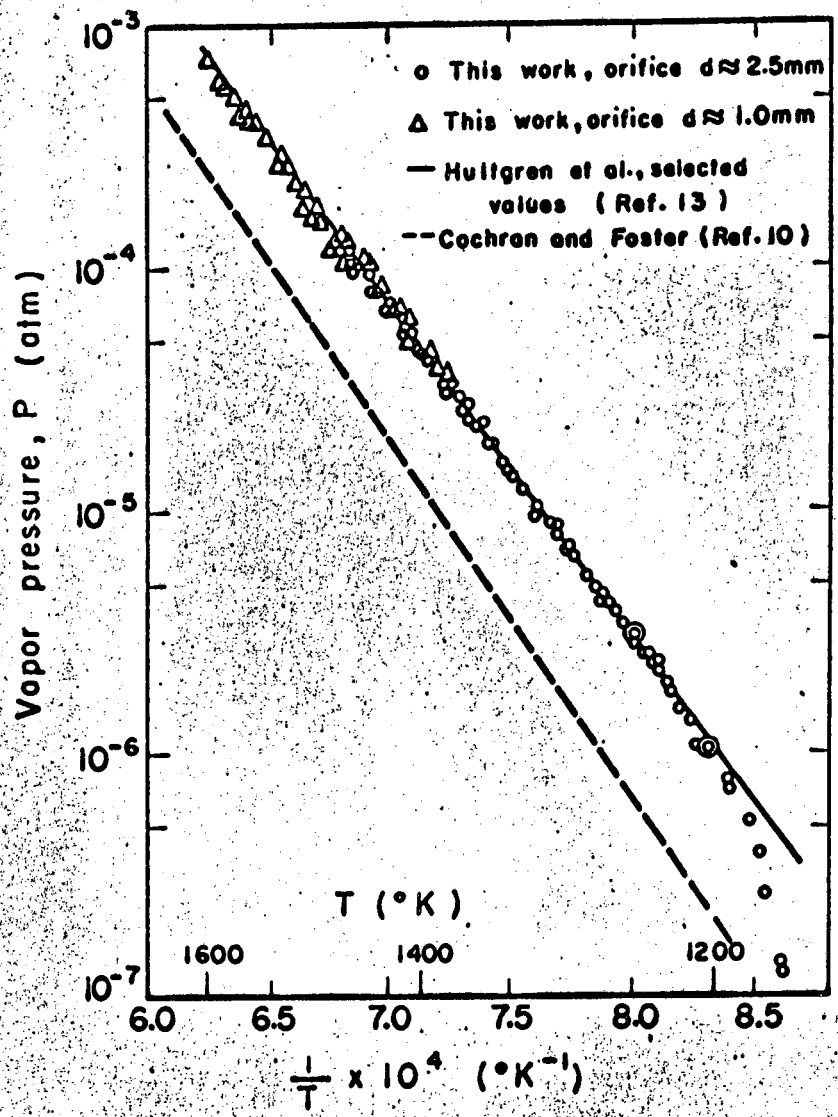
o This work, orifice d≈2.5mm
Δ This work, orifice d≈1.0mm
— Hultgren et al., selected values (Ref. 13)
-- Cochran and Foster (Ref. 10)
Vapor pressure, P (atm)
10^-3
10^-4
10^-5
10^-6
10^-7
T (°K)
1600
1400
1200
6.0
6.5
7.0
7.5
8.0
8.5
1/T x 10^4 (°K^-1)
MU-29970

Figure 2

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