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Saturated Vapour Pressure and Enthalpy of Sublimation of Germanium

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The vapour pressure of germanium has been determined over the temperature interval 1134–1647 K.

The literature data[1–5] on the sublimation enthalpy of germanium (Table 1) are in sharp contradiction with the values that have been calculated from the dissociation energy of GeS(g) and the enthalpies of formation and sublimation of GeS(cr) (see ref. 7, pp. 307 and 342).

We measured the vapour pressure of crystalline and liquid germanium over a wide temperature interval because the enthalpy of sublimation of germanium is the key value in the thermochemistry of the gaseous compounds of germanium. The vapour pressure over solid germanium has been measured for the first time.

The vapour pressure of germanium was determined by means of an integral variant of the Knudsen method in a hydrocarbon-free vacuum 10^{-6}–10^{-7} Pa. The operating principle and design of the device have been described previously.[8] The effusion cell and the diaphragm were of graphite MPG-6

Table 1 Enthalpy of sublimation of germanium according to data obtained by various authors

Author, ref.	Method	No. of measurements	Temp. range T/K	Enthalpy of sublimation at 298.15 K/kJ mol^{-1} 2nd Law	3rd Law
Searcy, 1	Knudsen	13	1510–1882	389 ± 25	371.7 ± 1.2
Searcy, 2	Knudsen	6	1418–1686	350 ± 54	375.1 ± 3.3
Searcy, 3	Knudsen	10	1608–1885	398 ± 23	379.5 ± 1.1
	Torsional	10	1608–1885	367 ± 47	377.3 ± 1.9
Nesmeyanov, 4	Open crucible	4	1270–1403	363 ± 59	378.1 ± 2.6
Tseplyaeva, 6	Knudsen	68	1263–1647	370 ± 7	367.4 ± 0.3
Timokhin, 5	Knudsen	4	1450–1755	362 ± 73	375.0 ± 5.0

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Table 2 Constants for eqn. (2), $\lg P = (A - B)T^{-1}$, and values for the enthalpy of the sublimation of germanium

No.	Ge sample	Temp. range T/K	No. of measurements	$\lg P/\mathrm{Pa} = [(A \pm \Delta A) - (B \pm \Delta B)]T^{-1}$ $A \pm \Delta A$	$B \pm \Delta B$	$\Delta_s H°$ (Ge, cr, 298.15 K)/kJ mol^{-1} 2nd Law	3rd Law
1	Molten, monocrystalline	1134–1201	19	12.4 ± 0.7	19300 ± 800	367 ± 15	367.8 ± 0.3
2	Melted, monocristalline	1162–1206	8	12.0 ± 0.8	19000 ± 900	362 ± 26	367.7 ± 0.4
3	Polycrystalline, bar	1153–1193	10	12.3 ± 0.7	19230 ± 860	367 ± 17	367.8 ± 0.3
4	Summary data for solid Ge	1134–1206	37	12.31 ± 0.35	19210 ± 420	366 ± 8	367.8 ± 0.1
5	Starting monocrystalline	1213–1303	7	10.7 ± 0.8	17260 ± 1050	366 ± 20	367.6 ± 0.5
6	The data of this work	1263–1647	68	10.81 ± 0.24	17400 ± 370	370 ± 7	367.4 ± 0.3
7	Summary of data for liquid Ge	1213–1647	75	10.83 ± 0.16	17410 ± 230	368 ± 8	367.6 ± 0.3
8[a]	Starting monocrystal	1409–1540	6	10.7 ± 1.0	18100 ± 1800	383 ± 35	376.6 ± 1.5
9[a]	Starting monocrystal	1477–1521	2	—	—	345	371.2

[a] In series 8 and 9 effusion cells are made of porous graphite.

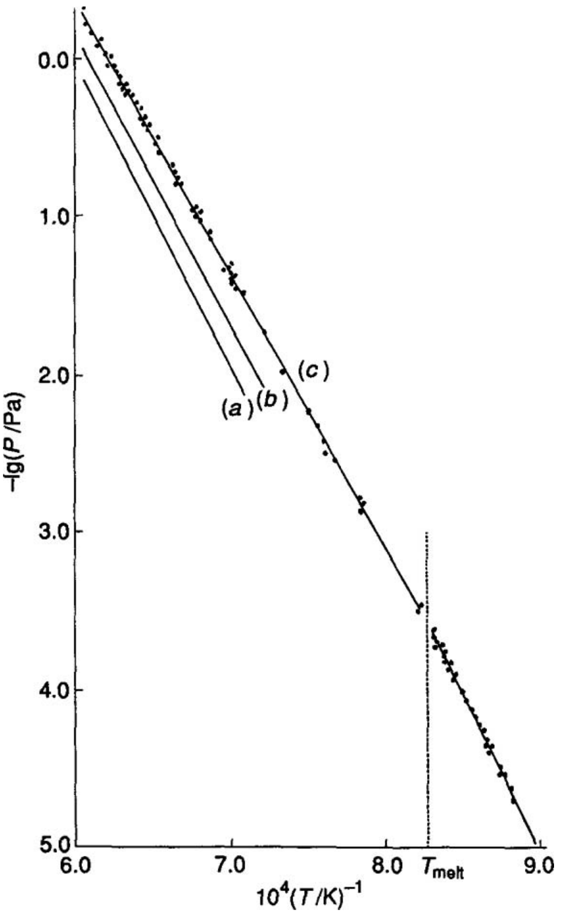

Fig. 1 The temperature dependence of vapour pressure for germanium, showing data from (*a*) Searcy,[3] (*b*) Searcy[1] (*c*) the present work

with closed pores and were degassed *in vacuo* at 2300 K. Two samples of germanium were used, monocrystalline (99.99% pure) and polycrystalline (99.999% pure). The amount of evaporated germanium was determined by a colorimetric method.[9]

The saturated vapour pressure of germanium was calculated according to eqn. (1), where σ is the area of the effusion orifices,

$$P = m(K\sigma\tau)^{-1}(2\pi RTM^{-1})^{1/2} \quad (1)$$

K is Clausings' factor and M is the molecular weight of germanium vapour (72.6). The results obtained are given in Tables 2 and 3 and Fig. 1.

In order to test whether equilibrium was established in the Knudsen cell the experiments were carried out using germanium samples with various areas of evaporating surface, using the same effusion orifice (Table 2). Statistical treatment[10,11] revealed the statistical equivalence of the results for the vapour pressure of solid germanium. Similarly, statistical equivalence was shown by the data for the vapour pressure of liquid germanium with the results which we had obtained previously.[6]

The enthalpy of sublimation of germanium was calculated in accordance with the second and third laws of thermodynamics at 298.15 K, using thermodynamic functions[7] for solid and liquid germanium. The corresponding regression equations have been obtained (Table 2). The statistical equivalence of the data calculated for the enthalpy of sublimation of germanium at 298.15 K from the vapour pressures of liquid and solid germanium was demonstrated, and a value of $\Delta_s H°$ (Ge, cr, 298.15 K) = 367.7 ± 0.1 kJ mol^{-1} was obtained. It follows from Table 1 that this value differs from the previously reported values for the enthalpy of formation of gaseous germanium. In our view the reason for the lower value obtained for the vapour pressure of germanium is the use of porous graphite for effusion cells in refs. 1–3, 5. Our own experiments with the use of porous graphite as a material for the effusion cells have confirmed this assumption (Table 2).

The results obtained can be written as eqns. (2) and (3) (the

$$\lg P_{\mathrm{sol}} = (12.31 \pm 0.35) - (19210 \pm 420)T^{-1} \quad (2)$$

$$\lg P_{\mathrm{liq}} = (10.83 \pm 0.16) - (17410 \pm 230)T^{-1} \quad (3)$$

corresponding absolute errors are given by confidence limits 0.95).

On the basis of eqns. (2) and (3) for the temperature dependence of the vapour pressure of solid and liquid germanium the enthalpy of melting was estimated. The value of 34.4 ± 9.2 kJ mol^{-1} obtained does not contradict the accepted value of 37.03 ± 0.20 kJ mol^{-1}.[7]

The data stated above allow us to propose a value for the enthalpy of formation of gaseous germanium (enthalpy of sublimation) at 298.15 K of $\Delta_s H°$ (Ge, cr, 298.15 K) = 368.0 ± 1.0 kJ mol^{-1} (taking into account errors in the thermodynamic functions).

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Table 3 Experimental data on vapour pressure and corresponding 3rd law enthalpy of sublimation for germanium

No.	Temp. T/K	Evaporation time τ/s	Mass of condensate, 10^9 (m/kg)	Vapour pressure, 10^5 (P/Pa)	$\Delta_s H^\circ$ (Ge, cr, 298.15 K)/kJ mol^{-1}
Series 1[a]					
1	1154	30700	11.0	4.896	367.076
2	1154	25200	8.3	4.500	367.882
3	1169	14700	8.5	7.950	367.151
4	1171	14400	8.8	7.670	368.134
5	1213	7200	16.0	31.13	367.136
6	1213	3600	7.0	27.24	368.482
7	1193	6540	7.0	15.08	368.380
8	1194	3600	4.2	16.21	367.968
9	1205	3600	6.0	23.26	367.631
10	1206	3600	6.5	25.21	367.230
11	1277	1200	12.5	149.7	368.020
12	1277	1200	13.0	155.7	367.604
13	1303	1200	24.0	290.4	367.567
Series 2[a]					
14	1134	39600	6.5	2.222	368.108
15	1135	36000	6.5	2.446	367.548
16	1153	23160	7.0	4.128	368.386
17	1163	14400	7.2	6.857	366.693
18	1184	7200	6.0	11.53	368.229
19	1189	7200	8.0	15.41	366.927
20	1201	7500	10.5	19.52	368.267
21	1213	4800	11.0	32.10	366.825
22	1213	3600	7.5	29.18	367.786
23	1199	7200	10.0	19.35	367.736
24	1190	10800	11.0	14.13	368.093
25	1184	18000	16.0	12.30	367.705
26	1162	18000	8.0	6.09	367.519
Series 3[a]					
27	1153	18000	5.8	4.400	367.773
28	1152	18000	5.6	4.246	367.720
29	1174	10800	7.0	8.931	367.596
30	1174	10800	6.9	8.803	367.738
31	1189	7200	7.4	14.25	367.697
32	1189	7200	7.6	14.64	367.438
33	1197	7200	9.2	17.79	367.981
34	1195	7200	8.7	16.80	367.924
Series 4[a]					
35	1153	18000	5.7	4.324	367.940
36	1153	18360	5.9	4.388	367.799
37	1163	14400	6.5	6.190	367.682
38	1163	14400	6.4	6.095	367.813
39	1175	10800	7.5	9.573	367.232
40	1175	10800	7.0	8.935	367.905
41	1186	7200	6.5	12.49	368.170
42	1186	10980	9.8	12.36	368.056
43	1191	12660	14.0	15.35	367.584
44	1192	7200	8.0	15.43	367.845
Series 5[b,c]					
45	1409	1200	54	129.9	374.275
46	1428	900	60	193.7	374.137
47	1466	910	126	407.7	374.185
48	1485	900	180	599.6	373.913
49	1501	600	161	799.4	373.851
50	1540	605	316	1589.2	373.892
Series 6[b,c]					
51	1477	600	113	7251	370.644
52	1521	600	230	14990	371.845

[a] In series 1–4 the diameter of the effusion orifice is 0.318 cm. [b] The effusion cell is made of porous graphite in series 5 and 6. [c] In series 5 the diameter of the effusion orifice is 0.305 cm and in series 6 it is 0.20 cm.

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