[CONTRIBUTION FROM THE CRYOGENIC LABORATORY, DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

The Vapor Pressures of Inorganic Substances. I. Beryllium[1]

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The need for more complete data on the vapor pressure and thermodynamic properties of many elementary substances has prompted us to determine the vapor pressure of solid beryllium over a wide temperature range. For these measurements both the Langmuir and Knudsen methods were used and the data obtained by these two methods are in good agreement. Intercomparison of these data affords a means of determining the value of the condensation coefficient for this substance. The theory and use of these methods are described by other investigators.[2,3,4a]

In Langmuir's method the vapor pressure of a substance is determined by the relationship

$$m = \alpha P \sqrt{M/2\pi RT} \qquad (1)$$

where m is the rate at which the material evaporates into a vacuum per unit area of surface, P is the vapor pressure, M is the molecular weight of the evaporating particle, R is the gas constant per mole, T is the absolute temperature and α is the condensation coefficient.[4] The necessary relationship for determining the vapor pressure of a substance by Knudsen's method is

$$m = P \sqrt{M/2\pi RT} \qquad (2)$$

where m is the rate at which the vapor under its equilibrium pressure will effuse through an orifice, and the other symbols have the same meaning as before.

Experimental

The measurements consisted in the measurement of the rate at which a metal surface evaporates into a vacuum (Langmuir method) and the determination of the rate at which metal vapor at its equilibrium pressure effuses through an orifice (Knudsen method). For the former measurements the samples were in the form of either cylinders or annular rings; for the latter the finely divided material was placed inside buckets constructed of sheet molybdenum. The annular rings were approximately 2.8 cm. o.d. × 1.3 cm. i.d. × 1.0 cm. thick; the cylinders were approximately 2.5 cm. long × 2.3 cm. diameter. The molybdenum buckets were approximately 1.9 cm. long × 1.9 cm. diameter and had effusion holes 0.318 cm. and 0.398 cm. in dia., respectively. Since the solid samples changed size due to evaporation they were measured between runs. The areas were corrected to take into account the increase due to thermal expansion.

The beryllium samples used were of two sorts: vacuum cast and experimentally sintered. Both of these materials were used for the Langmuir type measurements whereas for the Knudsen measurements the vacuum cast material was used exclusively. All of the vacuum cast material used was of high purity. The analysis of the material used in the Langmuir runs is Al 0.06%, Cr 0.01%, Cu 0.01%, Fe 0.07%, Mg 0.01%, Ni 0.01%, Si 0.03%, together with entirely negligible amounts of several other impurities, and that of the material used in the Knudsen runs is Al 0.14%, Cr 0.01%, Cu 0.01%, Fe 0.07%, Mg 0.02%, Na 0.01%, Ni 0.01%, Si 0.04%, Zn 0.01%, together with entirely negligible amounts of several other impurities. The experimentally sintered material was of lower purity; however, any effects this might introduce were diminished by a preliminary evaporation treatment.

The apparatus and general technique employed was essentially that of Marshall and co-workers.[3,4a] Particular modifications were the mounting of the observation port on a ball joint so that it could be inclined to the axis of the cell to protect the window from condensing vapors when pyrometric measurements were not being made, and the incorporation of a removable sample holder.

The temperatures were measured under black body conditions by means of a Leeds and Northrup No. 8620 C optical pyrometer. These black body conditions were determined in an auxiliary experiment by measuring the apparent temperature of a series of holes drilled into a beryllium ring. When the dimensions were such that increasing the ratio of length to diameter caused no increase in apparent temperature the conditions were essentially black body; in our actual experiments a considerable safety factor was allowed in addition in constructing the black body sighting hole on our samples. In the case of the Knudsen cell, the pyrometer was sighted through the orifice into the interior of the cell which approximated a very good hohlraum. It was found that with some practice the pyrometer readings could be reproduced to ±1°. The pyrometer was calibrated against a standard lamp furnished by the General Electric Company.

The samples were heated by means of high frequency induction and the temperature was controlled by means of a device[5] which consisted of a variable inductance placed in series with the output coil. This inductance was varied in such a way as to compensate for fluctuations in the output of the radio frequency oscillator.

Data and Thermodynamic Treatment[6]

The experimental results are recorded in Tables I and II and in Fig. 1. In determining the effective time at the temperature of measurement the evaporation during periods of initial heating and final cooling was taken into account by a process of graphical integration. The effective internal areas of the annular rings were determined in accord with the expression

$$\text{Eff. area} = \pi b\left(\sqrt{a^2 + b^2} - b\right) \qquad (3)$$

where a is the inside diameter, and b is the thickness. This expression was derived from the assumptions that the evaporation follows the cosine law and that the condensation coefficient is unity.

The curve shown in Fig. 1 was determined by using only the data for vacuum cast material. It

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[2] (a) Langmuir, *Phys. Rev.*, **2**, 329 (1913); (b) Knudsen, *Ann. Physik*, **29**, 179 (1909).

[3] Marshall, Dornte and Norton, THIS JOURNAL, **59**, 1161 (1937).

[4] The coefficient, α, is the condensation coefficient—sometimes called the accommodation coefficient; however, since this is ambiguous in that the term has been preempted for the thermal accommodation, we feel that the more descriptive term "condensation coefficient" is preferable.

[4a] Johnston and Marshall, *ibid.*, **62**, 1382 (1940).

[5] R. Speiser, G. W. Ziegler, Jr., and H. L. Johnston, manuscript in preparation.

[6] Birge's values of the fundamental constants have been used throughout: R. T. Birge, *Rev. Mod. Phys.*, **13**, 233 (1941).

TABLE I

RATES OF EVAPORATION AND VAPOR PRESSURES OF VACUUM CAST BERYLLIUM

Run	Temp., °K.	Wt. loss, g.	Eff. time, min.	Rate g./sq. cm./sec. × 10^7	−log P (atm.)
26	1172[a]	0.01042	178.8	0.329	8.0726
25	1206[a]	.00883	55.9	0.891	7.6337
36	1209[a]	.02108	88.4	1.35	7.4528
24	1245[a]	.01940	44.6	2.45	7.1875
21	1263[a]	.02462	35.3	3.92	6.9803
23	1265[b]	.02467	27.3	5.06	6.8692
35	1268[a]	.03463	31.8	6.15	6.7838
20	1274[a]	.04170	34.4	6.79	6.7398
33	1284[a]	.03647	26.5	7.76	6.6801
29	1320[c]	.00121	77.7	19.8	6.2673
22	1326[b]	.04921	11.3	24.3	6.1774
30	1343[c]	.00239	81.3	37.3	5.9886
37	1419[c]	.00692	78.5	183	5.2859
31	1448[c]	.00632	36.1	222	5.1975
38	1457[c]	.00954	60.1	329	5.0254
39	1537[c]	.00888	15.2	1210	4.4482
40	1552[c]	.01209	16.5	1520	4.3471

[a] Solid cylinder. [b] Drilled cylinder. [c] Knudsen cell.

TABLE II

RATES OF EVAPORATION AND VAPOR PRESSURES OF EXPERIMENTALLY SINTERED BERYLLIUM[a]

Run	Temp., °K.	Wt. loss, g.	Eff. time, min.	Rate, g./sq. cm./sec. × 10^7	−log P (atm.)
7	1213	0.04000	234.1	1.37	7.4457
9	1243	.01946	61.4	2.54	7.1723
14	1256	.02926	65.3	3.62	7.0161
15	1273	.03098	49.9	5.03	6.8703
19	1281	.03633	47.9	6.19	6.7788
11	1291	.03346	24.0	11.2	6.5196
12	1299	.03427	24.0	11.5	6.5078
13	1302	.03135	21.8	11.6	6.5035
18	1317	.05235	32.9	12.9	6.4539
17	1326	.04339	21.0	16.8	6.3377
16	1333	.04195	16.5	20.6	6.2480
10	1365	.04837	7.8	49.5	5.8621

[a] These samples were all in the form of annular rings.

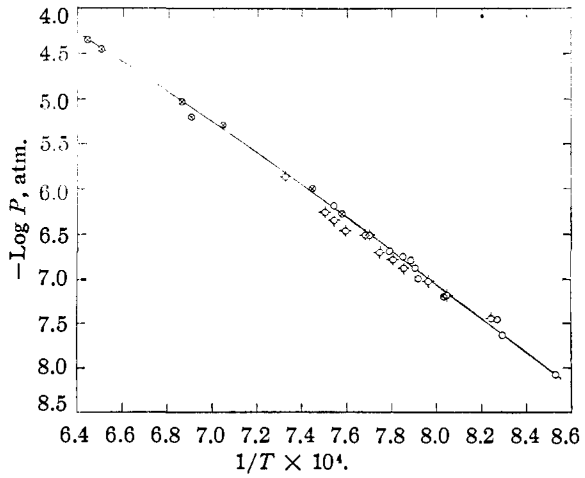

Fig. 1.—⊙, Pure vacuum cast; -ϕ-, exp. sintered; ⊗, Knudsen cell, vacuum cast.

is seen that there is no marked difference between the pressures exerted by vacuum cast beryllium and by sintered beryllium. It is to be noted, however, that these values are higher than the values reported by Schuman and Garrett[7] by a factor of approximately three.

The values of ΔH_0^0 for the evaporation process

$$\text{Be (solid)} = \text{Be (monatomic vapor)} \qquad (4)$$

have been calculated in accordance with the formula

$$\Delta H_0^0/T = -R\ln P - (F^0 - H_0^0)\ \text{gas} + (F^0 - H_0^0/T)\ \text{solid} \qquad (5)$$

for all of the data obtained with vacuum cast beryllium and are given in Table III. The free energy functions of the gas were computed from spectroscopic data,[8] and the free energy functions of the solid material were obtained from heat capacity data. The value for the entropy at 298.1°K. was taken to be 2.28 e.u.[9] Unfortunately heat capacity data are not available for the range in which these measurements were made, so in order to make the calculations it was necessary to extrapolate the equation of K. K. Kelley.[10] This introduces some uncertainty into the ΔH_0^0 values; however, since the free energy function of the solid is small compared to the other terms the relative error introduced on this account will be considerably less than the relative error in the heat capacity extrapolation.

TABLE III

THERMODYNAMIC CALCULATIONS FOR VACUUM CAST BERYLLIUM

Temp., °K.	$-(F^0 - H_0^0)/T$ solid	$-(F^0 - H_0^0)/T$ gas	$-R \ln P$	ΔH_0^0/kcal.
1172	5.26	34.381	36.925	77.41
1206	5.39	34.523	34.917	77.24
1209	5.40	34.536	34.090	76.45
1245	5.51	34.681	32.876	77.25
1263	5.58	34.753	31.929	77.17
1265	5.58	34.760	31.420	76.66
1268	5.59	34.772	31.030	76.35
1274	5.61	34.796	30.829	76.47
1284	5.65	34.834	30.555	76.70
1320	5.77	34.972	28.667	76.39
1326	5.80	34.994	28.256	76.18
1343	5.85	35.058	27.390	76.01
1419	6.03	35.331	24.178	75.89
1448	6.19	35.431	23.774	76.77
1457	6.23	35.462	22.987	76.08
1537	6.46	35.728	20.347	76.27
1552	6.52	35.776	19.884	76.27
				Mean 76.57 ± 0.37

The equation for the vapor pressure has been determined by inserting the average value of ΔH_0^0 into equation (5) and expanding the term

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[7] Schuman and Garrett, THIS JOURNAL, **66**, 442 (1944).

[8] Moore, Nat'l Bur. Stand. Circular **467**, Vol. 1, Section 1 (1948).

[9] Kelley, *Bur. Mines Bull.*, **434**, 25 (1941).

[10] Kelley, *Bur. Mines Bull.*, **371**, 13 (1934).

$\Delta(F^0 - H^0_0/T)$ as a linear function of the temperature

$$\log P(\text{atm.}) = 6.186 + 1.454 \times 10^{-4}T - (16{,}734 \pm 80)/T$$

The Condensation Coefficient.—As pointed out by Johnston and Marshall[4a] the value of the condensation coefficient, α, may be tested by observing any drift in values for ΔH^0_0 calculated over a temperature range with the supposition that this coefficient is unity. If this supposition is contrary to fact, the values of ΔH^0_0 will exhibit a drift in accordance with the term $RT \ln \alpha$. However, there are more direct methods which we employed in these measurements. The first was to compare the rate of evaporation of two cylinders, one solid and one perforated with holes drilled longitudinally into it. The rate calculations were performed considering the area of the perforated cylinder to be the same as though the holes had not been drilled. The results for the two cylinders calculated in this fashion were the same within experimental error which indicates that the condensation coefficient is not far removed from unity.

A more sensitive method for the determination of the condensation coefficient consists in comparing the rate at which saturated metal vapor effuses through an orifice with the rate at which a metal surface evaporates *in vacuo*, since it is given simply by the ratio of these two rates. We found these to be the same within experimental error, also indicating that the condensation coefficient is unity within the accuracy of our measurement.

Other Data.—To our knowledge the only other published data on the vapor pressure of beryllium are those of Bauer and Brunner[11] and those of Schuman and Garrett.[7] Since the former measurements are on liquid beryllium and are at relatively high pressures, it is difficult to make a direct comparison. Since the range of the Schuman and Garrett measurements is included within the range of our measurements the results may be directly compared, and, as previously pointed out, their results are considerably lower than ours. We believe the explanation may be as follows: Schuman and Garrett obtained their temperatures by sighting on the surface of their specimen and correcting to black body temperature by using the emissivity. They determined this emissivity for a polished sample. However, due to the anisotropic nature of beryllium it leaves a progressively irregular surface on evaporation and the apparent emission temperature will increase markedly in the course of the evaporation.[12] Thus if the emissivity determined for a polished specimen is applied to apparent temperatures of an evaporating sample, the calculated black body temperature will be too high, and correspondingly the vapor pressures obtained will be too low if these temperatures are assumed to be correct. In our measurements this difficulty was avoided by making all temperature measurements under black body conditions.[13]

Summary

The vapor pressure of solid beryllium has been measured in the temperature range 1171–1552°K. by measurement of both the rate at which the metal surface evaporates into a vacuum and the rate at which saturated metal vapor effuses through an orifice. The results obtained by these methods are in good agreement, and intercomparison of results indicates that the condensation coefficient is unity within experimental error. The ΔH^0_0 values have been calculated and show no appreciable drift with temperature, the mean value being 76,560 ± 370 cal. By combining this value of ΔH^0_0 with the standard free energy functions of solid and gaseous beryllium, the vapor pressure equation $\log P\ (\text{atm.}) = 6.186 + 1.454 \times 10^{-4}T - (16{,}734 \pm 80)/T$ was obtained.

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[11] Bauer and Brunner, *Helv. Chim. Acta*, **17**, 958 (1934).

[12] We have found that the emissivity of a sample whose surface is irregular due to evaporation is about 0.80 at 1150°K. Calculation of the emissivity from the empirical equation given by Schuman and Garrett yields a value of 0.59 at 1150°K. for a polished surface.

[13] A difference in the purity of the samples of beryllium used by the authors and Schuman and Garrett may be an additional explanation for the differences in vapor pressure observed. Since the war, there have been significant improvements in the purification of beryllium and in the quantitative determination of the impurities occurring in the metal.