[CONTRIBUTION FROM PHYSIKALISCH-CHEMISCHES INSTITUT DER TECHNISCHEN HOCHSCHULE, BRESLAU]

I. THE SPECIFIC HEATS OF THALLIUM, CALCIUM AND MAGNESIUM MEASURED TO 10° ABSOLUTE

II. THE ENTROPY AND CHEMICAL CONSTANTS OF MAGNESIUM FROM SPECTROSCOPIC DATA

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This paper presents the results of the measurement of specific heats from 10 to 200° absolute, of thallium, calcium and magnesium. The specific heats of these metals have indeed been measured in the low-temperature range, yet in no case have they been measured to a sufficiently low temperature to permit a safe extrapolation to the absolute zero, which is necessary in the calculation of the entropy. Because of the peculiarity of the entropy function, the chief interest in these measurements has been in the region under 80°A. The apparatus, however, was capable of rendering exact results even at a temperature as high as 250°A.

Of special interest is a comparison between the entropy values obtained from calorimetric and from spectroscopic data, respectively. In order to make such a comparison, it is necessary to calculate the entropy of the substance as a gas, which requires the values for the heat of vaporization, and for the specific heats at higher temperatures. The heat of vaporization may be calculated from the vapor pressure curve. At the present time, recent measurements of these quantities make it possible to calculate the entropy of magnesium vapor.

Experimental Details

The experimental method used is essentially that of the vacuum calorimeter, in which the material whose specific heat is to be measured served as the calorimeter. The apparatus pictured in Fig. 1 was made for a previous investigation[1] and is capable of reaching a temperature of 9.4°A. The bulbs A and B are made of thin glass, bulb B having a *double-walled construction.* The space formed in the double bulb B serves to hold liquid hydrogen, which is condensed by applying several atmospheres' pressure and cooling the outer bulb A with boiling hydrogen. The heat transfer is effected by 2–5-mm. pressure of pure helium in the space between the two bulbs. All other gases are ineffective for this purpose because they are either condensed or are strongly adsorbed at these low temperatures, so that rapid removal by pumping is impossible.[2] When the space between A and B is evacuated by means of a mercury diffusion pump, the inner parts of the apparatus are thermally well insulated. Then if vacuum from a Gaede steel mercury pump and a heavy-duty oil pump in series is applied to the condensed hydrogen so that it boils under 1 mm. pressure, the temperature of the hydrogen decreases rapidly to about 9.4°A.

The block of material to be investigated (K) is suspended freely in a protecting

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[1] Clusius, *Z. physik. Chem.*, Abt. B, **3**, 41 (1929).

[2] Eucken, *Sitz. Berl. Akad. Wiss.*, 682 (1914); Clusius and Harteck, *Z. physik. Chem.*, **134**, 243 (1928).

mantle of copper, which has a block of lead in the upper end to increase its heat capacity. The cable, containing the wires which carry the heating current and the connections to the resistance thermometer, is made of four silk-covered copper wires 0.1 mm. in diameter. The cable, after being wound with thread, was boiled in a mixture of beeswax and resin. No disturbing gases are evolved under vacuum from a cable prepared in this way. To prevent any heat conduction to the block from the outside by the copper wires, the cable is connected thermally with the protecting mantle by imbedding it in a trough of Wood's metal.

In the block of metal a thread-like groove of suitable pitch and depth was cut to accommodate a 0.03 mm. constantan wire having a resistance of 500–800 ohms. Over this winding of the heating element was wrapped a layer of thin tissue paper, which served to insulate the constantan from the next winding of 0.05 mm. lead wire, which formed the resistance thermometer. To give good thermal contact between the block and the two windings, a small amount of lacquer was used. The quantity of lacquer, lead, constantan and paper was determined by weight and considered in the calculation of the specific heat of the metal.

Before undertaking this investigation, the qualifications of the lead resistance thermometer were again carefully determined[3] by comparing its resistance with that of a pure platinum wire between 20 and 80° absolute. The measured resistance of the platinum wire was recalculated by Henning's formula[4] to the exact temperature values given by K. Onnes and Tuyn.[5] The agreement between the lead and platinum thermometers is completely satisfactory considering the difficulty of calibration in this low temperature range.

The completely wound and lacquered block of metal was heated for several hours at 150° in order to harden the lacquer and to age the lead wire, which is necessary for a reproducible resistance value at 0.0°. As can be seen from the following table, a satisfactory behavior of the thermometer was obtained in every case. It was calibrated in the range of liquid air by means of an oxygen vapor-pressure thermometer, and in the range of liquid hydrogen by the boiling point of the latter substance in the chamber of bulb B under a known pressure. The deviations from the normal wire table were limited (maximum 0.1°A.) and were taken into account by means of the Nernst α-rule.[6]

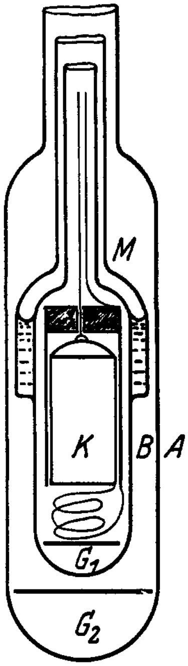

Fig. 1.

Date	Resistance at 0.0°	Sample
1-15-29	277.8 ohms	Magnesium
1-20-29	Used at 10°A.	
1-28-29	277.7 ohms	
2-5-29	555.0 ohms	Calcium
2-8-29	Used at 10°A.	
2-9-29	555.5 ohms	
2-20-29	134.2 ohms	Thallium I
2-21-29	Used at 10°A.	
2-22-29	134.3 ohms	

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[3] Clusius and Vaughen, *Z. ges. Kälte-Ind.*, **36**, 215 (1929).

[4] Henning, *Naturwissenschaften*, **16**, 617 (1928).

[5] Onnes and Tuyn, *Comm. Leiden Suppl.*, 58 (1926).

[6] Nernst, *Ann. phys.*, **36**, 432 (1911).

Date	Resistance at 0.0°	Sample
4-27-29	200.3 ohms Used at 90°A. 200.3 ohms	Thallium II

The determination of the energy supplied to the sample consisted in measuring the voltage, the resistance of the circuit, and the time of current flow. A standardized stop watch was used in an apparatus which made or broke the circuit precisely as the watch was started or stopped. A storage battery of large capacity was used as a source of current. The circuit included a precision resistance box, the potential across the terminals of which was kept constant by balancing it against that of a standard cell. A second standard cell was at times substituted to serve as a check. The e. m. f. of the cell was taken as 1.0185 volts at 20° and a difference between the two cells greater than 0.0002 volt was never detected. The current flow was regulated by means of two parallel sliding resistances, one of which had ten times the resistance of the other. This regulation was not difficult because of the limited change in resistance of the constantan wire due to temperature changes. Before and after each individual heating, the resistance of the constantan wire was determined with an accuracy of 0.1% by means of a precision bridge. The same bridge was used to measure the resistance of the lead wire thermometer. The value, 4.1842 watt seconds = 1 calorie, as given by Jaeger and Steinwehr,[7] was used in the calculation of the heat quantities.

The various sources of error in these measurements are as follows.

(1) **Measurement of the Temperature Rise in an Individual Experiment.**—The rate at which the temperature increases, due to heat leaks, during the intervals before and after the energy input, was uniform and could be measured accurately even at the lowest temperature. Until after the heat capacity of the sample reached 0.4 calorie, the temperature was read every fifteen seconds. Later readings were taken every thirty seconds.

(2) **Error in Determining the Energy Input.**—The energy introduced into the sample may be regarded as being correct to within 0.3% for the shorter heating intervals (five to ten seconds), and within 0.03% for the longer intervals (thirty to one hundred twenty seconds).

(3) **Error in the Correction for the Accessory Material.**—The corrections for the various foreign materials such as the lead wire, constantan wire, thread and lacquer, are as follows.

A = percentage of the total heat capacity due to foreign materials
B = percentage error due to foreign materials

		10°A.	20°A.	80°A.	200°A.
Magnesium	A	39	16	2	2.2
	B	2	0.8	0.1	0.1
Calcium	A	15	5	2	2.5
	B	0.75	0.25	0.1	0.1
Thallium	A	1	.6	1.4	2.2
	B	0.06	.03	0.07	0.1

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[7] Jaeger and Steinwehr, *Ber. Sitzungsberichte*, 424 (1915).

(4) **Errors in the Measurement of Temperature.**—Taking into account the slight error due to the temperature measurement, the total error in the results for calcium at the lowest temperatures probably does not exceed 1.5%. At 20°A. this error amounts to 0.8%, and at 80°A. it is probably within 0.3%. These errors are somewhat lower for the thallium measurements, and are slightly larger for those of magnesium because of the larger error due to corrections for the foreign materials present in the latter sample.

Source of Materials.—The magnesium was presented to us as a very pure sample by Dr. Grützner of the I. G. Farbenindustrie. The analysis of the material is as follows:

Element	Si	Al	Fe	Mn	Cu	Zn	Total
Percentage	0.02	0.06	0.018	0.035	..	..	0.133

The sample of magnesium was turned to a cylindrical block 17 mm. in diameter and 83 mm. long weighing 31.989 g. Considering an atomic weight of 24.32 for magnesium, the block contained 1.316 mole.

The calcium block was of similar dimensions and was turned out of a sample of the purest commercial metal. Traces of iron, silicon, nitrogen and calcium chloride were found by the analysis. The block weighed 28.617 g., corresponding to 0.7139 mole at an atomic weight of 40.07.

Two thallium samples coming from different sources were used in these measurements. No difference in the specific heat curves for these two samples could be detected, which is worthy of mention because our measurements differ from those to be found in the literature. One sample was made by the reduction of pure thallium oxide with charcoal powder in a stream of hydrogen. The other sample came from Kahlbaum, and contained only traces of iron and aluminum according to the analysis furnished. Later, however, the presence of lead was discovered, yet the presence of this element in such limited quantities can hardly have affected the calculation of the specific heat because the atomic weights as well as the characteristic temperature of thallium and lead are similar. In consideration of the appreciably smaller heat conductivity of thallium, blocks of only 12 mm. in diameter and 64 mm. and 47.5 mm., respectively, in length were used. The first sample weighed 84.943 g. (0.4158 mole) and the second 63.671 g. (0.3115 mole), using an atomic weight of 204.39.

Results

The results of these measurements are assembled in Table I, which contains the absolute temperature and the directly measured C_p values. To picture the completeness of the results, the Debye characteristic temperature Θ has been calculated, which required the value of C_v. This value was obtained from the approximate equation[8]

$$C_p - C_v = AC_p^2T$$

In order to use this equation, the value of $C_p - C_v$ must be known exactly for at least one temperature, and since the equation

$$C_p - C_v = T\frac{\alpha^2V_0^2}{XV}$$

requires data which are not known for calcium and magnesium, the following simplification according to Mie and Grüneisen was used

$$\frac{C_p}{C_v} \simeq 1 + 2.0\ \alpha\ T$$

This equation gives results correct to within 10% for monatomic substances, and the correction here is only about 1.5–2.5% of the C_p value.

The following values were obtained

$$A_{\mathrm{Tl}} = 2.85 \times 10^{-5}$$
$$A_{\mathrm{Ca}} = 2.42 \times 10^{-5}$$
$$A_{\mathrm{Mg}} = 2.61 \times 10^{-5}$$

The Θ-values were calculated for values of C_v under 5 calories. Because of the form of the Debye curve, and the increasing errors in C_p and $C_p - C_v$, a further comparison is uncertain.

TABLE I

THALLIUM (TWO SAMPLES)

Sample	$T°$	C_p	C_v	$C_p - C_v$	Θ_D
I	11.18	0.976		...	84
II	11.40	1.069		...	82
I	11.98	1.099		...	85
II	12.64	1.193		...	87
II	12.88	1.234		...	87
I	13.22	1.318		...	87
I	13.94	1.436		...	88
I	13.98	1.552		...	85
II	14.86	1.560		...	90
II	14.93	1.581		...	90
II	15.32	1.637	1.636	0.001	90
I	15.66	1.743	1.742	.001	90
I	16.08	1.800	1.799	.001	90
II	17.50	1.975	1.973	.002	93
II	17.78	2.009	2.007	.002	94
I	18.24	2.130	2.218	.002	94
II	18.36	2.105	2.103	.002	94

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[8] Cf. "Handbuch der Experimental Physik," Vol. VIII, p. 208.

C_p = Molecular heat at constant pressure
C_v = Molecular heat at constant volume
α = Cubical coefficient of expansion
X = Compressibility
V_0 = Normal volume
V = Volume at the temperature T

TABLE I (*Continued*)

Sample	$T°$	C_p	C_v	$C_p - C_v$	Θ_D
I	18.80	2.225	2.222	0.003	93
I	19.86	2.385	2.382	.003	94
II	20.6	2.456	2.453	.003	95
II	20.7	2.457	2.454	.003	96
I	21.7	2.704	2.700	.004	94
II	23.6	3.075	3.069	.006	93
I	25.0	3.176	3.169	.007	95
II	27.5	3.625	3.615	.010	92
I	29.2	3.717	3.706	.011	95
II	33.0	4.105	4.098	.017	94
I	34.5	4.225	4.208	.017	95
II	38.7	4.571	4.548	.023	93
I	40.6	4.675	4.650	.025	93
II	44.9	4.878	4.848	.030	93
I	47.2	4.960	4.927	.033	94
II	52.3	5.175	5.135	.040	92
I	54.0	5.225	5.133	.042	92
II	59.2	5.342	5.294	.048	92
I	61.4	5.319	5.270	.049	97
II	66.1	5.452	5.396	.056	94
I	69.0	5.530	5.470	.060	91
I	77.5	5.632	5.552	.070	93
I	94.0	5.763	5.674	.089	
II	96.2	5.725	5.635	.090	
II	103.5	5.80	5.70	.10	
II	118.4	5.94	5.82	.12	
II	123.2	5.96	5.84	.12	
II	132.8	6.01	5.87	.14	
II	139.8	6.04	5.89	.15	
II	147.8	6.16	6.00	.16	
II	236.6	6.29	6.02	.27	
II	246.6	6.34	6.06	.28	
II	249.0	6.34	6.06	.28	

MAGNESIUM

$T°$	C_p	C_v	$C_p - C_v$	Θ_D
11.31	0.013		...	(450)
11.43	.013		...	(457)
14.14	.026		...	370
14.28	.028		...	364
16.94	.049		...	360
17.24	.051		...	361
19.50	.075		...	360
19.64	.073		...	364
21.7	.112		...	348
24.3	.169		...	340
27.1	.246		...	335
30.2	.353		...	329
34.2	.533		...	323
37.6	.696		...	321

TABLE I (*Continued*)

$T°$	C_p	C_v	$C_p - C_v$	Θ_D
41.7	0.919		...	319
45.2	1.122		...	319
48.7	1.330	1.328	0.002	318
51.8	1.518	1.515	.003	318
55.1	1.724	1.720	.004	317
63.7	2.214	2.206	.008	318
86.7	3.247	3.223	.024	325
93.2	3.546	3.515	.031	321
99.2	3.718	3.682	.036	324
106.7	3.878	3.836	.042	332
115.4	4.200	4.147	.053	324
124.2	4.426	4.363	.063	321
136.2	4.640	4.564	.076	326
145.4	4.830	4.742	.088	320
163.4	5.070	4.960	.110	319
172.6	5.192	5.071	.121	315
182.0	5.229	5.100	.129	...
191.2	5.329	5.118	.141	...
217.2	5.460	5.291	.169	...
228.4	5.520	5.339	.181	...

CALCIUM

$T°$	C_p	C_v	$C_p = aT^3$ 4.41×10^{-5}	$C_p - C_v$	Θ_D
10.16	0.044		0.046	...	223
10.66	.055		.053	...	218
11.72	.071		.071	...	220
11.76	.072		.072	...	220
13.02	.097		.097	...	220
13.49	.116		.118	...	215
15.34	.162		.159	...	219
16.58	.203		.201	...	218
17.43	.233		.234	...	219
18.73	.290		.290	...	219
19.36	.320		.320	...	318
21.40	.405		(.432)	...	222
24.2	.581		...	...	221
27.6	.833		...	...	219
31.7	1.094		...	...	226
34.8	1.378	1.376	...	0.002	224
38.8	1.704	1.701	...	.003	225
43.3	2.076	2.072	...	.004	224
52.2	2.744	2.735	...	.009	225
59.6	3.190	3.175	...	.015	227
67.7	3.546	3.525	...	.021	232
75.7	3.879	3.852	...	.027	234
83.5	4.195	4.160	...	.035	233
92.7	4.470	4.425	...	.045	234
102.2	4.700	4.645	...	.055	235
111.5	4.915	4.850	...	.065	233

TABLE I (*Concluded*)

$T°$	C_p	C_v	$C_p = aT^3$ 4.41×10^{-5}	$C_p - C_v$	Θ_D
118.4	5.053	4.980	...	0.073	229
128.6	5.234	5.149	...	.085	...
138.8	5.347	5.251	...	.096	...
147.2	5.480	5.373	...	.107	...
157.0	5.586	5.468	...	.118	...
168.0	5.653	5.523	...	.130	...
178.0	5.779	5.635	...	.144	...
189.4	5.803	5.649	...	.154	...
200.8	5.930	5.763	...	.167	...

Figure 2 presents the curves of the data. The results of earlier investigations are also entered,[9] which in the case of thallium are too low, and with calcium and magnesium are too high, when compared with our data. With samples of thallium from different sources, however, we obtained the same values. The difference between the measurements with calcium and magnesium as recorded here, and those reported by earlier investigators,

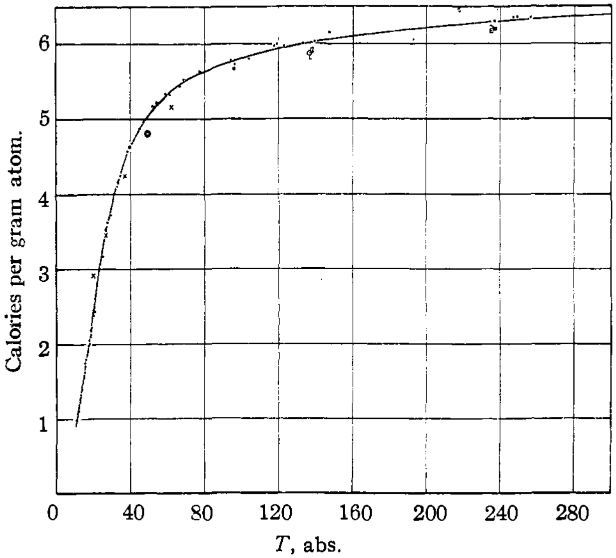

Fig. 2.—Thallium: ⊙, Dewar, average; ⊡, Ewald, average; ♀, Schimpf, average; ×, Nernst and Schwers; ●, Clusius and Vaughen.

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[9] Dewar (Tl, Ca, Mg), *Proc. Roy. Soc.* (London), **89**, 158 (1913); Günther (Ca), *Ann. Phys.*, [4] 51, 828 (1916); Eastman and Rodebush (Ca and Mg), THIS JOURNAL, **40**, 496 (1918); Nordmeyer (Ca), *Verhandl. deut. physik. Ges.*, **10**, 202 (1908); Nernst and Schwers (Tl and Mg), *Ber. Sitzb.*, 355 (1914); Richards and Jackson (Tl and Mg), *Z. physik. Chem.*, **70**, 414 (1910); Ewald (Tl and Mg), *Ann. Physik*, **44**, 1213 (1914); Russell (Tl), *Physik. Z.*, **13**, 59 (1912); Schimpff (Mg), *Z. physik. Chem.*, **71**, 257 (1910).

which also differ among themselves, is surely not due to the use of impure samples.

In the case of thallium, direct reproduction of the specific heat values is possible from 17°A. on, by using $\Theta = 94°$ in the Debye function. Below this temperature, the Θ value decreases to about 84°, indicating a deceleration of the atomic vibrations. Lead, which is so similar to thallium as regards its elastic constants, its density and its melting point, possesses this characteristic also. With lead, between 20 and 80°A., the specific heat is given correctly by a Debye function with a Θ of 88,[10] but at lower temperatures $\Theta = 85$.[11] Keesom and van den Ende,[12] in reporting earlier experiments,[13] mention that at liquid helium temperatures no further variation from the Θ-value, determined at 10°A., is apparent.

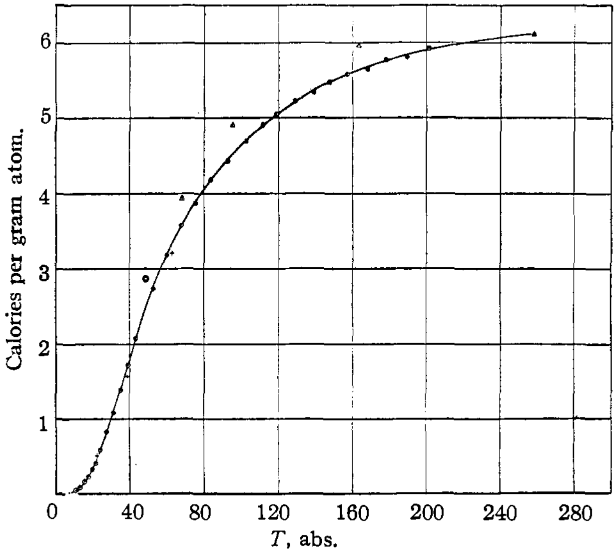

Fig. 3.—Calcium: ◉, Dewar, average; △, Eastman and Rodebush; +, Günther; ⊙, Clusius and Vaughen.

In all probability thallium behaves in a similar manner, and an extrapolation of the specific heat curve to the absolute zero (using a Θ value of 84) for the calculation of the absolute entropy, seems justifiable without introducing a large error.

In the measurements with calcium, special care was used in obtaining a high vacuum. Only after several days of continuous pumping did the hydrogen evolution from the calcium block cease. The Θ value of calcium

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[10] Eucken and Schwers, *Verhandl. deut. physik. Ges.*, **15**, 581 (1913).

[11] Simon, *Z. physik. Chem.*, **110**, 572 (1924).

[12] Keesom and van den Ende, *Physik. Z.*, **29**, 896 (1928).

[13] Keesom and Andrews, *Comm. Phys. Lab. Univ. Leiden*, No. 185.

exhibits the comparatively moderate slope of about 6%, and therefore belongs to the class of elements whose specific heats are reproduced approximately by the Debye function.[14] Especially noteworthy is the fact that the Θ-value approaches a constant of about 219 at low temperatures, indicating that the T^3 rule of Debye is probably valid. In fact, the data for C_p, calculated from the equation

$$C_p \simeq C_v = 4.41 \times 10^{-5} T^3$$

agree remarkably well with the directly measured values of C_p below a C_p value of 0.3 calorie. It appears that the extrapolation to the absolute zero can be performed with safety.

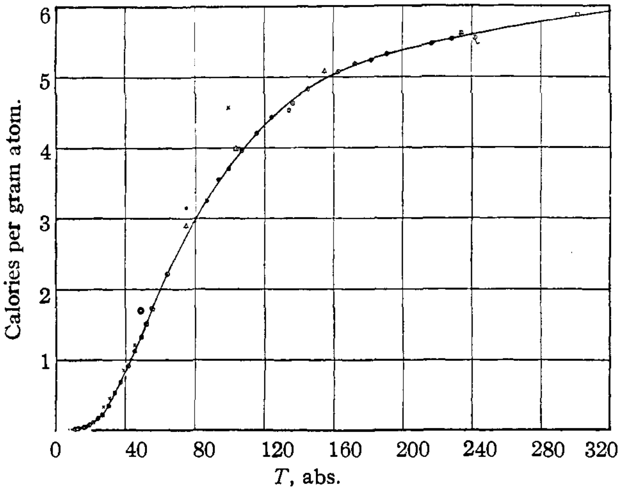

Fig. 4.—Magnesium: ◉, Dewar, average; ⊡, Ewald, average; ♀, Schimpf, average; △, Eastman and Rodebush; ×, Nernst and Schwers; ⊙, Clusius and Vaughen.

With magnesium, on the other hand, the Θ-values increase with decreasing temperature, and above 30°A. a Θ-value of 322 reproduces a fairly satisfactory atomic heat value. Even when it is considered that the difficulties of measurement at the low temperatures (due to the extremely small heat capacity of the substance) strongly magnify the possibilities of error, the reality of the effect remains indeed unquestionable. At the lowest temperatures, the points on the curve due to separate series of measurements lie very close together, indicating very good reproducibility. If any appreciable experimental error were present, too high a specific heat value would probably be obtained. A more rapid decrease of the specific heat curve than is to be expected from the T^3 law has been noted only in

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[14] Compare the assembly of Professor Eucken in "Handbuch der Experimental Physik," Vol. VIII, p. 245.

the case of copper and tungsten.[15] With copper at 14.51°A., a specific heat of 0.0396 cal. was determined, whereas the calculated value is 0.044 cal. The specific heat of tungsten decreases even more suddenly. The variations with magnesium are of the same order of magnitude. An explanation of this behavior, which might indicate a failure of the fundamental T^3 law, is not at present available.

For the calculation of the entropy under standard conditions, the curves were extrapolated to 298.1°A., by making use of the existing data (see Fig. 2). The following values for the integral $S_0 (S_0 = \int C_p \, \mathrm{d}t/T)$ were obtained.

	Calculated	Lewis and Randall[16]
Thallium S_0	= 15.51	14.6
Calcium S_0	= 9.72	10.64
Magnesium S_0	= 7.76	8.3

VAPOR PRESSURE CONSTANTS OF MAGNESIUM

The existing data for magnesium are sufficient to permit the calculation of the vapor pressure constants. The general vapor pressure curve for this element, whose vapor is probably monatomic, is as follows:[17]

$$\log p = -\frac{L_0}{4.573T} + \frac{5}{2}\log T - \frac{1}{4.573}\int_0^T \frac{\mathrm{d}T}{T^2}\int C_{p_{\text{cond.}}}\,\mathrm{d}T + J_p \qquad (1)$$

where p is the saturation pressure at the temperature T, L_0 is the heat of vaporization at the absolute zero, $C_{p_{\text{cond.}}}$ is the specific heat of the condensate, and J_p is the vapor pressure constant. The required values are calculated as follows.

The heat of vaporization at absolute zero may be calculated from the data of Hartmann and Schneider.[18] Since these values were obtained by the boiling method, in which the zone of condensation is located by determining the region of constant temperature, their results may be considered to be free from systematic errors. From the slope of their vapor pressure curve, these authors obtain a value of the heat of vaporization of L_T = 32,800 calories at an average temperature of 1100°A. Using for the triple point 924°A.,[19] the following is obtained as the heat of vaporization at the absolute zero

$$\overline{L}_T = L_0 + \int_0^T C_{p_{\text{gas}}}\cdot\mathrm{d}T - \int_0^T T\,C_{p_{\text{cond.}}}\,\mathrm{d}T - L_e \qquad (2)$$

$$L_0 = L_T + L_e + \int_0^T C_{p_{\text{cond.}}}\,\mathrm{d}T - 5/2\,RT$$

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[15] Keesom and K. Onnes, *Comm. Phys. Lab. Univ. Leiden*, 147a (Cu); Lange, *Z. physik. Chem.*, **110**, 360 (1921) (W).

[16] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw Hill Book Co., Inc., New York, **1923**.

[17] *Cf.* Eucken, "Lehrbuch der Chemischen Physik," **1930**, p. 234.

[18] Hartmann and Schneider, *Z. anorg. Chem.*, **180**, 275 (1929).

[19] Landolt-Börnstein, "Tabellen " Vol. I, 82g (1923).

where L_e is the heat of fusion (1130 calories),[20] C_p is the specific heat of the condensate, which we have supplied for low temperatures, and for values above room temperature those reported by Eastman, Williams and Young[21] have been used. The results of these authors are given correctly enough between 300 and 900°A. by the equation $C_p = 2.62 \times 10^{-3}T + 5.27$. The specific heat of the liquid has been taken as 7 calories.[22] Then

$$L_0 = 32800 + 1130 + 7365 - 5965 = 35330 \text{ cal.} \tag{2a}$$

The logarithm of the triple point vapor pressure is -0.339 when the value of the saturation pressure at 1163°A. is taken as 84 mm. of mercury according to Hartmann and Schneider

$$\log p_2 - \log p_1 = \frac{L_T}{4.573}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{3}$$

The evaluation of the double integral of Equation 1 is easiest in this case by the transformation

$$\int_0^T \frac{\mathrm{d}T}{T^2}\int_0^T C_p\,\mathrm{d}T = \int_0^T \frac{C_p}{T}\,\mathrm{d}T - \frac{1}{T}\int_0^T C_p\,\mathrm{d}T \tag{4}$$

The entropy at 298°A. is known as 7.76. The remainder of the equation follows

$$S_{298}^{924} = \int_{298}^{924} 2.62 \times 10^{-3}\,\mathrm{d}T + \int_{298}^{924} \frac{5.27}{T}\,\mathrm{d}T = 7.63$$

The value of the second integral in Equation 4 appears as 5455 calories from the calculation of L_0; therefore the second member of the above equation becomes 5.89. The double integral is then

$$\int_0^T \frac{\mathrm{d}T}{T^2}\int_0^T C_p\,\mathrm{d}T = 7.76 + 7.63 - 5.89 = 9.50$$

Combining the various values in the vapor pressure formula

$$jp = \frac{35330}{4.573 \times 927} - 2.5 \times 2.967 + \frac{9.50}{4.573} + 0.339$$

$$jp_{\text{mm.}} = 3.324$$

Calculating the pressure in atmospheres

$$jp_{\text{atm.}} = 3.324 - \log 760 = 0.443 \pm 0.1$$

The limit of error which has been given is a result of the uncertainty of the energy content of the condensate.

From statistical considerations, the chemical constant value for jk is[23]

$$jk = -1.587 + 1.5 \log M + \log g$$

where M is the atomic weight of the gas, and g is the degree of freedom of the atom in a magnetic field, its quantum weight. For magnesium in particular $g = 1$, and $jk = 0.493$.

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[20] Auberry and Griffiths, *Proc. Phys. Soc.* (London), **38,** 378 (1926).

[21] Eastman, Williams and Young, THIS JOURNAL, **46,** 1178 (1924).

[22] Zalesinski and Zulinski, *Bull. intern. l'acad. Polonaise,* **9–10,** 479 (1928).

[23] A. Eucken, "Lehrbuch der chemischen Physik," **1930,** pp. 243–248.

In order to compare the entropy of magnesium vapor, as calculated from these experimental data, with the theoretical value under standard conditions, the data must be rearranged somewhat. Let one mole of magnesium vaporize at 298°A. From Equation 2 the heat of vaporization is

$$\begin{aligned} L_{298} &= 35330 + 298 \times 2.5 \times R - 1155 \\ &= 35655 \text{ calories} \end{aligned}$$

if the value 1155 cal. is assigned to the energy content of the condensate (from the specific heat measurements). The entropy increase in vaporizing under equilibrium pressure is 35655/298 = 119.65 cal. per degree. The equilibrium pressure is obtained from Equations 1 and 4 and from the value of *jp*.

$$\begin{aligned} \log p_{298} &= \frac{-35330}{4.573 \times 298} + \frac{5}{2} \log 298 - \left(7.76 - \frac{1155}{298}\right) \frac{1}{4.573} + 0.443 \\ &= -25.92_5 + 6.18_6 - 0.84_8 + 0.44_3 = 20.14_4 \end{aligned}$$

This value corresponds to a vapor pressure of 0.717×10^{-21} atmospheres. In compressing this vapor to atmospheric pressure, the following entropy change takes place

$$\Delta S = -4.573 \times 20.144 = -92.12 \text{ cal. per degree}$$

The entropy of magnesium vapor at 25° is empirically

$$S^{\circ}_{\mathrm{Mg}} = 7.76 + 119.65 - 92.12 = 35.2_9 \text{ cal. per degree}$$

We obtain from the theoretical equation

$$S^{\circ}_{\mathrm{Mg}} \text{ theor.} = 4.573\, ja + 6.699 \times 2.5 \times R = 35.5_2 \text{ cal. per degree}$$

Considering the tendency for double molecule formation, the agreement is satisfactory.

The data necessary for a similar comparison of the spectroscopic and calorimetric values in the cases of calcium and thallium are not at present available. These two metals have transition points somewhere above room temperature that have not been investigated thoroughly. In this Institute, however, experiments are in progress to supply the necessary data.

Many thanks are due Professor Eucken for the use of the property of the Institute, and for his interest and suggestions in the completion of this investigation.

Summary

1. An apparatus is described which was used in measuring specific heats from 10 to 200°A.

2. The specific heats of thallium, calcium and magnesium have been measured from 10 to 200°A. The Debye function has been discussed in the light of these experimental data.

3. The vapor pressure constant of magnesium has been determined as 0.443 ± 0.1 and is found to agree very well with the statistically calculated

value 0.493. The entropy of monatomic magnesium vapor at atmospheric pressure and 25° has been determined empirically at 35.29 units, while the theoretical value is 35.5_1.

BRESLAU, GERMANY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PRINCETON UNIVERSITY]

THE INFLUENCE OF THE PERIOD OF HEATING UPON THE BOILING POINT OF CERTAIN LIQUIDS USED IN EBULLIOSCOPY, WITH A NOTE ON TESTING THE PURITY OF VOLATILE LIQUIDS BY ISOTHERMAL DISTILLATION[1]

BY SYDNEY L. WRIGHT, JR., AND ALAN W. C. MENZIES

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This paper describes a series of experiments designed to determine as accurately as possible whether the boiling point of a liquid is dependent upon the liquid's previous thermal history, *i. e.*, whether a liquid which has been boiling for several hours, boils at exactly the same temperature as one recently elevated from a lower temperature. It is obvious, as pointed out by Smits and others, that in associated liquids there might be a delay in attaining the degree of association appropriate to the higher temperature. This would usually result in a slightly higher boiling point at the beginning of ebullition than would be observed several hours later. For purposes of investigation two associated liquids, bromine and acetic acid, and two supposedly non-associated liquids, benzene and carbon tetrachloride, were used.

We also briefly refer to a method of testing the purity of volatile liquids, far more sensitive than the ordinary methods of boiling point and distillation range.

This study was prompted by experiments reported by H. B. Baker,[2] who believed that they demonstrate a delay in the attainment of internal equilibrium in the case of bromine and acetic acid. These observations, if confirmed, might serve to explain several difficulties previously encountered in ebullioscopic work, such as (1) the frequently mentioned necessity of allowing an astonishingly long period of time for the pure solvent to attain a constant boiling point in Beckmann's ebullioscopic method of determining molecular weights,[3] (2) the classical controversy[4]

[1] From the thesis of Sydney L. Wright, Jr., presented in partial fulfilment of the requirement of the degree of Doctor of Philosophy, 1928.

[2] Baker, *J. Chem. Soc.*, **129**, 949 (1927).

[3] Beckmann, *Z. physik. Chem.*, **6**, 473 (1890); **8**, 225 (1891). Biltz, translated by Jones and King, "Practical Methods for Determining Molecular Weights," 1912, p. 155; Jones, "The Elements of Physical Chemistry," 4th ed., 1915, p. 133; Walker, "Introduction to Physical Chemistry," 9th ed., 1922, p. 200; Findlay, "Practical Physical Chemistry," 4th ed., 1923, p. 264.

[4] Reference to the extensive literature on this subject may be found in Ostwald's "Lehrbuch der Allgemeinen Chemie," Vol. I, p. 308.