

Chemistry. — *The Exact Measurement of the Specific Heats of Solid Substances at Higher Temperatures. XIX. The Specific Heats of Zinc, Magnesium and their Binary Alloy: MgZn₂.* By T. J. POPPEMA and F. M. JAEGER.

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§ 1. In connection with previous papers from this laboratory¹⁾ on the validity of the law of NEUMANN, KOPP, etc. concerning the additivity of the atomic heats of the elements in their compounds, in the present paper the results are communicated obtained in the study of the metals *zinc* and *magnesium* and of their binary compound *MgZn₂*.

I. *Zinc*. The question about the exact values of the specific heats of *zinc* at higher temperatures has, up till now, not yet been completely settled, as a consequence of the fact that no perfect certainty exists about the occurrence of allotropic forms of this metal. Allotropic changes at temperatures below 200° C. are signalled by COHEN²⁾ and *Collab.*, by JÄNECKE³⁾, BENEDICKS⁴⁾, BINGHAM⁵⁾ and LOSANA⁶⁾; the existence of a transformation-point at temperatures higher than 300° C. is suggested by LE CHATELIER⁷⁾, BENEDICKS⁸⁾, WERNER⁹⁾, MÖNCKEMEYER¹⁰⁾, SCHÜBEL¹¹⁾, LASTCHENKO¹²⁾, BINGHAM¹³⁾, and LOSANA¹⁴⁾.

As to the right interpretation of the phenomena observed, the opinions of the numerous authors on the subject still differ. Thus, for instance, BENEDICKS and ARPI¹⁵⁾ emphasize the fact that the discontinuities in the temperature-curve of the electrical conductivity of the metal do not manifest themselves if the metal is perfectly pure, but they can be clearly stated at 160°, 270° and 350° C., when it contains 0,52 % of *cadmium*.

1) F. M. JAEGER and J. A. BOTTEMA, *Recueil d. Trav. Chim. Pays-Bas*, **52**, 89 (1933).

2) E. COHEN and W. D. HELDERMAN, *Zeits. f. phys. Chem.*, **89**, 742 (1915); **87**, 426 (1914).

3) E. JÄNECKE, *ibid.*, **90**, 321 (1915).

4) C. BENEDICKS, *Die Metallurgie*, **7**, 531 (1910).

5) K. E. BINGHAM, *Met. Ind. London*, **17**, 346 (1920).

6) L. LOSANA, *Gazz. Chim. Ital.*, **53**, 539 (1923).

7) H. LE CHATELIER, *Compt. rend. Paris*, **111**, 454 (1890).

8) C. BENEDICKS, *loco cit.*

9) M. WERNER, *Zeits. f. anorg. Chem.*, **83**, 301, 321 (1913).

10) K. MÖNCKEMEYER, *ibid.*, **43**, 182 (1908).

11) P. SCHÜBEL, *ibid.*, **87**, 31 (1914).

12) M. P. LASTCHENKO, *Zeits. f. Metallk.*, **10**, 253 (1919).

13) K. E. BINGHAM, *loco cit.*

14) L. LOSANA, *loc. cit.*

15) C. BENEDICKS and R. ARPI, *Zeits. f. anorg. Chem.*, **88**, 237 (1914).

COHEN¹⁾ considers the metal at ordinary temperatures as a "metastable" system, consisting of allotropic forms produced at higher temperatures and very slowly changing into some other form at room-temperature. However, the X-ray-analysis of the metal by SIMON and VOHSEN²⁾ and others at different temperatures does not yield any indication of the occurrence of allotropic modifications, neither is this corroborated by a study of the metal in this laboratory by means of SALADIN's method, when the metal is slowly heated in hydrogen and by means of a differential thermo-element is compared with a normally behaving substance like *copper* or *magnesium*. PETRENKO³⁾ also attributes the discontinuous change observed at 175° C. rather to a change in the size of the crystals of the polycrystalline metal than to an allotropic change. Some investigators observed no such discontinuities at all, neither with respect to the electrical conductivity, nor to the thermal one in its dependence on the temperature⁴⁾. Other observers tend to ascribe the discontinuous changes occasionally found to admixtures or to the preliminary treatment of the metal⁵⁾.

From our measurements of the specific heats of the metal between 100° and 360° C. it has become quite sure that between 160° and 170° C. there really occurs a discontinuous change in the metal and equally so between 330° and 340° C. In the first case, however, the \bar{c}_p - t -curve at 180° C. evidently re-assumes its former course; the discontinuity at 340° C., on the other hand, disappears if the metal is heated at 360° C., and on repeating the experiment at the former temperature the new value of \bar{c}_p at 340° is located exactly on the smooth curve passing through the points at 270° and 360° C. On repeating the experiments at 170° C., the discontinuity at 170° proves, however, still to exist; but the value at 100° C. has remained unchanged after and before the heating of the metal at 360° C. No discontinuous changes are observed, moreover, at 170° or at 340° C., if the metal is heated in hydrogen and investigated by means of SALADIN's device, although it makes the impression that a general retardation in the heating-curve over the whole interval between 100° and 360° is present. Whether this phenomenon is caused by some recrystallization-process or not, is not certain; no unambiguous indications of the occurrence of allotropic changes, however, were found in the way described.

§ 2. The pure *zinc* used in our experiments was fused in a hydrogen-atmosphere and a lump of the metal thus prepared was brought into the

¹⁾ E. COHEN and K. INOUE, *Zeits. f. phys. Chem.*, **71**, 306 (1910).

²⁾ F. SIMON and E. VOHSEN, *Zeits. f. phys. Chem.*, **133**, 165 (1928); J. R. FREEMAN, F. SILLERS and P. F. BRANDT, *Scient. Papers Bur. Stand.* **522**, 661 (1926).

³⁾ G. J. PETRENKO, *Zeits. f. anorg. Chem.*, **167**, 411 (1927).

⁴⁾ A. SCHULZE, *Zeits. f. Metallk.*, **22**, 194 (1930); L. C. BAILEY, *Proc. R. Soc. London, A*, **134**, 57 (1931).

⁵⁾ H. SIEGLERSCHMIDT, *Zeits. f. Metallk.*, **24**, 198 (1932); J. B. AUSTIN, *Physics*, **3**, 240 (1932).

shape of the crucibles ordinarily used in the calorimeter. The zinc was electrolytically coated with a thin film of *silver*, — for the purpose of protecting the metal against superficial oxidation, — and measurements

TABLE I.
The Mean Specific Heats \bar{c}_p of Zinc between 100° and 360° C.

No of the Experm.:	Tempera- ture t in °C.:	Final tempe- rature t' of the Ca- lorimeter:	Increase of temperature Δt in M.V.	Heat Q_0 developed be- tween t° and 0° C. by 1 Gr. of Zinc.:	Mean Specific Heat \bar{c}_p between t° and 0° C.:
1	100.34	21.196	709.1	9.401	} 0.09376
2	100.34	21.372	708.8	9.414	
3	160.17	21.665	1251.4	15.137	0.09451
4	164.84	21.646	1292.1	15.555	} 0.09437 (Disc.)
5	170.08	21.713	1336.9	16.031	
6	174.98	21.493	1388.1	16.546	0.09456
7	180.20	21.636	1437.1	17.074	0.09475
8	170.31	21.419	716.8	16.057	0.09429
9	220.30	21.680	966.1	21.000	} 0.09530
10	220.03	21.515	964.8	20.965	
11	269.90	21.403	1218.9	25.964	0.09620
12	310.16	21.830	1427.2	30.153	0.09722
13	320.31	21.958	1482.1	31.259	0.09759
14	330.49	21.511	1536.4	32.287	0.09770
15	338.35	21.765	1572.1	32.993	0.09751 (Disc.)
16	320.18	21.712	1482.8	31.252	↑ 0.09761 0.09852 0.09816 *
17	361.00	21.910	1698.6	35.564	
18	340.65	21.916	1590.4	33.439	
19	270.26	21.635	1219.3	25.993	0.09618
20	180.18	21.485	766.1	17.038	0.09456
21	170.24	21.396	715.8	16.030	0.09416
22	139.49	21.525	566.6	13.134	0.09418
23	99.41 ²	21.227	374.6	9.327	} 0.09381
24	99.60	21.246	375.2	9.342	

with it were made up to 180° C. 1) Above this temperature the measurements were executed with a lump of zinc of 31,1555 grammes, fitting in an evacuated platinum crucible weighing 28,5345 grammes; the maximum temperature of the calorimeter in these experiments was commonly reached within 1 to 2 minutes. In all these experiments it was observed, that the normal course of the calorimeter was only re-established 2 to 2,5 hours after the moment of introduction into the instrument; if, however, the metal was preliminarily heated at 360° C., this interval of time proved to be reduced to about 1,5 hours. No measurements above 360° C. were made, because of the volatility of the metal and the danger of an alloy being produced with the platinum of the crucible-wall.

The data thus obtained are collected in the table I; for the reduction of Q_{20° to Q_0 , the value of \bar{c}_p in this interval was assumed to be: 0,0927. The values of \bar{c}_p obtained are in fairly good agreement with those of former investigators 2).

The quantities of heat developed Q_0 can fairly well be represented by the equation:

$$Q_0 = 0,093335 \cdot t - 0,389 \cdot 10^{-6} \cdot t^2 + 0,4236 \cdot 10^{-7} \cdot t^3.$$

The mean specific heats between 100° and 360° C. therefore, by:

$$\bar{c}_p = 0,93335 - 0,389 \cdot 10^{-6} \cdot t + 0,4236 \cdot 10^{-7} \cdot t^2.$$

The true specific heats c_p are given by the equation:

$$c_p = 0,93335 - 0,778 \cdot 10^{-6} \cdot t + 0,12708 \cdot 10^{-6} \cdot t^2,$$

and the atomic heats C_p by:

$$C_p = 6,1013 - 0,50858 \cdot 10^{-4} \cdot t + 0,83073 \cdot 10^{-5} \cdot t^2.$$

It should be remarked, however, that these formulae can neither be applied between 165° and 175° C. nor between 330° and 340° and at temperatures below 100° C.

The values of the atomic heats C_p thus calculated are:

t :	C_p	C_p (appr.):
100°	6.1793	5.528
200°	6.4234	5.548
300°	6.8337	5.714
400°	7.4102	6.022

1) The lump of zinc weighed 76,141 grammes; the silver suspensionhook 0.594 grammes. The maximum temperature of the calorimeter was reached within 3 to 4 minutes.

2) Cf.: W. JAEGER and C. DIESSELHORST, *Abh. phys. techn. Reichsanst.*, **3**, 269 (1900); W. GAEDE, *Phys. Zeits.*, **4**, 105 (1902); R. RUER and K. KREMERS *Zeits. f. anorg. Chem.*, **185**, 208 (1929); W. U. BEHRENS and C. DRUCKER, *Zeits. f. phys. Chem.*, **113**, 100 (1924); K. CLUSIUS and P. HARTECK, *ibid.*, **134**, 256 (1928). The deviations generally do not surpass, 0,05 tot 0,3% of the total value of \bar{c}_p .

At 0° C. the atomic heat C_p is 5,935, — smaller than the value deduced from the above formula.

§ 3. With respect to the approximate calculation of C_p , it can be remarked that some data concerning the thermal expansion-coefficient 3α of zinc¹⁾ and the compressibility κ are available²⁾ in the literature, although rather incomplete. The approximate values of C_p thus calculated are also given with those of C_p .

§ 4. II. *Magnesium.*

A bar of *magnesium* was brought into the shape of the vacuum-crucibles, ordinarily used in our calorimetric measurements. On heating the metal in the open air — even after prolonged heating at 450° C. during 6 hours — only a slight superficial oxidation proved to have occurred: the increase of the weight was less than 0,1 %. The weight of the metal used was 18,438 grammes, that of its platinum suspension-hook 1,289 grammes. An analysis of the metal yielded 99,93 %—100 % Mg. A second series of measurements was started with a lump of the metal weighing 7,0955 grammes, closely fitted within an evacuated platinum crucible of the usual form, weighing 27,4830 grammes. No measurements at higher temperatures than 550° C. could be made, because between 595° and 670° C. a violent reaction with the platinum sets in, leading under an appreciable heat-effect, to a complete destruction of the crucible and the forming of a magnesium-platinum-alloy. Tentatives made with the powdered metal enclosed in an evacuated crucible had no result, no reproducible data being obtained in this way.

The values obtained with the massive, unprotected lump are collected in Table II sub *A*, those obtained with the metal enclosed in the vacuum-crucible are mentioned sub *B*.

The values sub *B* are situated on an almost straight line; those sub *A* are, from 349° C. upwards, about 0,3 % to 0,7 % higher, — evidently as a consequence of the slight superficial oxidation of the unprotected lump of the metal. The values of \bar{c}_p obtained with the powder of the metal enclosed in a vacuum crucible were too uncertain and variable to allow a direct comparison with those sub *B* or *A*. From the latter the mean specific heat of magnesium between 0° and 20° C. is deduced: 0,2423. The value of \bar{c}_p between 20° and 100° C. obtained by us (0,2477) is 0,3 % lower than that of RICHARDS and JACKSON³⁾ and identical with that of SCHIMPF⁴⁾,

¹⁾ A. SCHULZE, *Phys. Zeits.*, **22**, 403 (1921); S. MATTHIESEN, *Pogg. Ann. d. Phys.*, **130**, 50 (1867); P. HIDNERT, *Scient-Papers Bur. Stand.*, **497**, 25.

²⁾ TH. W. RICHARDS, *Zeits. f. Electrochem.*, **13**, 519 (1907).

³⁾ TH. W. RICHARDS and F. G. JACKSON, *Zeits. f. phys. Chem.*, **70**, 447 (1910).

⁴⁾ H. SCHIMPF, *Zeits. phys. Chem.*, **71**, 270 (1910).

TABLE II.
The Mean Specific Heats \bar{c}_p of Magnesium between 100° and 550° C.

A.						
No.	Temperature t in °C.:	Final temperature t' of the Calorimeter:	Increase of temperature Δt in Microvolts:	Amount of Heat Q developed by 1 gramme between t and t' :	Amount of Heat Q_0 developed between t° and 0° C.:	Mean specific Heat \bar{c}_p between t° and 0° C.:
1	99.902	21.110	453.2	19.540	24.655	} 0.2466
2	99.717	20.932	452.1	19.492	24.564	
3	247.20	21.584	1335.2	57.579	62.809	} 0.2539
4	247.05	21.683	1332.0	57.444	62.698	
5	348.97	21.981	1976.1	85.214	90.504	} 0.2596
6	348.92*)	21.989	1924.1	85.328	90.656	
7	455.24	21.238	2607.2	115.61	121.00	} 0.2660
8	455.34	22.125	2612.0	115.84	121.20	
*) Before this experiment the lump of metal was once more turned off on the lathe. The temperature-maximum of the calorimeter was always reached within 1—2 minutes after dropping the metal into the instrument.						
B						
17	349.47	21.512	1127.3	85.760	90.972	} 0.2600
18	349.42	21.711	1124.8	85.498	90.759	
13	456.24	21.404	1517.9	115.76	120.95	} 0.2653
14	456.24	21.706	1518.8	115.89	121.15	
15	550.24	21.788	1873.1	143.31	148.59	} 0.2702
16	550.20	21.785	1874.3	143.46	148.74	
The maximum temperature of the calorimeter is here reached 1—2 minutes after dropping the crucible into the instrument.						

while the c_p - t -curve of MAGNUS¹⁾ between 100° and 540° C. proves to be appreciably (1—7%) steeper.

¹⁾ A. MAGNUS, Ann. d. Phys., (4), 31, 597 (1910); cf. also: W. VOIGT, Wied. Ann., 49, 709 (1893); N. STÜCKER, Wien. Akad. Sitz. Ber., (1903), 114.

Within the limits of error the amount of heat Q_0 developed by 1 gramme of magnesium between t° and 0° C. can be represented by the formula:

$$Q_0 = 0,241306 \cdot t + 0,526418 \cdot 10^{-4} \cdot t^2 - 0,1575 \cdot 10^{-10} \cdot t^3.$$

The true specific heat c_p of magnesium, therefore, by

$$c_p = 0,241306 + 0,1052836 \cdot 10^{-3} \cdot t - 0,4725 \cdot 10^{-10} \cdot t^2,$$

and the atomic heat C_p of the metal by:

$$C_p = 5,8637 + 0,25585 \cdot 10^{-2} \cdot t - 0,1148 \cdot 10^{-8} \cdot t^2.$$

Some values of C_p thus calculated are here given:

Temperature t in $^\circ\text{C}.$:	True specific Heat c_p :	Atomic Heat C_p :
0	0.2413	5.864
100	0.2518	6.120
200	0.2624	6.375
300	0.2729	6.631
400	0.2834	6.887
500	0.2939	7.143
600	0.3045	7.398

§ 5. III. The Compound: $MgZn_2$.

This compound was obtained by melting together the two components in the appropriate quantities in an atmosphere of hydrogen; after solidification the mass was re-melted in vacuo and allowed to cool down slowly. The X-ray-spectrogram shows no other diffraction-lines than those characteristic¹⁾ of the alloy itself, as may be seen from the following data: (See table following page).

The substance was carefully analysed; this analysis yielded the following data: 84,20 % Zn and 15,80 % Mg; calculated for $MgZn_2$: 84,3 % Zn and 15,7 % Mg. In connection with the results of the X-ray-analysis we can conclude from these data that the crystalline mass really consisted of the pure alloy, with practically no admixture of the free components.

The binary system: zinc-magnesium was studied by means of the method of thermal analysis by ROTHERY and ROUNSEFELL²⁾). The diagram published proves the existence of three compounds: $MgZn_5$, $MgZn_2$ and $MgZn$, of which only $MgZn_2$ possesses a congruent melting-point at 590° C. The temperatures of the coexistence of $MgZn_2$, $MgZn_5$ and a liquid phase,

1) J. B. TRIAUF, Phys. Review, 29, 353 (1927).

2) W. H. ROTHERY and E. O. ROUNSEFELL, Journ. Inst. of Metals, 41, 119 (1929).

X-Ray-Spectrogram of the Compound: $MgZn_2$							
No.	Distances 2. d in mM.:	Estim. In- tensities:	Wave- length:	Angle θ :	$\sin^2 \theta$ (observed):	$\sin^2 \theta$ (calculated):	Indices { hkl }:
1	35.52	1	β	8°53'	0.0238	0.0242	(100)
2	39.32	4	α	9 50	0.0292	0.0298	(100)
3	42.16	1	α	10 32	0.0334	0.0329	(002)
4	44.78	3	α	11 12	0.0377	0.0380	(101)
5	58.16	1—	α	14 32	0.0630	0.0627	(102)
6	62.22	1—	α	15 33	0.0719	0.0741	(003)
7	66.90	2	α	16 43	0.0828	0.0846	(103)
8	69.16	2	α	17 17	0.0883	0.0893	(110)
9	73.00	2	α	18 15	0.0981	0.0975	(111)
10	74.60	8	α	18 39	0.1023	0.1039	(103)
11	75.94	1	β	18 59	0.1058	0.1071	(004)
12	80.90	10	α	20 13	0.1195	0.1191	(200)
13	82.40	10	α	20 36	0.1238	0.1222	(112)
14	83.96	10	α	20 59	0.1283	0.1273	(201)
15	85.42	4	α	21 21	0.1325	0.1317	(004)
16	91.34	8	α	22 50	0.1506	0.1520	(202)
17	94.30	3	α	23 34	0.1600	0.1615	(104)
18	103.66	6	α	25 55	0.1910	0.1932	(203)
19	107.74	2	α	26 56	0.2052	0.2058	(005)
20	110.24	1	α	27 34	0.2141	0.2166	(211)
21	113.46	1—	β	28 22	0.2257	0.2250	(301)
22	118.00	1	α	29 30	0.2425	0.2413	(212)
23	123.22	2—	β	30 48	0.2625	0.2646	(205)
24	127.62	3	α	31 54	0.2793	0.2762	(301)
25	132.32	5	α	33 5	0.2980	0.2964	(006)
26	138.54	6	α	34 38	0.3230	0.3009 0.3249	(302) (205)
27	141.80	3	α	35 27	0.3364	0.3401	(214)
28	145.72	6	α	36 26	0.3527	0.3572	(220)
29	152.98	2	α	38 15	0.3832	0.3857 0.3870	(116) (310)
30	155.18	1	α	38 48	0.3926	0.3952	(311)
31	159.78	4	α	39 57	0.4122	0.4122 0.4155	(215) (206)
32	169.42	2	α	42 21	0.4539	0.4611	(313)
33	175.88	6	α	43 58	0.4820	0.4845 0.4890	(401) (224)

Radius of the Camera: 57.2 mM. Exposure: 70 m.A. hours.
Wave-lengths: $\lambda_\alpha = 1.539$ A.U.; $\lambda_\beta = 1.339$ A.U.
The diffraction-lines with $\theta > 44^\circ$ are omitted.
Quadratic Equations: $\sin^2 \theta = 0.0298 (h^2 + k^2 + hk) + 0.00823.1^2 \dots (\alpha)$.
 $\sin^2 \theta = 0.0242 (h^2 + k^2 + hk) + 0.00671.1^2 \dots (\beta)$.
Hexagonal; cell-dimensions: $a_0 = 5.15$ A.U.; $c_0 = 8.48$ A.U.; $a : c = 1 : 1.6469$.

and of the coexistence of $MgZn_2$, $MgZn$ and liquid, are $380^\circ C.$ and $354^\circ C.$ respectively; the two eutectic temperatures present are $364^\circ C.$ and $340^\circ C.$ respectively. Zn takes up Mg in solid solution to a small percentage, as well as Mg takes up some Zn . The pure compound $MgZn_2$ does not show any polymorphic transformation; notwithstanding this, its calorimetric study soon revealed the fact, that it gives off its heat at a rather small rate, so that the maximum temperature of the calorimeter was only reached after 8 or 10 minutes, while the normal value of the cooling modulus of the instrument was not re-established until more than a full hour after the moment of introduction into the calorimeter. If, however, attention is paid to the latter minimum lapse of time, the values obtained prove to be quite reproducible; they are collected in the following Table III.

Sequence of the Experiments:	Temperature t in $^\circ Cent.$:	Final temperature t' of the Calorim.:	Rise of Temperature Δt of the Calorimeter in Mikro-Volts:	Amount of Heat Q_0 between t° and $0^\circ C.$ in Calories pro Gr.	Mean Specific Heat \bar{c}_p between t° and $0^\circ C.$
10	99.450	21.189	212.9	11.525	0.1158 ⁸
11	99.860	20.961	214.9	11.594	0.1161
12	99.711	21.116	213.4	11.526	0.1155 ⁹
8	200.53	21.469	494.7	23.654	0.1179 ⁶
9	200.75	21.378	495.4	23.672	0.1179 ²
7	300.28	21.294	782.9	36.099	0.1202 ²
6	300.27	21.282	781.8	36.019	0.1199 ⁵
4	374.95	21.527	1001.1	45.560	0.1215
5	375.24	21.463	1003.4	45.694	0.1217 ⁷
3	425.34	21.546	1153.8	52.272	0.1228 ⁹
2	425.24	21.519	1153.1	52.227	0.1228 ²
1	500.20	21.521	1381.7	62.242	0.1244 ³
13	500.33	21.655	1380.7	62.189	0.1242 ⁹

For \bar{c}_p between 0° and $20^\circ C.$ the value: $\bar{c}_p = 0.1140$ was used. The measurements were not continued above $500^\circ C.$, as we feared that the platinum would react with the alloy.

In this connection, it may be remarked that some values of \bar{c}_p of this compound were previously determined by SCHIMPF 1) and by SCHÜBEL 2). The latter author found:

\bar{c}_p between 100° and 18° C.: 0,1155; our value being: 0,1164.

\bar{c}_p between 200° and 18° C.: 0,1182; our value being: 0,1184.

\bar{c}_p between 300° and 18° C.: 0,1208; our value being: 0,1205.

The agreement is fairly satisfactory.

From these data the values of Q_0 appeared to be most satisfactorily represented for each temperature t by the formula:

$$Q_0 = 0,113545 \cdot t + 0,21902 \cdot 10^{-4} \cdot t^2,$$

so that the mean specific heats c_p in function of t can be represented by the linear equation:

$$\bar{c}_p = 0,113545 + 0,21902 \cdot 10^{-4} \cdot t,$$

and the true specific heats c_p by:

$$c_p = 0,113545 + 0,43804 \cdot 10^{-4} \cdot t.$$

The molecular heats C'_p are consequently:

$$C'_p = 17,60604 + 0,679216 \cdot 10^{-2} \cdot t.$$

Some of the values thus calculated are the following:

Molecular Heats C'_p of $MgZn_2$.			
Temperature t in °Cent.:	Molecular Heats C'_p :	Calculated from the Additive Law of NEUMANN-KOPP:	Differences Δ in Percentages:
0°	17.606	17.734	— 0.72%
100	18.285	18.479	— 1.06%
200	18.964	19.222	— 1.36%
300	19.644	20.298	— 3.32%
400	20.323	21.707	— 6.81%
500	21.002	—	—
590	21.613	—	—

1) H. SCHIMPF, Zeits. f. phys. Chem., 71, 257 (1910).

2) P. SCHÜBEL, Zeits. f. anorg. Chem., 87, 81 (1914).

The differences ($C'_p - \Sigma$) are *negative* and, exactly as in the cases previously studied, they prove to augment rapidly with increasing temperatures t , as may be seen from Fig. 1.

As far as a comparison of the specific volumes of the free metals and

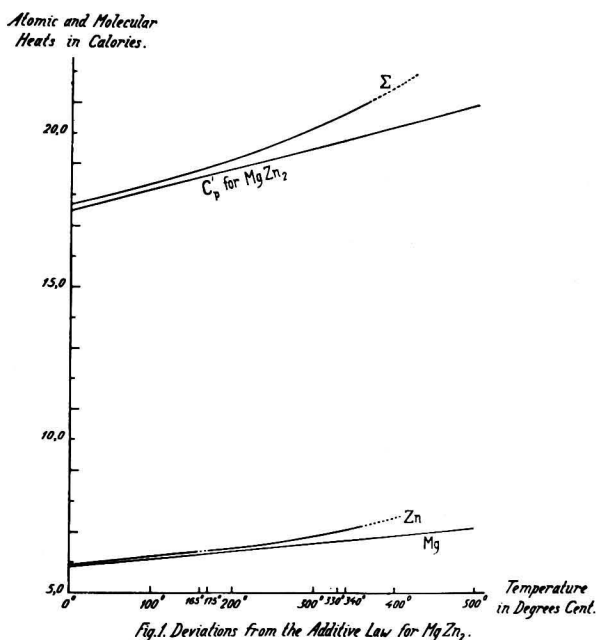


Fig. 1. Atomic and Molecular Heats of Zinc, Magnesium and the Alloy $MgZn_2$.

their binary compound ¹⁾ in the solid state can be made, it can be remarked here that evidently the specific volume of the compound in this case is somewhat smaller than that calculated from those of the free metals according to the additive law, so that a "contraction" of about 8 % may be supposed to occur during the formation of the compound from its components.

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Physical Chemistry of the University.*

¹⁾ The specific gravity of zinc is 7,13, that of magnesium: 1,748, and that of the compound: 5,161, as deduced from the X-ray-measurements. The molecular volume observed is 48,7; calculated from the atomic volumes of the components it would be: 53,1.