Chemistry. — *"Investigations in the Field of Silicate-Chemistry. IV. Some data on the Meta- and Ortho-Silicates of the bivalent Metals: Beryllium, Magnesium, Calcium, Strontium, Barium, Zinc, Cadmium, and Manganese."* By Prof. JAEGER and Dr. VAN KLOOSTER.

(Communicated in the meeting of Nov. 27, 1915.)

§ 1. In connection with the investigations into the crystallisation-phenomena of complex, molten silicate-magmas, as they were commenced in this laboratory, but stopped for some time since August 1914, — it was necessary for our purpose to study in the first place again the solidifying phenomena of the pure silicates of the alcaline earths and of zinc, cadmium, and manganese.

The data about the melting- and solidifying-points and about several properties of the just named substances found in literature are rather discordant and often contradictory. As far as the silicates of *calcium* and *magnesium* are concerned, definite results can be said to have been obtained now in the very accurate investigations from the Geophysical Laboratory in *Washington* [1]). Some of the data obtained there are once more reviewed at the end of this note for the purpose of comparison with those established here.

About the melting- and solidifying-points of the silicates of the other bivalent metals: *Sr, Ba, Zn, Cd* and *Be*, there has not yet been obtained any certainty, while about those of *Mn*, only a few, rather uncertain data are available.

Indeed several investigations [2]) of these silicates have been published; but the experimental methods were in all those cases such, that no reliable results could be expected, as will appear clearly in the following pages.

For without any exception, *cooling*-curves were always used in these determinations, which, — as has been already repeatedly proved, and is again stated here by us, — can never give any reliable result in the case of *silicates*, not even in the most favourable circumstances. Furthermore in not one of these cases sufficient attention was given to the preparation of completely pure products, nor to the complete chemical homogeneity of the molten substances; neither was a reducing atmosphere avoided with respect to the

[1]) ALLEN, WHITE and WRIGHT, Amer. Journ. of Science **21**, 89. (1906); ALLEN, WRIGHT and CLEMENT, ibid. **22**, 385. (1906); A. L. DAY and SHEPHERD, Amer. Journ. of Science **22**, 265 (1906); ALLEN and WHITE ibid, **27**, 1. (1907); SHEPHERD and RANKIN, ibid. **28**, 293. (1909).

[2]) STEIN, WALLACE, LEBEDEW, Zeits. f. anorg. Chem. **55**, 63, 70. See the literature given further on.

presence of the silicate and the thermo-element. Finally in no case the infection of the used thermo-elements was controlled, neither were the obtained data reduced on the nitrogen-gasthermometer of *Washington*. A short review of the data given in literature will soon persuade the reader of the facts mentioned.

§ 2. According to STEIN [1]) a molten mass of the composition $SrSiO_3$ crystallises at 1287° C. He prepared the compound by melting together the oxides, carbonates and hydroxides with silica in tubes of *carbon*, while in his measurements the porcelain protecting tube of the thermo-element was placed in most cases quite bare into the molten mass. As he mentions, the colour of his products was indeed more or less dark-gray, as a consequence of the admixed carbon. The specific gravity should be 3,89 or 3,91; no glass was obtained. According to WALLACE [2]) however the solidifying-point of $SrSiO_3$ should be 1529° C.; he worked in an analogous way, and says, that the solidified substances were always greatly contaminated by admixed carbon, their colour being thus *black* or *bluish-black*. The crystallised product should be very analogous to calcium-metasilicate: very strongly birefringent, obliquely or normally extinguishing monoclinic prisms. Evidently this analogy must be present between this compound and the *pseudo-wollastonite*, the common solidifying-product of the molten calcium-metasilicate. The last modification being typically pseudo-hexagonal, the same should be the case with $SrSiO_3$; however, this is nowhere mentioned by the author, and thus needs more detailed study.

According to STEIN $BaSiO_3$ crystallises at 1368° C.; the product should possess a specific gravity of 3.77, and also be obtained in the form of a glass with a specific weight of 3.74. In this case also all experiments were made in *carbon*-tubes, and all solidifying-points were determined by means of *cooling*-curves.

According to LEBEDEW [3]) the solidifying-temperature is: 1438° C.; the method used was the same. The product is according to this author monoclinic, and isomorphous with $CaSiO_3$; but it is not said with which modification of it.

On the contrary WALLACE finds 1490° C. for the solidifying-point, and in contrast to STEIN's experience, only a single crystalline modification, instead of two different ones.

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[1]) G. STEIN, Zeits. f. Anorg. Chem **55**. 159. 163. (1907).

[2]) R. C. WALLACE. Zeits. f. Anorg. Chem., **63**, 9. 10. 11. (1909).

[3]) P. LEBEDEW, Zeits. f. Anorg. Chemie, **70**, 301, 317 (1911).

A meltingpoint of 1494° C. for $BaSiO_3$ is also given by VOLOSKOV, Ann. Instit. Polyt. St. Petersburg, **15**. 421. (1911).

$ZnSiO_3$, prepared by melting together ZnO and SiO_2 in porcelain crucibles, is said to crystallise at 1429° C.; the glass of this silicate should possess a greater specific weight (3,86) than the crystals (3,42). Finally STEIN gives as solidifying-temperature of Sr_2SiO_4: 1593° C.; the specific gravity being 3,84, and for the glass: 3,57. In the same way Zn_2SiO_4 would crystallise at 1484° C., and show a specific weight of 3,7.

About Ba_2SiO_4 it is only mentioned, that products soiled by carbon were obtained; no data about melting-temperature or properties are given. Data about *beryllium*-silicates: $BeSiO_3$ and Be_2SiO_4 are only few: STEIN mentions, that the meltingpoint of $BeSiO_3$ was too high, to be determined by means of the thermo-element. Above 2000° C. the substance becomes a thin liquid; the specific gravity of the crystalline product is given as 2,35. Be_2SiO_4 has evidently a very high meltingpoint, and crystallises readily; more detailed data are absent.

On the silicates of *manganese* an investigation is published by DOERINCKEL [1]); he mentions the compounds $MnSiO_3$ and Mn_2SiO_4, and says, that they melt under partial decomposition. However for $MnSiO_3$ the composition of the molten mass can only differ slightly from that of the pure compound. The temperatures are related as follows: for $MnSiO_3$: 1215° C., and for Mn_2SiO_4: about 1323° C. Between the two compounds there would be a eutectic point at 1185° C.

If we now consider, that the data given for $SrSiO_3$ differ 242° C., for $BaSiO_3$ 122° C. from each other with different authors; that in no case the influence of the heating in an atmosphere of carbon-monoxide on these products and on the thermo-elements was investigated, and that always the unreliable cooling-method was used in the study of these silicates, — then a renewed study of the phenomena here occurring can hardly be said to be superfluous. Some few data about these substances, although yet incomplete, may therefore be given already in the following pages.

§ 3. The pure silicates were prepared by repeatedly heating and melting together the purest, finely powdered quartz, and chemically pure $SrCO_3$ and $BaCO_3$ in the calculated quantities. The employed $SrCO_3$ was free from barium-oxide, the $BaCO_3$ free from strontium-oxide. Both substances appeared to have no other impurity than an

[1]) F. DOERINCKEL, Die Metallurgie, **8**. 201. (1911).

insignificant trace of iron. The quartz was of American origin, and may be considered to be almost 100 % SiO_2.

The finely powdered and well mixed materials were several times heated in the platinum-resistance-furnace in iridium-free platinum-crucibles, and then melted in the FLETCHER-furnace.

Then they were ground and sieved, and these manipulations were repeated, as commonly, three or four times. Notwithstanding all care, an analysis of the products proved, that the composition again differed from the theoretical one. Thus the calculated quantity of carbonate or silica was added, and all mentioned manipulations were again repeated several times. If analysis showed the composition of the finely ground product not yet to be the true one, the deficient quantity of one of the components was again added, etc. If by at least two analyses it was proved, that the product showed the right composition, it was used for the final determinations. To study the influence of a slight excess of one of the components on the melting-point, we investigated also in some cases a not yet quite pure preparation.

All thus prepared compounds of *Ba*, *Sr*, *Be*, *Zn* and *Cd* were stainlessly white, and beautifully crystallised; only in the preparing of the *zinc*-salts sometimes a slight bluish or pink tinge was observed, evidently caused by the introduction of a trace of platinum from the walls of the crucibles; in the case of the pink manganese-compounds a partial brown colouring appeared to be unavoidable in the repeated heatings.

§ 4. *Strontium-metasilicate.* A preparation of $SrSiO_3$, whose analysis gave the following numbers:

	Observed:		*Calculated:*
SiO_2	37,59 %	37,70 %	36,78 %
SrO	62,40 %	62,35 %	63,22 %

and which thus showed yet an excess of 0,87 % SiO_2, was first used for the meltingpoint-determinations. With thermo-element III we found successively:

16509 M.V., with a furnace-gradient of 30 M.V., per minute.
16501 M.V., „ „ „ „ 45 M.V., „ „
16495 M.V., „ „ „ „ 40 M.V., „ „
16505 M.V., „ „ „ „ 70 M.V., „ „

mean.: 16502 M.V.. ± 7 M.V. (uncorr.).

The correction for this thermo-element at this temperature being

— 26 M.V., the melting-point can thus be fixed at 16476 M.V. ± 7 M.V., this being: 1577,°5 ± 0,5 C. on the nitrogen-gasthermometer.

This compound crystallises perfectly, although perhaps not so extraordinarily rapidly as the barium-silicate. In cooling-experiments, where the molten mass was shaken continually by oscillations produced by repeatedly tapping and knocking the MARQUARDT-tube, even with a gradient of 3°,5 or 5° C. per minute, the liquid could be undercooled down to 1239° C., a spontaneous crystallisation afterwards occurring, in which the temperature rose to 1339° C. because of the relatively great heat-effect. In another experiment undercooling was produced to about 1264° C. in this way, a rise of temperature thereupon being observed after crystallisation, up to 1347° C. Two refractive indices of the solidified substance were measured: $n_1 = 1{,}595 \pm 0.001$, and $n_2 = 1{,}625 \pm 0{,}001$.

Now the preparation was improved by addition of the calculated amount of $SrCO_3$, the mixture repeatedly heated and melted, and again several times analysed. The data obtained were now:

	Observed:		*calculated:*
SiO_2	36,4%	36.5%	36,78%
SrO	63,6%	63,5%	63,22%

The deviation from the theoretical composition is only about 0,3 %; the influence on the meltingpoint appeared to be without significance.

In the usual way we now determined the melting-point of this beautifully crystallised, irreproachably white product; with the same element *III* we found successively the following values for the E. M. F. of it at the meltingpoint:

16515 M.V., with a furnace-gradient of 45 M.V, per minute.
16496 M.V., „ „ „ „ 50 M.V. „ „
16501 M.V., „ „ „ „ 50 M.V. „ „

Mean: 16504 M.V., ± 10 M.V. (uncorr.)

After correction (—26 M.V.), the true melting-temperature may thus be fixed at 16478 M.V. ± 10 M.V., this corresponding with: 1578° C. ± 1°. An excess of 0,9 % (weight proc.) of SiO_2 seems to cause a lowering of the meltingpoint of about 1° C.

On cooling the molten mass it was observed, that with undercooling to about 12200 M.V. and with continual tapping of the crucible, *every* solidifying-temperature between 1306° and 1364° C. could be found. So e.g. we cooled in one of the experiments with a velocity of 4,°5 per minute; the result was an undercooling to 1225° C., and

crystallisation at 1364° C.; in a second experiment crystallisation occurred at 1306° C., after undercooling to 1222° C., with a gradient of 3,°5 C., per minute. Here also the cooling-curves did not give in any case a reliable temperature for the equilibrium liquid $\rightleftarrows$ solid: *all thus obtained data appeared to be* 230° *or* 240° *C. lower than the real temperature of equilibrium for the transition solid* $\rightleftarrows$ *liquid.* These experiments and the analogous ones in the case of the *Ba*-silicate and other objects, must prove, that even mechanical stirring of the liquid during its cooling, e.g. by means of electro-magnetic stirrers, as proposed by some investigators, is not able to produce the reaching of equilibrium in the case of such silicate in a sufficient way. Even under those circumstances the cooling-method remains an unreliable one.

Strontium-metasilicate crystallises on slow cooling of the molten mass in glittering, irregularly bounded, flat crystals. In most cases these are penetration-twins or again more complicated aggregations, which are also produced in more rapid cooling of the liquid. Often the boundaries of the different united crystals are irregular, sometimes however clearly rectilinear. Every crystal shows a fine twin-striation, parallel to the extinction-directions. Very probably the silicate is monoclinic.

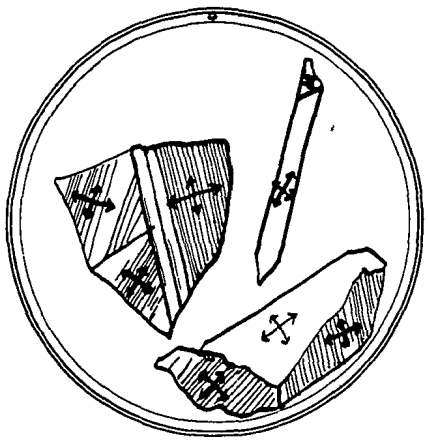

Fig 1. *Strontium-Metasilicate,* molten and solidified.

On the border of the field in convergent polarized light a single branch of an hyperbola is visible. The refractive index in the direction of the striation is about: 1 590; perpendicular to it: 1.620. Sometimes also long flat needles were found, with oblique extinction.

The angle of extinction is about 18° with respect to the length-direction of the needle. The crystals are very strongly birefringent; by means of the immersion-method two refractive-indices were determined to be: $n_1 = 8.595 \pm 0.003$, and $n_2 = 1.624 \pm 3.003$. The double refraction is about; 0.029 to 0.030; at another time we found: $n_1 = 1.590 \pm 0.003$, and $n_2 = 1{,}620 \pm \pm 0.003$.

The specific gravity of the solidified product was pycnometrically determined in ortho-chlorotoluene to be: $d_{4^\circ} = 3.652$ at 25°.1 C.

By quenching the molten substance, heated to 1637° C., in mercury or water, a beautiful colourless, and almost perfectly

isotropous glass was obtained. However the substance will crystallise so easily, that also here some crystalline particles always appear to be present. The refractive index of the glass was: $n_D = 1.618 \pm \pm 0.002$; in the immersion liquid used it produced a beautiful pink colour (monochrome-effect). At 25°.2 C. the glass possesses a specific weight of: $d_{4^\circ} = 3.540$; the specific volume thus being greater than that of the crystalline substance. On carefully heating the glass becomes gradually opaque under transformation into a microcrystalline mass.

§ 5. *Barium-Metasilicate* · $BaSiO_3$.

This compound was prepared in a quite analogous way as in the case of the strontium-salt. It may be remarked here, that the purest bariumsilicates of commerce, e.g. the product of KAHLBAUM, always contain an appreciable quantity of water (11 or 12 %); if this is eliminated, the substance appears furthermore never to contain more than about 70 % of BaO, i.e. about 1.8 % less than corresponds with the theoretical composition. Often also some sodium is found as an impurity.

The heated mixtures of the components were melted three times at 1650° C., ground, sieved and again melted. The thus obtained product, with refractive indices of about 1.666 to 1.669, was analysed. The numbers found are:

	Observed:		*Calculated*:
SiO_2	29,48 %	29,44 %	28,22 %
BaO	70,50 %	70,53 %	71,78 %

In the case of this substance the meltingpoint was determined several times with the aid of thermo-element IV. The following values were found:

16799 M.V., with a furnace-gradient of 30 M.V. per min.
16783 „ „ „ „ „ „ „ 26 „ „ „
16812 „ „ „ „ „ „ „ 50 „ „ „
16799 „ „ „ „ „ „ „ 19 „ „ „

Mean: 16799 M.V. ± 13 M.V. (uncorr.).

The correction for this thermoelement at this temperature being — 8 M.V., the melting-point of this product can be fixed upon: 16791 M.V. ± 13 M.V., corresponding with 1603° ± 1° C. on the nitrogen-gasthermometer.

Because the substance could not yet be considered as a perfectly pure $BaSiO_3$, it was improved by addition of $BaCO_3$, repeatedly heated and then analysed. We found the following numbers:

	Observed:		*Calculated*:
SiO_2	28,24 %	28,19 %	28,22 %
BaO	71,75 %	71,85 %	71,78 %

The product could now indeed be considered as a chemically pure $BaSiO_3$. The determination of the meltingpoint was now repeated, and gave with element III the following values:

16823 M.V., with a furnace-gradient of 40 M.V. per minute
16825 „ „ „ „ „ „ 33 „ „ „
16838 „ „ „ „ „ „ 45 „ „ „

Mean: 16838 M.V. ± 6 M.V. (uncorr.).

The correction being here —26 M.V., the meltingpoint of pure $BaSiO_3$ can thus be fixed at: 16803 M.V. ± 6 M.V., corresponding with 1604° ± 0°,5 C. (G. Th.). An excess of 1,7 % weight proc. SiO_2 thus lowers the meltingpoint about 1° C.

The specific gravity of the crystalline product appeared at 25°,1 C. to be $d_{4^\circ} = 4.435$. It crystallises on slow cooling of the molten mass in flat, small crystals, which only show a feeble birefringence: 0.003 or 0.004; this is consequently 7 or 10 times smaller than in the case of the strontiumsalt. For the refractive indices we found: 1.667 and 1.670, both numbers with deviations of about ± 0.001; greater crystals often show an irregular extinction.

To obtain a glass, the substance was heated to 1650° C. and then suddenly quenched in cold mercury. Notwithstanding all endeavour, we did not succeed in changing the molten product into a glass, because of the exceedingly rapid crystallisation of the substance. The melting-point is according to this so sharp, that $BaSiO_3$ may be recommended as a new substance for the calibration of thermoelements.

After all attempts to get some information about a polymorphic transition with $SrSiO_3$ and $BoSiO_3$ had been without success, we tried to obtain yet a second modification of these compounds by means of fluxes. For that purpose 0,5 gram of pure $BaSiO_3$ were mixed with 1 gram of sodium-wolframate, and in the same way 0,5 gram of pure $SrSiO_3$ with 1 or 2 grams of the same salt, and then heated at 860° C. during 72 hours. Neither in these experiments, nor in others, where we started with $SrSiO_3$-glass, did we succeed in obtaining other crystals than those formerly obtained by the melting of the salts.

Finally we wish to draw attention here also to the results, which were obtained by means of the cooling-method, just because one would perhaps expect to find here in this favourable case some

agreement between the thus obtained solidifying-points and the true temperature of equilibrium.

At 14000 M. V. (1371° C.) the whole mass was again a viscous liquid, while the cooling-velocity was 3°,5 C. per minute; after an undercooling to 1365° C., the liquid crystallised by shaking and tapping the crucible, and the temperature increased to 1376° C. Another time we observed undercooling to 1349° C. and a crystallisation at 1364° C.; in yet another experiment, with varied temperature-gradient, undercooling occurred down to 1306° C., crystallisation setting in at 1326° C.; etc. Thus even in this extraordinarily favourable case the temperature of crystallisation appears to be completely dependent upon the preliminary treatment of the molten mass, and upon the particular way, in which the heat is withdrawn: *it is possible to find as solidifying-point any arbitrary temperature.*

The complete impracticability of the cooling-method is here also proved in an indisputable manner.

§ 6. By the way it merits attention, that the temperatures of observation in this and the foregoing case, are close to the extreme limit, to which the platinum-resistance-furnaces can again be applied. The effect of electricity-leakage out of the heating-coil, which occurs by the transport of the ions in the white-hot air-column, appeared to be rather appreciable; and it was absolutely necessary now to eliminate these disturbances by means of a protecting shield of zero-potential round the thermo-elements, by conducting the electrical charges to the earth-surface. The conduction-wires of the FARADAY-cage were therefore lengthened, and soldered to the platinum-crucibles by means of the oxygen-flame. Only by these precautions it appeared possible to make the final measurements, without being troubled by leakage-phenomena any more.

§ 7. We prepared by synthesis also the *ortho-silicates* of barium and strontium. However the meltingpoints appeared to be here so high, that the substances could no longer be melted in platinum-crucibles, while all attempts to determine some reliable melting-point by means of the optical pyrometer, using a carbon-shortcircuiting furnace, had to be given up because of the reaction between the carbon and the silicates.

§ 8. *Zinc-Metasilicate*: $ZnSiO_3$; *Zinc-Orthosilikate*: Zn_2SiO_4, and *Willemite*.

These compounds were all prepared from pure ZnO and SiO_2

by melting them together in iridiumfree platinum-crucibles. The crystallised products are in most cases slightly pink or pale blue tinged by metal extracted from the walls of the crucibles. We used in the synthesis also $ZnCO_3$, but with less result. Analysis of the products proved, that originally too much SiO_2 was present; but the evaporation of the ZnO appeared however to be only very slight, if the crucible was covered [1]). After several improvements, we obtained a product, whose analysis gave:

	Observed:		*Calculated*:
ZnO	42.43 %	42.24 %	42.55 %
SiO_2	57.80 %	57.68 %	57.45 %

The obtained, stainless white substance could thus be considered to be pure $ZnSiO_3$. With thermoelement II the E.M.F. at the melting-temperature was determined to be:

14786 M.V., with a furnace-gradient of 75 M.V. per minute.
14804 M.V., „ „ „ „ 70 M.V. „ „
14780 M.V., „ „ „ „ 50 M.V. „ „

Mean: 14799 M.V. ± 12 M.V. (uncorr.).

The correction of this thermoelement being at this temperature about —10 M.V., the reduced E. M. F. can be fixed upon 14789 M.V. ± 12 M. V., corresponding with a meltingpoint of 1437° ± 1° C. According to STEIN [2]) the meltingpoint is: 1429° C.; according to VAN KLOOSTER [3]): 1419° C., but in both cases the experiments were made in the accustomed way. In cooling-experiments a solidifying-point was observed beneath 13700 M.V.; nor did we get any positive result in experiments, where the strongly heated substance was suddenly quenched in cold mercury, because in the quenching-product there were always crystals found besides the glassy substance.

The solidified mass is weakly birefringent and has often a porcelain-like aspect, the grains of it being thus only transparent at the extreme borders. Evidently the product consists of very complicated parallel aggregations of thin, felty needles. The refractive indices were: $n_1 = 1.623 \pm 0.006$, and $n_2 = 1.616 \pm 0.006$, the birefringence thus being 0.007. The determination of the indices is very troublesome; for the *glass* we found a mean value of 1.650. The specific gravity of the crystallised $ZnSiO_3$ at 25° C. is: $d_{4^0} = 3{,}52$.

[1]) Using $ZnCO_3$ instead of ZnO with the synthesis, the loss of ZnO by *flying away*, appears to be much more appreciable.

[2]) STEIN, Z. f. Anorg, Chem. **55**. 165. (1907).

[3]) VAN KLOOSTER, Z. f. Anorg. Chem. **69**. 135. (1910).

In an analogous way we prepared also the *Zinc-ortho-silicate*: Zn_2SiO_4. Also here the loss of ZnO during melting appeared to be by no means appreciable. Analysis of the used final product gave the following values:

	Observed:	*Calculated*:
SiO_2	26.94 %	27.03 %
ZnO	73.12 %	72.97 %

In a series of experiments, in which the furnace-gradient was about 50—54 M.V. per minute, we found with thermoelement *II* at the meltingpoint an E. M. F. of: 15667 ± 5 M. V. (uncorr.). After reducing this value on the nitrogen-gasthermometer-scale (corr. — 9 M. V.), this E. M. F. can be fixed at: 15658 ± 5 M. V., corresponding to 1509.°5 C. ± 0°.5.

On cooling, a feeble effect was observed under 14900 M.V.; but neither in this way, nor by sudden quenching of the heated mass by cold mercury, we could obtain any reliable result. According to STEIN [1]) the solidifying-temperature is 1484° C.

The crystallised substance consists of irregularly bordered birefringent grains or scales; for the refractive-indices we found the following values: $n_1 = 1.719 \pm 0.003$ and $n_2 = 1.697 \pm 0.004$. The birefringence is: 0.022. For the purpose of comparison we investigated again a natural *Willemite* (from Moresnet); the indices and the birefringence appeared to have the same values as the mentioned ones; so that there can be no doubt whatever, that the two preparations are *identical*. Also we had at our disposal a beautifully crystallised preparation obtained by GORGEU [2]), which consisted of broad needles with rectangular extinction and positive birefringence. The refractive indices were: $n_1 = 1.720 \pm 0.003$ and $n_2 = 1.693 \pm 0{,}006$; the birefringence was about: 0.027. So all these preparations evidently represent one and the same modification of Zn_2SiO_4, identical with the *Willemite*.

§ 9. *Cadmium-metasilicate*: $CdSiO_3$ and *Cadmium-orthosilicate*: Cd_2SiO_4.

From a hydrated, crystallised cadmium-nitrate pure CdO was prepared by heating, and from this the ortho- and meta-silicates were obtained by melting it with SiO_2 in platinum-crucibles.

[1]) STEIN, Z. f Anorg. Chem. **55**. 165. (1907).

[2]) A. GORGEU, Bull. de la Soc. Min. de France **10**, 36, 264. (1887). We bring here once more our thanks to Prof. P. GAUBERT in *Paris*, who was so kind as to give us these preparations for our purpose.

CdO appeared always to volatilise in an appreciable quantity, the preparation of products of the right composition thus being highly impeded. In the case of the ortho-silicate, a beginning of layer-formation could be observed; however the layers disappeared finally after repeated melting.

Finally we found by analysis of the product:

For $CdSiO_3$	32,1 %	SiO_2;	calculated:	31,96 %
	67,8 %	CdO;	„	68,04 %
For Cd_2SiO_4	19,7 %	SiO_2;	„	19,1 %
	80,2 %	CdO;	„	80,9 %

The ortho-silicate thus may not be considered to be completely pure, containing about 0.5 % SiO_2 too much; because of the very rapid evaporation of CdO at 1400° C. however, it will only be accidentally possible to obtain a 100 % Cd_2SiO_4 in this way.

For $CdSiO_3$ we determinated in a series of successive experiments (with thermoelement *II*) the E. M. F. at the meltingpoint to be 12435 ± 5 M. V. (uncorr.). After correction this can be fixed at: 12426 ± 5 M. V., corresponding to 1241° ± 0°,5 C.

On cooling we found, after undercooling to 12240 M. V., a solidifying-point at 12285 M. V., i. e. at about 1229° C.

Experiments with the use of the quenching-method in mercury were also made; we found, that:

After heating at 12480 M. V. and quenching, *all was glassy.*
„ „ „ 12460 M. V. „ „ „ „ „
„ „ „ 12450 M. V. „ „ there were *crystals and glass present.*
„ „ „ 12440 M. V. „ „ idem.

The meltingpoint must therefore be situated at about 12455 M. V., (uncorr.), which after correction corresponds to 1243° C.

The crystallised product consists of beautiful, but irregularly bordered crystals with parallel extinction and strong birefringence. The refractive indices were both greater than 1,739, but the lack of liquids with higher refractive index made a more accurate determination momentaneously impossible.

The specific gravity of the molten and then solidified $CdSiO_3$ was: $d_{4^\circ} = 4{,}928$ at 25° C.

For Cd_2SiO_4 we found in the same way: E. M. F. = 12460 ± ± 10 M. V., or, after correction (— 10 M. V.): 1242° ± 1° C; this meltingtemperature being practically identical with that of the meta-silicate.

In cooling a heat-effect was observed at 12280 M. V., i. e. at

about 1228° C. Quenching-experiments gave no positive results; a single indication was obtained, which could lead to the conclusion, that the meltingpoint should lie in de neighbourhood of 12560 M. V. i. e. at about 1252° C. The crystallised substance consists of irregularly shaped, strongly birefringent grains, probably resembling those of artificial willemite, which probably is isomorphous with the *Cd*-compound. Both refractive-indices are greater than 1,739.

§ 10. *Manganese-Metasilicate; Manganese-Orthosilicate; Rhodonite and Tephroite.*

The ortho-, and meta-silicate of *manganese* were obtained from a basic manganese-carbonate, which, as analysis showed, contained 54,1 % *MnO*, and from pure quartz. Because on melting in platinum-crucibles in the open air, always black needles of higher oxides were observed, the components were then melted in the FLETCHER-furnace in graphite-crucibles, closed with a cover of the same material. Certainly a rose coloured product was now obtained; but the crucibles burnt very rapidly, and the carbon soiled the silicate too much, to continue the experiments any longer in this way. Thus the graphite-crucible in the FLETCHER-furnace was again replaced by a platinum-crucible, which was tightly closed by a cover of graphite, turned on the lathe. In this way we obtained a pure *rhodonite*, or by quenching in cold water, a pink *glass*, which on heating in the BUNSEN-flame was again transformed into a red crystalline mass. Analysis gave the following data:

	Crystals:	*Glass*:	*Calculated*:
SiO_2	46.25 %	46.20 %	45,95 %
MnO	53,8 %	53,8 %	54,0 %

So the product still contains 0,25 % SiO_2 too much; but it was only accidentally possible to approach nearer to the theoretical composition.

The preparation of the ortho-silicate occurred in quite the same way; after twofold correction, the analysis gave:

	Observed:	*Calculated*:
SiO_2	29,60 %	29,82 %
MnO	70,4 %	70,2 %

The product has a brownish-black colour, and consists of glittering crystals, which on grinding give a grey powder.

Besides the artificial *rhodonite*. $MnSiO_3$, we also investigated the meltingpoints, etc. of a number of natural, very pure and selected *rhodonites* from *Radau-Tal*, from *Franklin N. J.*, from *Auvergne*

and from *Langban* in *Sweden*. On melting them exposed to the air as well as in a nitrogen-atmosphere, they always become darker by a decomposition, and by a slight oxydation. However, this seems to have no appreciable influence on the meltingpoint, but only makes the localisation of the heat-effects on the curves more troublesome. In all cases we found on these curves *three* successive heat-effects, which however, on repeated melting of the mass were gradually effaced, a more detailed research must bring a full decision as regards the true significance of these successive effects. The measurements were made with thermoelement II; the results, after correction, are reviewed in the following table:

Effect:	*Artificial Rhodonite*		*From Radau-Tal*		*Natural Rhodonites.*					
					From Franklin, N. J. [1]		*From Auvergne*		*From Longban* [2]	
	M.V.	° C.	M.V.	° C.	M.V.	° C.	M.V. in air	° C.	M.V.	° C.
1	12820	1274°	12620	1257°	12185	1221°	12800	1272°	12740	1267°
2	12024	1208	—	—	11410	1156	—	—	—	—
3	10920	1115	—	—	—	—	—	—	—	—
							in nitrogen			
1	12810	1273°	12535	1259°	12175	1220°	12734	1267°	12710	1265°
2	12050	1210	—	—	11500	1164	12000	1206	—	—
3	—	—	—	—	—	—	—	—	—	—
1	12800	1272°					12770	1270°		
2	12020	1207	—	—	—	—			—	—
3	11180	1137								

In cooling-experiments undercooling of 10 or 40 M.V. below the maximum crystallisation-temperatures immediately following, appeared

[1]) The rhodonite from these places is analysed by PIRSSON; he determined: SiO_2: 46,1%; MnO: 34,3%; FeO: 3,6%; ZnO: 7,3%; CaO: 7,0%; MgO: 1,3%.

[2]) According to an analysis of LINDSTROM the rhodonite of *Langban* contains: SiO_2: 47,7%; MnO: 31,6%; FeO: 0,5%; CaO: 18,2%; MgO: 1,2%. The *Swedish* rhodonites seem to contain no ZnO or only traces of it.

to be possible; these crystallisation-temperatures were however always 260 to 700 M.V. *lower* than the melting temperatures; also in this case the said method can never lead to the knowledge of the equilibrium-temperatures.

The meltingpoint of pure *rhodonite* thus may be fixed at 1273° ± 1° C.; evidently there are two transition-temperatures at resp. 1208° C. and 1120° C. Furthermore the melting-points of all *natural rhodonites* appear to be *lower*: for the rhodonite from *Auvergne* it is almost equal to that of the artificial product, and the same can be said of the first transition-point:

	Meltingpoint:	*Transitionpoint*:
Auvergne:	1270°	1206°.
Sweden:	1266°	—
Radau-Tal:	1258°	—
Franklin N.J.:	1221°	1150°.

The optical properties of the solidified products with the artificial and natural rhodonites were also identical with each other: $n_1 = 1{,}739 \pm 0.003$ and $n_2 = 1{,}733 \pm 0.003$; the birefringence is only feeble, about 0,007. For the *glass* we found: $n = 1{,}700$. The beautiful crystals are parallelogrammatically shaped, with an obtuse angle of about 107°, and an extinction-angle of 14°. There can be no doubt about *identity* of both kinds of crystals. For the natural rhodonites some data are reviewed here:

Rhodonite from Radau-Tal		*Rhodonite from Auvergne*		*Rhodonite from Franklin, N. J.*		*Rhodonite from Lang*	
Natural Crystal	After being melted	Natural Crystal	After being melted	Natural Crystal	After being melted	Natural Crystal	After be melte
			in air				
$n_1 = 1.722$	$n_1 = 1.712$	$n_1 = 1.736$	$n_1 = 1.733$	$n_1 = 1.729$	$n_1 = 1.725$	$n_1 = 1.702$	$n_1 = 1.$
$n_2 = 1.709$	$n_2 = 1.705$	$n_2 = 1.729$	$n_2 = 1.722$	$n_2 = 1.722$	$n_2 = 1.716$	$n_2 = 1.693$	$n_2 = 1.$
$\delta = 0.013$	$\delta = 0.007$	$\delta = 0.007$	$\delta = 0.011$	$\delta = 0.007$	$\delta = 0.009$	$\delta = 0.009$	$\delta = 0.$
			in nitrogen				
—	—	—	$n_1 = 1.729$	—	—	—	—
			$n_2 = 1.722$				
			$\delta = 0.007$				

The specific gravity of the crystallised $MnSiO_3$ is $d_{4^\circ} = 3{,}716$ at 25° C.; for the *glass*: $d_{4^\circ} = 3{,}48$.

With artificial Mn_2SiO_4 no reliable meltingpoint could be found; the compound became gradually darker by decomposition. With a natural Mn_2SiO_4, a *tephroite* of *Sparta* (*N.J.*), we found with thermoelement *IV* successively:

E.M.F. at the meltingpoint: 13185 M.V., if the furnace-gradient was 60 M.V. per minute.

12991 M.V., if the furnace-gradient was 40 M.V. per minute.

Mean: 13088 M.V. ± 9 M.V. (uncorr.)

which, after correction, corresponds to: 1292° ± 8° C. The meltingpoint is *not* sharp; for the artificial, *pure* silicate it probably will be *higher*, in agreement with the temperature mentioned by DOERINCKEL (1323° C.).

The melted and again solidified artificial Mn_2SiO_4 differed rather appreciably from the natural *tephroite* used; while the latter had the refractive indices: $n_1 = 1{,}709$, and $n_2 = 1{,}693$, the birefringence being: 0,016, — the indices of the melted artificial product appeared *both* to be *greater* than 1,739. Whether this solidified product represents another modification of the substance, or an impure and partially decomposed tephroite, can now hardly be said; the specific weight of the artificial, melted and again solidified Mn_2SiO_4 is: $d_{4^\circ} = 4{,}043$ at 25° C.

For the purpose of comparison we investigated also a beautifully crystallised preparation of GORGEU [1]), which was obtained by the interaction of $MnCl_2$ and SiO_2, under co-operation of introduced water-vapour. This *rhodonite* consisted of optically negative, often irregularly extinguishing, triclinic needles; n_1 was greater than 1,739 and n_2 was 1,728; birefringence about: 0,013. The corresponding *tephroite* had the shape of greyish-brown, flat, metallic looking needles, which probably were of rhombic symmetry, and whose refractive indices appeared both to be greater than 1,739.

§ 11. If now we summarise the results of these and former determinations, we can give the following survey:

1) GORGEU, loc. cit.

Compound	Meltingpoint	Specific Weight	Observers	Refraction, etc.
$BeSiO_3$	>1750° C.		JAEGER and VAN KLOOSTER	—
$MgSiO_3$	1554° C.	3.175	ALLEN and WRIGHT	$n_1 = 1.641$; $n_2 = 1.648$; $n_3 = 1.663$
Mg_2SiO_4	>1750° C.	—	—	—
$CaSiO_3$	1540° C.	—	DAY, ALLEN, SHEPHERD and WHITE	$n_1 = 1\,609$; $n_2 = 1.650$
Ca_2SiO_4	2130° C.	3.27	id.	$n_1 = 1.714$; $n_2 = 1.720$; $n_3 = 1.737$
$SrSiO_3$	1578° ± 1° C.	3.652	JAEGER and VAN KLOOSTER	$n_1 = 1.620$; $n_2 = 1.590$
Sr_2SiO_4	>1750° C.	—	id.	—
$BaSiO_3$	1604° ± 0.°5 C.	4.435	id.	$n_1 = 1.670$; $n_2 = 1.667$
Ba_2SiO_4	>1750° C.	—	id.	—
$ZnSiO_3$	1437° ± 1° C.	3.52	id.	$n_1 = 1.623$; $n_2 = 1.616$
Zn_2SiO_4	1509°.5 ± 0.°5 C.	—	Id.	$n_1 = 1.719$; $n_2 = 1.697$
$CdSiO_3$	1242° ± 0.°5 C.	4.928	id.	Both greater than 1.739
Cd_2SiO_4	1252° tot 1243° ± 1° C.	—	id.	Both greater than 1.739
$MnSiO_3$	1273° ± 1° C.	3.716	id.	$n_1 = 1\,739$; $n_2 = 1.733$
Mn_2SiO_4 (*tephroite*)	1290° tot 1300° C.	4.044	id.	Both greater than 1.739
$CaMg(SiO_3)_2$	1391° C.	3.275	ALLEN and WHITE	$n_1 = 1.664$; $n_2 = 1.671$; $n_3 = 1.694$

Very remarkable is the high specific gravity of the *cadmium*-metasilicate.

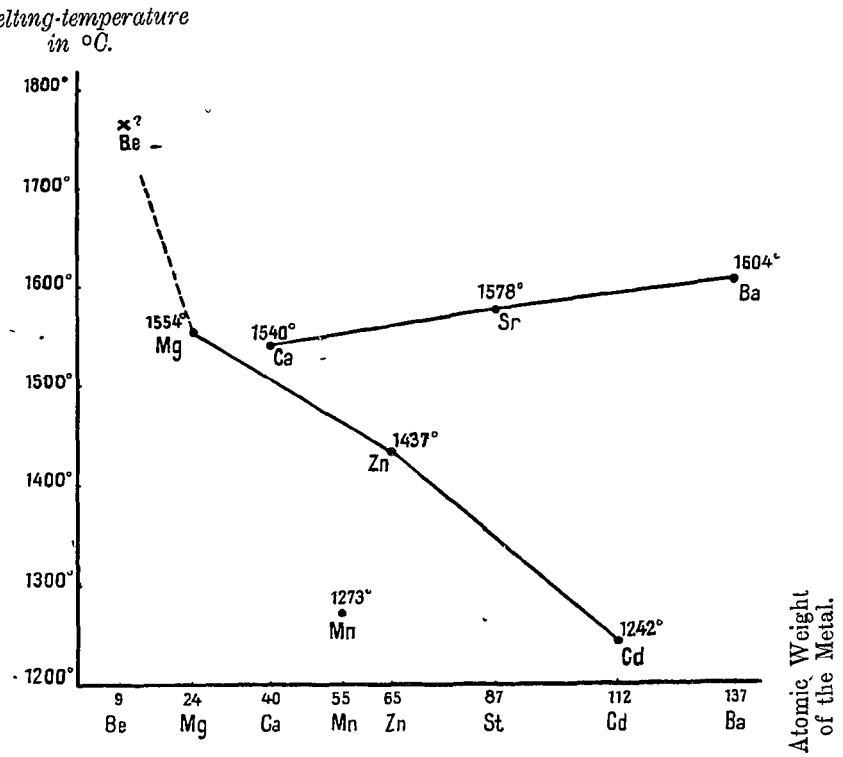

Fig. 2.

With respect to the melting-points of the *meta-silicates* (fig. 2), it may yet be remarked, that those of the *Ca*-, *Sr*-, and *Ba*-silicates *increase* in an almost *rectilinear* way with *increasing* atomic weight of the corresponding metal, while those of the *Mg*-, *Zn*-, and *Cd*-salts appear to *decrease* in an analogous way with increasing atomic weight of the metal. $BeSiO_3$ on the one side, $MnSiO_3$ on the other side seem, however, to be quite apart from both these homologous groups.

For the *ortho-silicates* the available data are too few, to obtain an analogous classification with any certainty. In every case evidently the meltingpoints of Sr_2SiO_4 and Ba_2SiO_4 are probably situated in the vicinity of 2200° C., while that of Be_2SiO_4 must be even much higher. In connection with this it would be interesting to investigate, if perhaps Be_2SiO_4 does not possess further properties, which would make it recommendable as an extremely refractory material.

Groningen, October 1915. *University-Laboratory for Inorganic and Physical Chemistry.*

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