Chemistry. — *The Structure of the Ammonium-, Rubidium- and Thallium-Osmiamates.* By F. M. JAEGER and J. E. ZANSTRA.

§ 1. In a previous paper [1]) we established the structure of *potassium-osmiamate* and demonstrated that the constitution of this tetragonal-bipyramidal salt is quite analogous to that of *potassium-periodate,* of *potassium-perrhenate* and of the *tungstates* and *molybdates* of the *scheelite-wulfenite*-group; more in particular that this constitution in the case of *potassium-osmiamate* can be expressed by:

$$\left\{ [O]''_3 [Os^{VIII}] [N]''' \right\}' \ldots K^{\cdot},$$

all composing ions having the electronic configurations of inert gases.

In the present paper we wish to communicate the results obtained in the analogous study of some other *alkali*-salts of this series, more particularly of the *ammonium-, rubidium-,* and *thallo-osmiamate.* The investigation of the corresponding, but structurally deviating *cesium*-salt will be published in another paper.

§ 2. Although all these salts show a close analogy to the *potassium*-salt in so far, that they prove to possess a truly pseudo-tetragonal character, they deviate from the salt formerly studied by their lower symmetry, as in reality they all are rhombic, and more particularly, rhombic-bisphenoidal.

Crystallographical data.

1. *Ammonium-Osmiamate* crystallizes from its aqueous solutions in apparently tetragonal crystals (Fig. 1), which on closer examination,
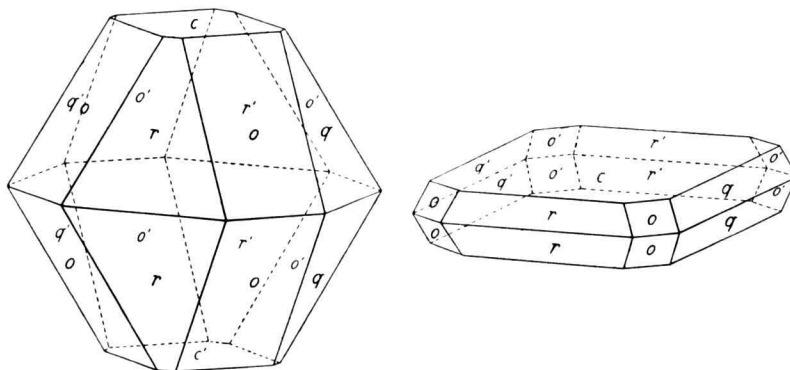

Fig. 1. Ammonium—Osmiamate.

[1]) F. M. JAEGER and J. E. ZANSTRA, these Proceedings, **35**, (1932), 610;

however, prove to be rhombic-pseudotetragonal. In their external appearance they are either analogous to the *potassium*-salt, only differing from them by the occurrence of the basal plane (001), or they are tabular parallel to this face (001), which at the same time is a direction of a not perfect, but good cleavability. The angular values are not quite constant.

Rhombic-bisphenoidal;   pseudo-tetragonal.

$$a : b : c = 0,9437 : 1 : 2,3106.$$

Forms observed: o = {112}, narrower than r and q, but yielding good reflections; r = {101} and q = {011}, both lustrous and about equally broad; c = {001}, either small or predominant, very lustrous.

Angular values:	Observed:	Calculated:
		(from the spectrogr. data):
c : o = (001) : (112) =*	58° 13'—59° 44'	59° 17'
c : q = (001) : (011) =*	66 42	66 36
c : r = (001) : (101) =	—	67 47
q : q' = (011) : (01$\bar{1}$) =	44 2 —45 35	44 26
r : r' = (101) : (10$\bar{1}$) =	—	46 48

Cleavage parallel to {001}, distinct, but not so perfect as in the case of the *rubidium*-salt. The specific weight at 16° C. is: 4.0.

The crystals are biaxial, with a very small optical angle. For red rays, they are almost uniaxial; the plane of the optical axes for the yellow rays is parallel to {100}, for the green and blue rays parallel to {010}. The first bisectrix is parallel to the c-axis; the character of the double refraction is positive.

2. *Rubidium-Osmiamate.* The *rubidium*-salt also is rhombic and shows the closest analogy with the *ammonium*-salt just described. However, the habitus of the crystals here is always tabular parallel to (001), this face being a direction of a perfect cleavability. The crystals are often elongated parallel to the edge (001) : (112); but also regular octagonally or tetragonally limited plates occur (Fig. 2).
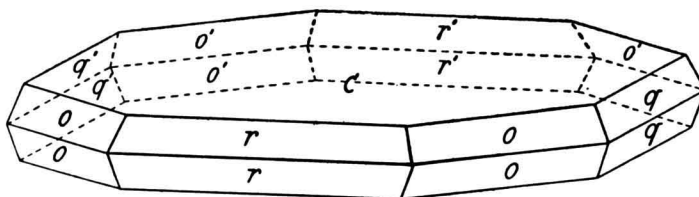

Fig. 2. Rubidium—Osmiamate.

Rhombic-bisphenoidal; pseudo-tetragonal.

$$a : b : c = 0,9539 : 1 : 2,3356.$$

Forms observed: $c = \{001\}$, always predominant, very lustrous; $o = \{112\}$, $r = \{101\}$ and $q = \{011\}$, almost equally well developed and yielding excellent reflections.

Angular values:	*Observed:*	*Calculated:*
		(from the spectrogr. data):
$c : q = (001) : (011) =$*	66° 58'—67° 58'	67° 42'
$c : o = (001) : (112) =$*	59 28	59 25
$c : r = (001) : (101) =$	66 29 —67 0	66 49½
$q : q' = (011) : (01\bar{1}) =$	44 4 —46 14	44 36
$o : o = (112) : (11\bar{2}) =$	61 4	61 10

The angular values oscillate not unappreciably. The crystals possess a perfect cleavability parallel to $\{001\}$. The specific weight at 18° C. is about: 5.0. Optically biaxial; the birefringence is positive. The plane of the optical axes for red and yellow rays is parallel to $\{100\}$, that for the green and blue rays parallel to $\{010\}$. The first bisectrix is parallel to the c-axis; the angle of the optical axes is only small.

Sometimes plates cut parallel to $\{001\}$ shows a subdivision in four weakly birefringent and biaxial sectors. In this case the angular values oscillate even more than in the ordinary case. Most probably this anomalous optical behaviour is caused by a slight admixture of the potassiumsalt; if a potassiumfree rubidiumsalt is used in the preparation of the osmiamate, no such anomalies manifest themselves any longer.

3. Thallium-Osmiamate.

The *thallous* salt, — which is almost insoluble in cold, better soluble in boiling water, — crystallizes, on cooling, in very small, flat crystals, which evidently are quite analogous to the *rubidium*-salt. They are biaxial; their powder spectrogram appeared almost identical with that of the *rubidium*-salt. The axial ratio is: $a : b : c = 0,9542 : 1 : 2,3679$.

The bisphenoidal symmetry is attributed to all three rhombic salts, in connection with the experiences gained in the case of the *cesium*-salt, the bisphenoidal symmetry of which was proved in several ways, as will be shown in the following paper.

§ 2. For the purpose of controlling the rhombic symmetry of the *ammonium*-, and *rubidium*-salts, LAUE-patterns on $\{001\}$ we made with *tungsten*-radiation (40—44 K.V.). The image of the *Rb*-salt thus obtained, is reproduced in Fig. 3.

The analysis of this LAUE-pattern in the usual way gave the following results; the gnomonic projection of the image is reproduced in Fig. 4.
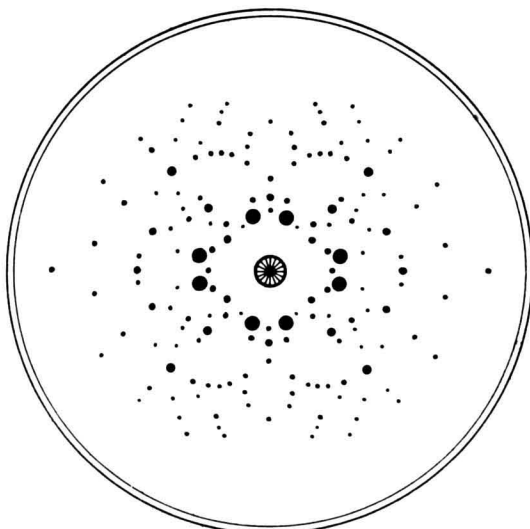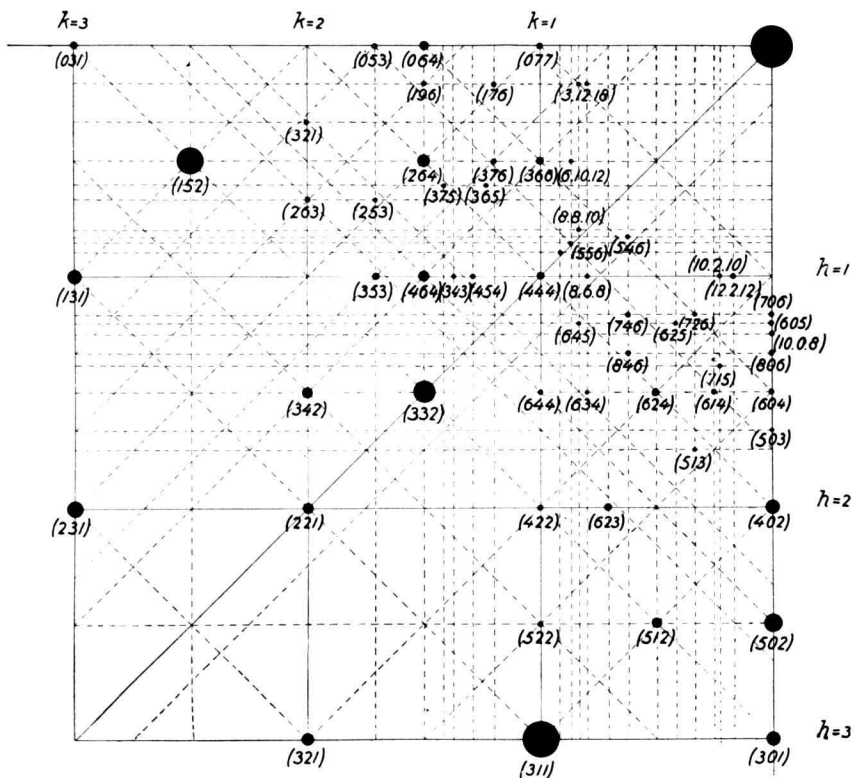

Fig. 3. LAUE-Pattern of Rubidium-Osmiamate on {001}.

Fig. 4. Gnomonic Projection of the LAUE-Pattern on {001} of Rubidium-Osmiamate.

TABLE I.
Analysis of the LAUE-pattern on (001) of the Rubidium-Salt.

Symbol {hkl} :	Estim. Int. :	Glancing Angle θ :		(1st order)	(2nd order)	(3d order)	(4th order)	(5th order)	(6th order)	(7th order)
(011)	1	22°	39'	4.1770	2.0885	1.3923	1.0442	0.8354	0.6962	0.5967
(356)	1	23	12	0.7231	0.3616	—	—	—	—	—
(122)	2	20	21	1.7086	0.8543	0.5695	—	—	—	—
(588)	1	19	41	0.3875	—	—	—	—	—	—
(546)	1	21	6	0.6074	—	—	—	—	—	—
(434)	1	18	15	0.6876	0.3438	—	—	—	—	—
(445)	1	20	1	0.6608	0.3304	—	—	—	—	—
(556)	1	19	31	0.5127	—	—	—	—	—	—
(778)	1	18	48	0.3523	—	—	—	—	—	—
(111)	2	16	19	2.2109	1.1055	0.7369	0.5528	—	—	—
(515)	1	21	46	0.7763	0.3882	—	—	—	—	—
(616)	1	21	55	0.6536	0.3268	—	—	—	—	—
(746)	1	16	54	0.4003	—	—	—	—	—	—
(645)	1	15	54	0.4228	—	—	—	—	—	—
(625)	1	17	53	0.5324	—	—	—	—	—	—
(726)	1	18	37	0.4779	—	—	—	—	—	—
(706)	1	19	37	0.5109	—	—	—	—	—	—
(605)	1	19	14	0.5827	—	—	—	—	—	—
(504)	1	18	31	0.6770	0.3385	—	—	—	—	—
(403)	1	16	55	0.8030	0.4015	—	—	—	—	—
(302)	1	15	11	0.9697	0.4848	—	—	—	—	—
(614)	2	14	56	0.4732	—	—	—	—	—	—
(715)	2	16	4	0.4329	—	—	—	—	—	—
(312)	2	14	25	0.8829	0.4415	—	—	—	—	—
(423)	1	15	19	0.6598	0.3299	—	—	—	—	—
(634)	1	13	44	0.3970	—	—	—	—	—	—
(322)	1	12	49	0.6960	0.3480	—	—	—	—	—
(513)	2	8	31	0.5112	—	—	—	—	—	—
(533)	3	11	53	0.4013	—	—	—	—	—	—
(211)	1	10	27	0.9169	0.4585	—	—	—	—	—
(623)	3	10	54	0.3407	—	—	—	—	—	—
(201)	5	11	42	1.1259	0.5630	—	—	—	—	—
(522)	1	8	37	0.3185	—	—	—	—	—	—

TABLE I (*Continued*). Analysis of the LAUE-pattern on (001) of the Rubidium-Salt.									
Symbol $\{hkl\}$:	Estim. Int. :	Glancing Angle θ :		(1st order)	(2nd order)	(3d order)	(4th order)	(5th order)	(6th order)	(7th order)
(512)	4	9°	8′	0.3526	—	—	—	—	—	—
(502)	6	9	14	0.3657	—	—	—	—	—	—
(311)	10	7	17	0.4640	—	—	—	—	—	—
(301)	5	8	46	0.5121	—	—	—	—	—	—
(032)	4	15	39	1.0145	0.5073	—	—	—	—	—
(146)	1	31	45	1.2579	0.6289	0.4169	—	—	—	—
(176)	2	19	30	0.5235	—	—	—	—	—	—
(132)	5	14	51	0.9157	0.4578	—	—	—	—	—
(365)	1	17	18	0.4935	—	—	—	—	—	—
(375)	1	15	16	0.3916	—	—	—	—	—	—
(465)	1	16	7	0.4302	—	—	—	—	—	—
(232)	3	12	55	0.7085	0.3543	—	—	—	—	—
(343)	1	14	1	0.5465	—	—	—	—	—	—
(454)	2	14	27	0.4414	—	—	—	—	—	—
(443)	4	12	38	0.4298	—	—	—	—	—	—
(332)	8	11	0	0.5145	—	—	—	—	—	—
(053)	1	14	5	0.5558	—	—	—	—	—	—
(152)	10	9	17	0.3684	—	—	—	—	—	—
(253)	1	13	3	0.4800	—	—	—	—	—	—
(353)	3	12	1	0.4101	—	—	—	—	—	—
(342)	4	7	17	0.3769	—	—	—	—	—	—
(221)	4	8	23	0.5885	—	—	—	—	—	—
(321)	4	6	29	0.3619	—	—	—	—	—	—
(031)	4	7	59	0.5372	—	—	—	—	—	—
(131)	4	7	34	0.4821	—	—	—	—	—	—
(231)	5	6	42	0.3686	—	—	—	—	—	—
(376)	2	18	15	0.4558	—	—	—	—	—	—
(321)	2	6	36	0.3619	—	—	—	—	—	—
(503)	1	14	6	0.5358	—	—	—	—	—	—
(196)	1	15	29	0.3343	—	—	—	—	—	—
(263)	1	11	23	0.3538	—	—	—	—	—	—
(566)	1	17	37	0.4236	—	—	—	—	—	—

The wave-lengths are calculated from the formula:

$$\lambda = \frac{2 \cdot l}{c_0} \left\{ \frac{1}{\left(\dfrac{h}{a_0}\right)^2 + \left(\dfrac{k}{b_0}\right)^2 + \left(\dfrac{l}{c_0}\right)^2} \right\}.$$

In the case of the *rubidium*-salt the wave-lengths produced lie between: 0,2796 Å. and about 0,68 Å. The underlying lattice proves to be *the simple rhombic* one.

The LAUE-pattern on (001) of the *ammonium*-salt was closely analogous to that of the *rubidium*-salt; it possessed rhombic symmetry, with a dyad axis and two symmetry-planes perpendicular to each other. The measurements of DUFET, who thought the *ammonium*-salt to be tetragonal, are, therefore, erroneous.

§ 3. *Rotation-spectrograms of the Rubidium-Salt.*

Rotation-spectrograms of the crystals were made by oscillating them round the principal crystallographical directions through different angles, using *copper*-radiation as the luminous source.

a. The rotationspectrogram round the *a*-axis showed a principal and two accessory spectra. $I_a = 5.55$ Å. The most intensive spots were: (004); (008); (028); (013); (026); (037); (048); (101); (103); (116); (118); (1.1.10); (116); (136); (138); (217); (228); (224) and (244).

b. The rotationspectrogram round the *b*-axis also showed a principal spectrum and two accessory spectra. $I_b = 5.70$ Å. The most intensive images were: (004); (008); (109); (0.0.12); (103); (204); (309); (017); (0.1.11); (112); (315); (316); (129); (121) and (224).

c. The rotationspectrogram round the *c*-axis showed a principal and seven accessory spectra. $I_c = 13.64$ Å. The most intensive spots ($\varphi = 60°$, being double that used in the previous cases) were: (200); (220); (020); (132); (332); (103); (123); (303); (024); (224); (244); (424) and (116). The 2nd, 4th and 6th spectra were more intensive than the 1st, 3d, 5th and 7th spectra.

d. Rotationspectrograms round [110], gave: $I_{(110)} = 8.1$ Å. A principal and three accessory spectra were present. With $\varphi = 60°$, the most intensive images were: (112); (116); (224); (228); (336); (338); (125); (129); (020); (024); (132); (136); (1.3.10); (0.0.12); (211); (200); (204); (310); (316) and (312). In another spectrogram of this kind, also: (2.2.10); (004); (008); (1.1.10); (208) and (3.1.10) were found to be rather intensive besides some of the spots already mentioned. In general, the spots of the highest intensities appear to be those for which $(h + k + l)$ is an *even* number; the triplets $(o\,k\,l)$ also occur only in such cases, where $(k + l)$ is an *even* number. Although the cell is evidently the simple rhombic one, these facts prove that at least the plane (100) is *almost* centred.

§ 4. *Powderspectrograms of the (NH₄)- and Rb-salts* were obtained by means of *iron-*, those of the *Tl*-salt by means of *copper*-radiation. The results obtained will be published later-on in detail in a more extensive paper. The data were not used for the determination of the intensities, as the diffraction-lines were too crowded, so that often several lines were practically coïnciding. For the purpose of comparison of the observed and calculated intensities, therefore, the intensities of the diffraction-spots of the rotationspectrograms were made use of. In general it may be pointed out that the data of the powderspectrograms were in perfect agreement with those obtained in the rotationspectrograms. The following Table II gives a survey of the principal data necessary for the final discussion of the structure of the salts here considered.

§ 5. *Discussion of the Structure of the (NH₄),- Rb- and Tl-Osmia-mates.*. As the (NH₄)- and Tl-salts show, in their behaviour, the closest analogy with the Rb-salt, it is sufficient here to limit our discussion to the latter compound.

In the spectrograms of this salt the reflections of (100), (010) and (001) in *odd* orders are absent. In connection with the simple rhombic lattice, its structure, therefore, must belong to the spacegroup V^4. In this group a tetravalent position occurs with the co-ordinates :

$$[x, y, z] \; ; \; [x + \tfrac{1}{2}, \tfrac{1}{2} - y, \bar{z}] \; ; \; [\bar{x}, y + \tfrac{1}{2}, \tfrac{1}{2} - z] \; ; \; [\tfrac{1}{2} - x, \bar{y}, z + \tfrac{1}{2}].$$

For $x = 0$; $y = \tfrac{1}{4}$; $z = {}^1/_8$ for the *Os*-atoms, the positions of the *Os*-atoms become :

$[0, \tfrac{1}{4}, {}^1/_8] \; ; \; [\tfrac{1}{2}, \tfrac{1}{4}, {}^7/_8] \; ; \; [0, \tfrac{3}{4}, {}^3/_8] \; ; \; [\tfrac{1}{2}, \tfrac{3}{4}, {}^5/_8]$; or, by shifting them over $y = -\tfrac{1}{4}$ and $z = -{}^1/_8$:

$[0, 0, 0] \; ; \; [\tfrac{1}{2}, 0, \tfrac{3}{4}] \; ; \; [0, \tfrac{1}{2}, \tfrac{1}{4}] \; ; \; [\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}]$, just as in the case of the *potassium*-salt.

In the same way, for $x = 0$; $y = \tfrac{1}{4}$; $z = {}^5/_8$ for the *Rb*-atoms in the *rubidium*-salt, their positions become :

$[0, \tfrac{1}{4}, {}^5/_8] \; ; \; [\tfrac{1}{2}, \tfrac{1}{4}, {}^3/_8] \; ; \; [0, \tfrac{3}{4}, {}^7/_8] \; ; \; [\tfrac{1}{2}, \tfrac{3}{4}, {}^1/_8]$; or, by the same shift :

$[0, 0, \tfrac{1}{2}] \; ; \; [\tfrac{1}{2}, 0, \tfrac{1}{4}] \; ; \; [0, \tfrac{1}{2}, \tfrac{3}{4}] \; ; \; [\tfrac{1}{2}, \tfrac{1}{2}, 0]$, also in analogy with those in the *potassium*-salt.

The *Rb*- and *Os*-atoms *are now placed with respect to each other in just the same way* as the *K*- and *Os*-atoms in the *potassium*-salt; the close analogy of this pseudo-tetragonal salt with the really tetragonal *potassium*-salt, beforehand makes it most probable that the deviations from these positions will only be very small.

Now the parameter : $z = \tfrac{1}{8}$ in the direction of the c-axis is certainly the correct one : for in the rotation-spectrograms, the reflections : (004), (008) and (00.12) are all very strong, while no trace of (002), (006) or (00.10) was ever observed ; moreover, the face (001) always occurs as a limiting crystal-face. The value of z must, therefore, be chosen in such a way that the path-difference of z and $\bar{z}$ will be exactly $\tfrac{1}{4} c_0$, and this occurs, if $z = \tfrac{1}{8}$.

TABLE II.

Synopsis of the Structures and Properties of the K-, (NH_4)-, Rb- and Tl-Osmiamates.

Salt:	Formula:	Symmetry:	Axial Ratio and Cleavability:	Optical Character:	Dimensions of the Elementary Cell:	Spec. Weight at 0° C.:	Number of Molecules pro Cell:	Character of Lattice:	Space-Group:
Potassium Osmiamate	$K\,Os\,NO_3$	Tetrag.-bipyr.	$a : c = 1 : 2,3123.$ No distinct cleavability.	Uniaxial; positive.	$a_0 = 5,65$ Å.; $a_0 = 5,65$ Å.; $c_0 = 13,08$ Å.	4.616	4 Mol.	Bodily centred tetrag. cell Γ'_t	C^6_{4H}
Ammonium- Osmiamate	$(NH_4)\,Os\,NO_3$	Rhomb.-bisphen. (pseudo-tetrag.)	$a : b : c = 0,9437 : 1 : 2,3106.$ Distinct cleavability ∥ (001).	Biaxial: positive	$a_0 = 5,53$ Å.; $b_0 = 5,86$ Å.; $c_0 = 13,54$ Å.	4.075	4 Mol.		
Rubidium- Osmiamate	$Rb\,Os\,NO_3$	Rhomb.-bisphen. (pseudo-tetrag.)	$a : b : c = 0,9539 : 1 : 2,3356.$ Good cleavability ∥ (001).	Small opt. angle. 1st Biss. ∥ c-axis.	$a_0 = 5,57$ Å.; $b_0 = 5,84$ Å.; $c_0 = 13,64$ Å.	5.033	4 Mol.	Simple rhomb. cell Γ_0.	V^4
Thallium Osmiamate	$Tl\,Os\,NO_3$	Rhomb.-bisphen. (pseudo-tetrag.)	$a : b : c = 0,9542 : 1 : 2,3679.$ Perfect cleavability ∥ (001).		$a_0 = 5,42$ Å.; $b_0 = 5,68$ Å.; $c_0 = 13,45$ Å.	7.281	4 Mol.		

The same reasoning for the equally strongly diffracting Rb-atoms, gives $z = \frac{1}{8}$.

That these values in the direction of the c-axis are the right ones, can also be deduced from the intensities of the reflections (011) and (101) in the powder-spectrogram, which in the Rb-salt are much weaker than in the case of the (NH_4)-salt; indeed, the strongly diffracting Rb-atoms (and in the case of the *thallium*-salt, also the Tl-atoms), — almost completely annihilate the diffraction-effect of the Os-atoms, if in the direction of the c-axis midway between two Os-atoms always a Rb-atom is placed. Of course, the much more weakly diffracting (NH_4)-groups will not have this annihilating effect.

Because reflections $(o\,k\,l)$ for which $(k+l)$ is *odd*, never occur, it must be clear that the y-parameter of the Os- and Rb-atoms must be $\frac{1}{4}$ and $\frac{3}{4}$ respectively; in that case the sum of the sinus-terms in the structure-factor becomes zero for such planes; and for $(o\,k\,l)$, in which $(k+l)$ is odd, also the sum of the cosinus-terms will always be zero.

Hence the principal difficulty remains the determination of the x-parameter. If x were really *zero*, we should again have the structure of the *potassium*-salt, in so far as the diffraction of the $(Os+Rb)$-atoms is concerned. But notwithstanding the analogy of the K- and Rb-salts, the differences between the two structures are evident: the structure of the latter salt certainly is no longer that of a bodily-centred cell and the occurrence of reflections for which $(h+k+l)$ is *odd*, as, for instance, (311), proves that this result cannot be completely explained by the co-operation of the oxygen- and nitrogen-atoms alone, because their intensity is too small, even in the most favourable case. Certainly, therefore, the said phenomenon must also be caused by the position of the Os- and Rb-atoms. From the intensity of (502), it follows that $0 < x < 0.10$; from that of (746), that $0 < 7x < 180°$, which gives for x a maximum value of 0.03.

Indeed, $x = 0.03$ proves to be in excellent agreement with the intensities observed, thus, for instance, for (512) and (152) in the LAUE-pattern.

The final co-ordinates (first set) of the Os- and Rb-atoms, thus become:

a. 4 Os-atoms at: $[0,03; \frac{1}{4}; ^1/_8]$; $[0,53; \frac{1}{4}; ^7/_8]$; $[0,97; \frac{3}{4}; ^3/_8]$; $[0,47; \frac{3}{4}; ^5/_8]$.

b. 4 Rb-atoms at: $[0,03; \frac{1}{4}; ^5/_8]$; $[0,53; \frac{1}{4}; ^3/_8]$; $[0,97; \frac{3}{4}; ^7/_8]$; $[0,47; \frac{3}{4}; ^1/_8]$.

The second set of co-ordinates can be obtained by a shift over: $y = -\frac{1}{4}$ and $z = -\frac{1}{8}$.

The number of the parameters of the O- and N-atoms surrounding the Os-atoms is very great: 12 parameters must be determined, so that great accuracy cannot be expected.

As in the series of reflections: (004), (008) and (0.0.12), the intensity of the latter is very much weakened in comparison of the others, evidently in the direction of the c-axis the total action of the $(O+N)$-atoms is opposite to that of he $(Os+Rb)$-atoms in that direction. This involves for half the height of the $(O+N)$-bisphenoid a value $= 0.04 \cdot c_0$.

It must be remarked that for a radius of the O''-ion of 1.32 Å., the plane (001) would be a direction of perfect cleavability, if z were $= 0.03$.

The reflections (202) and (402) are only caused by the action of the $(O + N)$-ions; they are more intensive than (118), (114), etc.; also (204) is more intensive than (220). The $(O + N)$-ions, therefore, must be situated nearer to the planes (010) and (100) than to (110); perhaps the line joining the ions O'' and N''' most probably has the direction of the a-axis, as also follows from a model in which these ions are represented by contiguous spheres of the appropriate diameters.

As a proof to what extent the intensities calculated in this way in general agree with those observed, the calculated and observed values for a number of planes are graphically plotted in Fig. 5 against the sixfold glancing angle $6 . \theta$.
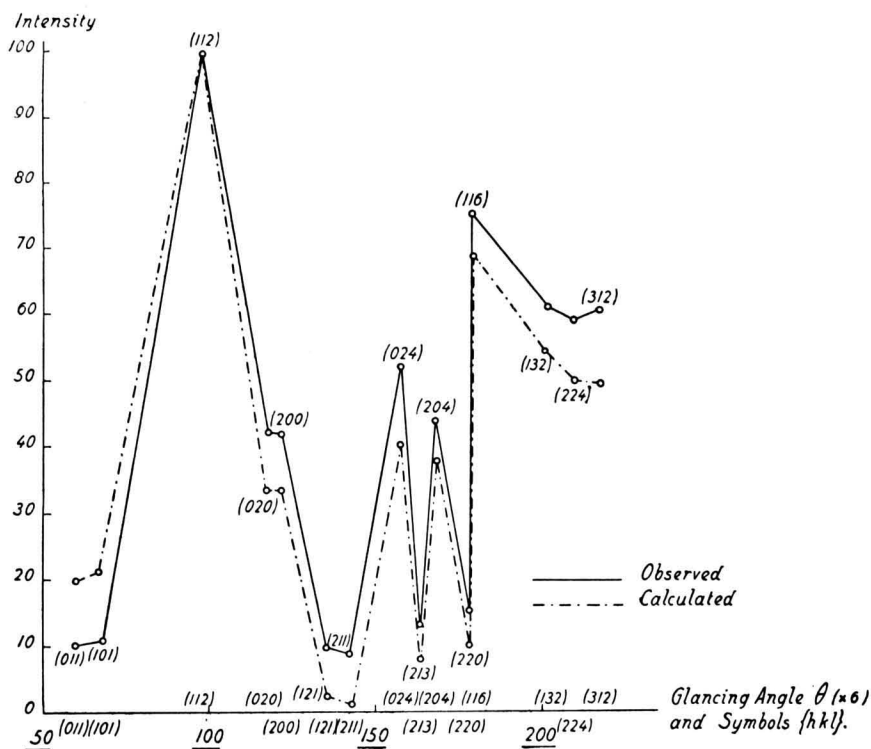
Fig. 5. Observed and calculated Intensities $(h\,k\,l)$ of Rubidium—Osmiamate.

The agreement, as expressed by the complete parallelism of the change in intensities of the subsequent planes, is really most satisfactory; so that there can be no doubt about the principal correctness of the structure adopted. That of the (NH_4)-salt and the Tl-salt are only slightly different from the structure mentioned, as is revealed by the very close analogy of their powder spectrograms with that of the Rb-salt.

In the next paper the structure of the more deviating *Cesium-Osmiamate* will be discussed and a comparison of the structures of all the *alkali-osmiamates* finally will be made.

Groningen, Laboratory for Inorganic and Physical Chemistry of the University.

Chemistry. — *Der Einfluss des Dispersitätsgrades auf physikalisch-chemische Konstanten.* (Zweite Mitteilung.) Von ERNST COHEN und C. THÖNNESSEN.

(Communicated at the meeting of June 25, 1932).

1. In einer kürzlich veröffentlichten Mitteilung [1]) konnten wir u.a. zeigen, dass sich Salizylsäure in so feindisperser Form herstellen lässt, dass dieselbe bei 25° C. eine bis zu etwa 15 % höhere Löslichkeit als die normale besitzt. Zu dieser feindispersen Form gelangten wir auf zwei Wegen, nämlich :

a) durch Abschrecken heiss gesättigter Salizylsäurelösungen ;

b) durch Schütteln der grobkristallinen Säure mit Goldkugeln in Gegenwart von Wasser.

In dieser ersten Mitteilung hatten wir bereits die Vermutung geäussert, dass für das von uns beobachtete Verhalten der Salizylsäure deren geringe Kristallisationsgeschwindigkeit oder wohl besser, deren geringe „Sammelkristallisationsgeschwindigkeit" [2]) verantwortlich gemacht werden muss. Es handelt sich nämlich darum, dass sehr kleine Kristalle in Lösung gehen und eine in Bezug auf die grossen Kristalle bei der herrschenden Temperatur übersättigte Lösung bilden. Die grossen Kristalle wachsen also infolgedessen auf Kosten der kleinen. Nun ist aber die Geschwindigkeit der Sammelkristallisation eine Funktion der Temperatur. In vorliegender Arbeit konnten wir einen solchen Einfluss der Temperatur dadurch nachweisen, dass wir die Versuche auf verschiedene Temperaturen ausdehnten.

2. Da wir zu Vergleichszwecken die Löslichkeitskurve der Salizylsäure benötigten und die in der Literatur von verschiedenen Autoren angegebenen Löslichkeitsdaten z.T. stark differieren [3]), musste die Löslichkeit der Säure bei verschiedenen Temperaturen sorgfältig neu bestimmt werden. Bei jeder Temperatur wurden stets mehrere Versuche ausgeführt in der Weise, wie sie bereits in der Abhandlung von ERNST COHEN und H. GOEDHART [3]) beschrieben wurde. Die zu sämtlichen Bestimmungen ver-

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[1]) Proc. Acad. Sci. Amsterdam **35**, 441 (1932).

[2]) Vergl. ERWIN SAUTER, Heterogene Katalyse, Bd. **23** der Wissenschaftlichen Forschungsberichte, STEINKOPF, Dresden und Leipzig 1930, Seite 20.

[3]) Proc. Acad. Sci. Amsterdam, **34**, 1 (1931).