

LXIII.—*Note on the Magnesium Vanadates.*

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VON HAUER described in 1860 (*J. pr. Chem.*, **80**, 329) a magnesium divanadate having the formula $\text{MgO} \cdot 2\text{VO}_3 + 8\text{HO}$ [$\text{V} = 68.6$, $\text{Mg} = 12$, $\text{O} = 8$], obtained by mixing solutions of magnesium sulphate and ammonium divanadate, and crystallising the sparingly soluble salt from hot water. On account of its slight solubility, it is difficult to obtain in large crystals, and furthermore its solution is somewhat readily decomposed on heating, with separation of vanadic acid. The description of this salt is concluded with the words:—*“Mit der genaueren Untersuchung dieser und mehrere anderer dreifach-vanadinsaurer Salze bin ich noch nicht zum Abschlusse gelangt, und behalte mir die Mittheilung für später vor.”* However, in none of the successive numbers of the Journal have we been able to find such a communication.

By boiling "magnesia alba" with water and amorphous vanadic acid, carbonic acid is rapidly evolved, and on filtering off the excess of magnesia alba, a colourless liquid is obtained. On evaporating this liquid a white mass is left, not sensibly crystalline, and giving discrepant results on analysis, whence it appears to be merely a mixture of magnesia and a neutral vanadate. If, on the other hand, acetic acid be added in excess, the liquid becomes deep red-brown, and on spontaneous evaporation it readily deposits crystals, leaving a syrupy solution of magnesium acetate. Two lots of crystals were thus obtained, one of a deep yellowish-brown, or almost black colour; and the other of a bright bichromate-red, both transparent.

I. *Brown Salt*.—A weighed portion of the crystals dissolved in water was precipitated with lead acetate. The washed precipitate was dissolved in nitric acid, and the solution precipitated with sulphuric acid; the filtrate after evaporation to a syrup was diluted with a very little water and the small quantity of lead sulphate filtered off; lastly this filtrate when evaporated and ignited left vanadic oxide. The filtrate from the lead vanadate, after precipitation with sulphuretted hydrogen, was concentrated, and the magnesia precipitated as usual with ammonium phosphate.

0.4025 substance lost 0.1315 on ignition; 0.3565 gave 0.0770 $\text{Mg}_2\text{P}_2\text{O}_7$; 0.3015 gave 0.1788 V_2O_5 , and 0.0692 $\text{Mg}_2\text{P}_2\text{O}_7$. Another preparation gave 60.02 p. c. V_2O_5 ; 7.66 p. c. MgO ; and 33.00 p. c. H_2O .

3MgO.5V ₂ O ₅ .28H ₂ O.		Found.			Mean.
V ₂ O ₅	59.40	—	59.30	60.02	59.66
MgO	7.82	7.78	8.27	7.66	7.90
H ₂ O.....	32.78	32.73	—	33.00	32.86
100.00					100.42

This salt forms crystals belonging to the triclinic system; the type is always short prismatic, through the predominance of the vertical prisms and pinacoids, of which the brachypinacoid is most developed; they are terminated by the basal planes and brachypinacoids. The forms observed are $\infty\text{P}\infty$. $\infty\text{P}'$. $\infty\text{P}\bar{2}'$. $\infty\text{P}\bar{2}$. $\infty\text{P}\infty$. $\frac{1}{2}\text{P}\infty'$. $\frac{1}{2}\text{P}\infty$. $+\text{P}\infty$. $+\text{P}'$ (Fig. 1). The prismatic faces, with the exception of the brachypinacoid, are often vertically striated, especially $\infty\text{P}\bar{2}'$ and $\infty\text{P}\infty$; the basal plane is nearly always deeply striated, parallel to the brachy-axis; the faces of $+\text{P}'$ are also striated parallel to their combination-edge with the brachypinacoid. The faces are always very lustrous, but do not generally give sharp images by reflection. The elements are:— $a : b : c = 1.000 : 1.003 : 1.012$; $\alpha = 89^\circ 24'$; $\beta = 104^\circ 20'$; $\gamma = 82^\circ 22'$; and the interfacial angles are:—

	Calculated.	Found.	No. of observations.
$\infty P\infty : \infty P\infty = (100) : (010) = 81^\circ 58'$	$81^\circ 58'$	$81^\circ 41'$	3
$\infty P\infty : \infty P' = (100) : (110) = 132 \quad 8$	132 8	132 4	1
$\infty P\infty : \infty P2' = (100) : (210) = 152 \quad 52$	152 52	151 50	2
$\infty P\infty : \infty P2 = (100) : (2\bar{1}0) = 155 \quad 51$	155 51	156 34	2
$\infty P\infty : \infty P' = (010) : (110) = 129 \quad 50$	129 50	129 54	4
$\infty P\infty : \infty P2' = (010) : (210) = 109 \quad 6$	109 6	109 6	1
$\infty P\infty : \infty P2 = (010) : (2\bar{1}0) = 122 \quad 11$	122 11	121 51	4
$\infty P' : \infty P2' = (110) : (210) = 159 \quad 16$	159 16	159 52	2
$\infty P\infty : \frac{1}{2}P\infty' = (010) : (012) = 114 \quad 10$	114 10	114 35	5
$\infty P\infty : 0P = (010) : (001) = 87 \quad 25$	87 25	87 3	3
$(\infty P\infty) : \frac{1}{2}P\infty = (0\bar{1}0) : (0\bar{1}2) = 118 \quad 18$	118 18	118 4	5
$0P : \frac{1}{2}P\infty' = (001) : (012) = 153 \quad 15$	153 15	153 23	5
$0P : \frac{1}{2}P\infty = (001) : (0\bar{1}2) = 154 \quad 17$	154 17	154 32	4
$\frac{1}{2}P\infty : \frac{1}{2}P\infty' = (0\bar{1}2) : (012) = 127 \quad 32$	127 32	127 39	2
$\infty P\infty : 0P = (100) : (001) = 104 \quad 33$	104 33	104 29	4
$\infty P\infty : +P\infty = (100) : (10\bar{1}) = 128 \quad 51$	128 51	128 52	2
$(0P) : +P\infty = (00\bar{1}) : (10\bar{1}) = 126 \quad 56$	126 56	126 40	2
$(\infty P\infty) : +P\infty = (0\bar{1}0) : (10\bar{1}) = 94 \quad 32$	94 32	95 2	6
$+P\infty : +P' = (10\bar{1}) : (11\bar{1}) = 139 \quad 41$	139 41	139 38	3
$\infty P\infty : +P' = (010) : (11\bar{1}) = 125 \quad 47$	125 47	125 30	3
$\infty P' : +P' = (110) : (11\bar{1}) = 139 \quad 32$	139 32	139 29	2
$\frac{1}{2}P\infty' : \infty P' = (012) : (110) = 115 \quad 50$	115 50	115 50	4
$\frac{1}{2}P\infty : (+P\infty) = (012) : (\bar{1}01) = 125 \quad 46$	125 46	125 33	1

The crystals are not uncommonly twinned in such a manner that the brachydomes of the second crystal fall in the same zone as the prismatic faces of the first, and conversely, and the brachypinacoids of the two individuals are parallel: hence the twin axis is the bisectrix of the axial angle β (Fig. 2).

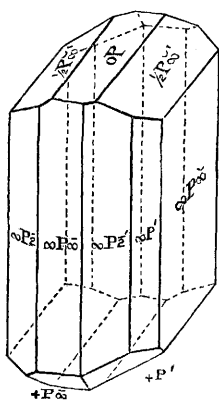


FIG. 1

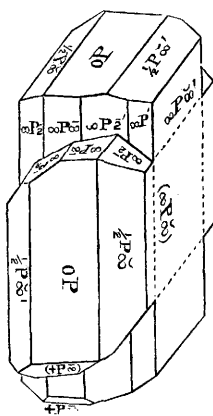


FIG. 2.

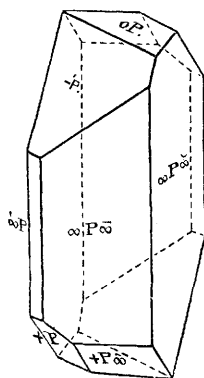


FIG. 3.

II. *Red Salt*.—The analyses of this salt gave the following results:—

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0.2880 gram lost 0.0942 on ignition; 0.3155 substance gave 0.1902 V_2O_5 = 59.73 V_2O_5 p. c.; this was fused with acid potassium sulphate, the fused mass dissolved in dilute sulphuric acid, and the solution after reduction with sodium sulphite and boiling was reoxidised with potassium permanganate solution (1 c.c. = 0.00611 V_2O_5), 30.75 c.c. were used, giving p. c. V_2O_5 = 59.55; mean, 59.64. 0.3375 gram substance lost 0.1091 gram on ignition, the residue fused with acid potassium sulphate and treated as above required 33.3 c.c. potassium permanganate solution.

3MgO.5V ₂ O ₅ .28H ₂ O.		Found.		Mean.
V ₂ O ₅	59.40	59.64	60.30	59.97
MgO	7.82	—	—	7.52 (by diff.)
H ₂ O	32.78	32.73	32.29	32.51

This red salt has, therefore, the same composition as the brown salt, and, like the latter, it also belongs to the triclinic system, but no relation between the two sets of forms is evident; the sp. gr. of the "brown salt" at 18° C., taken in benzene, was found to be 2.199, and that of the "red salt" 2.167; both forms are perfectly stable in the air.

The type of the red crystals is short prismatic, through predominance of the vertical pinacoids. Faces very lustrous, and, excepting the brachypinacoid, which is often bent, very well formed; none of the faces are striated. The occurring forms are $\infty P\infty.\infty P\infty.$ — $P.\infty P.$ + $P.0P.$ + $P\infty$ (Fig. 3). $a : b : c = 1.000 : 1.261 : 0.8525$, and the inclinations of the axes in the upper right octant are $\alpha = 93^\circ 35'$; $\beta = 101^\circ 30'$; $\gamma = 166^\circ 55'$; the interfacial angles are:—

	Calculated.	Found.	No. of observations.
$0P : \infty P\infty = (001) : (100) = 103^\circ 10'$	103° 10'	103° 10'	1
$+P\infty : \infty P\infty = (10\bar{1}) : (100) = 124 \ 11$	124 11	124 7	5
$+P\infty : (0P) = (10\bar{1}) : (00\bar{1}) = 132 \ 39$	132 39	132 38	1
$\infty P\infty : \infty P\infty = (100) : (010) = 108 \ 4$	108 4	108 13	5
$\infty P : (\infty P\infty) = (1\bar{1}0) : (010) = 116 \ 14$	116 14	116 16	3
$\infty P : \infty P\infty = (1\bar{1}0) : (100) = 135 \ 42$	135 42	136 5	2
$\infty P : -P = (1\bar{1}0) : (1\bar{1}1) = 136 \ 58$	136 58	136 58	3
$-P : 0P = (1\bar{1}1) : (001) = 139 \ 58$	139 58	139 54	1
$+P : 0P = (1\bar{1}1) : (00\bar{1}) = 133 \ 28$	133 28	133 3	2
$-P : (+P) = (1\bar{1}1) : (1\bar{1}1) = 93 \ 26$	93 26	93 24	2
$+P\infty : \infty P\infty = (10\bar{1}) : (010) = 97 \ 11$	97 11	97 7	3
$+P\infty : +P = (10\bar{1}) : (1\bar{1}1) = 147 \ 47$	147 47	147 44	2
$P : (+P\infty) = (1\bar{1}1) : (10\bar{1}) = 100 \ 29$	100 29	100 28	1
$(\infty P\infty) : +P = (010) : (1\bar{1}1) = 101 \ 26$	101 26	101 4	2
$\infty P\infty : +P = (100) : (1\bar{1}1) = 128 \ 20$	128 20	128 20	2
$\infty P\infty : -P = (100) : (1\bar{1}1) = 110 \ 16$	110 16	110 6	1

These observations show that the salt $3MgO.5V_2O_5.28H_2O$ is dimorphous; no other corresponding vanadate appears to be known.