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Studies on Rhenium Oxides

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The existence of the rhenium oxides ReO_3 and ReO_2 (MoO_2 type) has been confirmed. When rhenium metal and rhenium trioxide are heated together at 800° C only one intermediary phase forms, *viz.* an orthorhombic modification of the dioxide, which is the stable form of ReO_2 in the temperature interval 300° — 1 050° C.

The structure of orthorhombic ReO_2 has been studied by X-ray methods. The metal atom positions have been determined and a probable oxygen atom arrangement is proposed. The structure contains zigzag strings of ReO_6 octahedra joined by edges, the strings being mutually connected by octahedra sharing corners. The short Re-Re distance within the strings suggests the existence of covalent bonds between the metal atoms.

Rhenium trioxide was the first oxide of this metal to be studied by X-ray methods. Thus Meisel [1] found the crystal structure of this compound to be a cubic arrangement of ReO_6 octahedra joined by sharing corners (ReO_3-type structure). Rhenium dioxide, prepared by heating ammonium perrhenate at 500° C *in vacuo*, was investigated by Zachariasen [2], who was able to assign to this phase the MoO_2-structure type. Preliminary structural data on rhenium(VII) oxide have been reported by Wilhelmi [3].

The structural similarity between rhenium dioxide and wolfram dioxide (MoO_2 type) and between rhenium trioxide and wolfram trioxide (distorted ReO_3 type) made it of interest to find out if there exist intermediate oxides of rhenium as is the case with wolfram [4].

PHASE ANALYSIS

Starting materials were rhenium metal powder (Mackay, 99.9 % pure), rhenium trioxide and dirhenium heptoxide prepared from the metal according to Ref.[5] and ammonium perrhenate obtained by treating the latter oxide with ammonia.

Mixtures of rhenium metal and trioxide of gross compositions ranging from $ReO_{1.5}$ to $ReO_{2.5}$ were sealed in evacuated silica tubes and heated for a day at 300° C and then a day at 800° C. The results are summarized in Table 1.

Table 1. Results of the phase analysis.

Composition of the preparation	Appearance of the preparation	Evidence of X-ray powder pattern
Re	Dark, greyish powder	Re
$ReO_{1.50}$	» » »	X + Re
$ReO_{1.93}$	» » »	X + (Re)
$ReO_{2.00}$	» » »	X
$ReO_{2.14}$	» » » + small red grains	X + ReO_3
$ReO_{2.50}$	» » » »	X + ReO_3
ReO_3	Red powder	ReO_3

The only rhenium oxides that form under the conditions applied are the trioxide and the phase of composition close to $ReO_{2.0}$. The powder diagram of the latter is not in agreement with a MoO_2-type structure (*cf.* Table 2).

The powder patterns showed no displacements of the lines for samples of various compositions, which indicates that the ranges of homogeneity are narrow. The following unit cell dimensions were obtained *:

Re (hexagonal) $a = 2.762 \pm 0.001$ Å, $c = 4.457 \pm 0.001$ Å,
ReO_3 (cubic) $a = 3.7510 \pm 0.0005$ Å,

and for the new phase, the powder pattern of which could be indexed with an orthorhombic unit cell

$a = 4.8094 \pm 0.0005$ Å, $b = 5.6433 \pm 0.0005$ Å, $c = 4.6007 \pm 0.0005$ Å.

The density calculated for a cell content of four formula units of ReO_2 is 11.61 in excellent agreement with the density of 11.4 measured by Lehrer (in Biltz [7]) for a sample giving $ReO_{2.01}$ on analysis and prepared from rhenium and rhenium(VII) oxide at 600—650° C.

Rhenium dioxide evidently is dimorphic, forming a monoclinic and also an orthorhombic modification. Samples of the two phases, the former prepared according to Zachariasen [2], were sealed in evacuated silica tubes and heat-treated at various temperatures. While the orthorhombic form did not change within the interval 300—1 050° C, the monoclinic modification transformed into the former which is evidently the stable one in this region. At 300° C this reaction was almost completed in 3 days.

STRUCTURE OF ORTHORHOMBIC RHENIUM DIOXIDE

By heating rhenium dioxide at 1 050° C for a few weeks it was possible to grow crystals suitable for single crystal X-ray investigations. Rotation and Weissenberg photographs were taken with CuK radiation with [101] as rota-

* The X-ray powder data reported in this paper were obtained with a Guinier focusing camera of 80 mm diameter with strictly monochromatized CuKa_1 radiation. The temperature was about 20° C. Potassium chloride (Analar, British Drug Houses, $a = 6.2919$ Å) [6] was added to the specimens as an internal standard. Photographs of samples without admixture were used to reveal superpositions of lines.

Table 2. Powder photograph of orthorhombic rhenium dioxide. Cu$K\alpha_1$ radiation.

I_{obs}	$\sin^2\Theta_{obs}$	*hkl*	$\sin^2\Theta_{calc}$	$p\|F\|^2_{calc} \cdot 10^{-3}$
v st	0.04430	110	0.04428	170
v st	0.07236	111	0.07231	210
v w	0.07438	020	0.07452	3
st	0.10259	021	0.10255	180
		200	0.10260	80
st	0.11216	002	0.11212	160
v w	0.12832	121	0.12820	6
v w	0.13789	102	0.13777	5
—	—	211	0.14926	0
st	0.15651	112	0.15640	250
v w	0.17717	220	0.17712	8
v w	0.18644	022	0.18664	7
w	0.19331	130	0.19332	45
v st	0.20517	221	0.20515	440
—	—	122	0.21229	0
st	0.21466	202	0.21472	180
st	0.22137	131	0.22135	280
—	—	212	0.23335	0
m	0.24945	310	0.24947	100
m	0.27751	311	0.27750	140
v w	0.28930	222	0.28924	12
m	0.29649	113	0.29655	130
w	0.29798	040	0.29807	90
		231	0.29830	0
w	0.30539	132	0.30544	70
m	0.32669	041	0.32610	25
		023	0.32679	170
—	—	321	0.33339	2
—	—	302	0.34296	2
—	—	141	0.35175	0.3
—	—	123	0.35244	2
m	0.36159	312	0.36159	170
—	—	213	0.37350	0
—	—	232	0.38239	0
v w	0.39853	330	0.39851	30
w	0.40073	240	0.40067	90
m	0.41025	042	0.41019	120
		400	0.41039	80
—	—	322	0.41748	0.1
m	0.42638	331	0.42654	200
m	0.42903	241	0.42870	30
		223	0.42939	210
m	0.44562	133	0.44559	200
w	0.44854	004	0.44848	50

tion axis. The intensities were estimated visually and the intensity scales of the various photographs were correlated by means of reflexions, equivalent on account of symmetry relations. The structure amplitudes were calculated using the nomograms given by Lu [8].

The following reflexions were found to be systematically missing:

$$\begin{array}{lll} 0kl & \text{for } k & = 2n + 1 \\ h0l & \text{for } l & = 2n + 1 \\ hk0 & \text{for } h + k & = 2n + 1 \end{array}$$

This is characteristic of the space group *Pbcn* (No. 60).

The linear Harker sections suggested by this symmetry were calculated and found to have the following appearance:

$$\begin{array}{lll} \mathrm{P}(u\tfrac{1}{2}0): & \text{maximum at } u & = \tfrac{1}{2} \\ \mathrm{P}(0v\tfrac{1}{2}): & \text{maximum at } v & = 0.220 \\ \mathrm{P}(\tfrac{1}{2}\tfrac{1}{2}w): & \text{maximum at } w & = 0 \end{array}$$

This locates the rhenium atoms at the point position 4(*c*) with $y = v/2 = 0.110$, which corresponds to an arrangement of zigzag chains of metal atoms running parallel to the *c* axis. The distance between rhenium atoms within the chain is 2.61 Å, while adjacent rhenium atoms of different chains are 3.68 and 3.71 Å apart.

It is of interest to compare the interatomic distances thus obtained with those present in monoclinic rhenium dioxide, the atomic parameters of which, however, have not been determined. The close similarity between the unit cell dimensions of this phase and molybdenum dioxide seem to justify the assumption that the parameter values of these compounds are approximately the same. This leads to Re-Re distances within the straight chains of 2.48 and 3.08 Å and Re-Re distances between neighbouring chains of 3.7 Å.

The similar metal-metal distances present in the two forms of rhenium dioxide suggest that the arrangement of the oxygen atoms around the rhenium atoms in the orthorhombic modification is essentially the same as in the MoO_2-type form, *viz.* in ReO_6 octahedra with shared edges corresponding to the shorter rhenium-rhenium distances and shared corners corresponding to the longer ones. These conditions are fullfilled by the following structure:

Space group: *Pbcn* (No. 60)

4 Re in 4(*c*): $0,y,\tfrac{1}{4}$; $0,\bar{y},\tfrac{3}{4}$; $\tfrac{1}{2},\tfrac{1}{2}+y,\tfrac{1}{4}$; $\tfrac{1}{2},\tfrac{1}{2}-y,\tfrac{3}{4}$. $y = 0.110$

8 O in 8(*d*): x,y,z; $\tfrac{1}{2}-x,\tfrac{1}{2}-y,\tfrac{1}{2}+z$; $\tfrac{1}{2}+x,\tfrac{1}{2}-y,\bar{z}$; $\bar{x},y,\tfrac{1}{2}-z$; $\bar{x},\bar{y},\bar{z}$; $\tfrac{1}{2}+x,\tfrac{1}{2}+y,\tfrac{1}{2}-z$; $\tfrac{1}{2}-x,\tfrac{1}{2}+y,z$; $x,\bar{y},\tfrac{1}{2}+z$. $x = 0.25$, $y = 0.36$, $z = 0.125$.

The interatomic distances have reasonable values throughout, *viz.* Re—O 1.95 and 2.1 Å and O—O 2.6—3.1 Å. The distance of 3.1 Å is that of edges shared by two ReO_6 octahedra.

The influence of the oxygen atoms on the intensities of the X-ray reflexions is very low compared with that of the rhenium atoms. However, for reflexions *hkl* with $h+k = 2n+1$, the contributions of the metal atoms cancel out. The proposed oxygen arrangement gives fair agreement between calculated and observed intensities for this type of reflexions (*cf.* Table 2). As these reflexions are very weak and rather few, it is not, however, possible to improve the oxygen parameters from the experimental data.

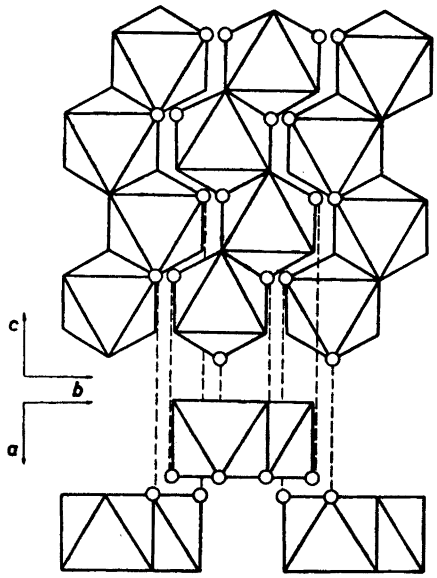

Fig. 1. The coupling of the ReO_6 octahedra of orthorhombic rhenium dioxide viewed along [100] and [001]. The strings of octahedra have been separated in order to reveal superimposed corners and edges. Corners shared by the strings are indicated by rings.

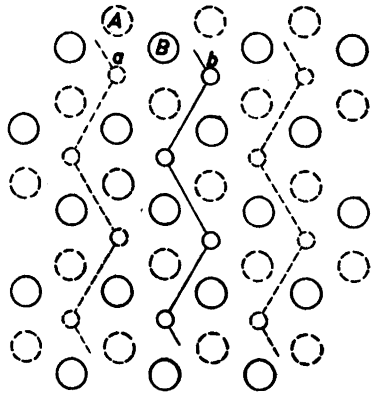

Fig. 2. The idealized structure of orthorhombic rhenium dioxide represented as hexagonal close-packing of the oxygen atoms (large circles). The rhenium atoms (small circles) are situated in octahedral holes. The sequence of the atoms normal to the plane of the figure is AaBbA.

The structure thus derived (*cf.* Fig. 1) has features in common with both the brookite and the rutile types. Thus both rhenium dioxide and brookite contain staggered strings formed by metal-oxygen octahedra having edges in common. While the strings of brookite are mutually connected by octahedra sharing edges and corners, those of rhenium dioxide are exclusively joined by corners as are the straight strings of rutile. No representative of this structure type seems to have been known before. However, as pointed out in a preliminary note [9] Pauling and Sturdivant [10] in connection with the determination of the brookite structure discussed a hypothetic structure, which is actually the same as the one now found for orthorhombic rhenium dioxide. The columbite structure is a superstructure of this type [11].

It is also possible to describe the structure as an hexagonal closepacking of oxygen atoms with rhenium atoms occupying certain of the octahedral interstices as illustrated in Fig. 2.

The pairwise arrangement of the metal atoms within the strings of the MoO_2 structure type has been ascribed to the existence of a homopolar bond between the metal atoms of the doublet [12]. In orthorhombic rhenium dioxide, the rhenium atoms within the staggered strings are uniformly distributed and at intervals (2.61 Å) which are longer than the short distance present in

Table 3. Metal-metal bond distances in some dioxides.

Compound	Structure type	Number of valence electrons available per metal-metal bond	Metal-metal distance Å
TiO_2	rutile	0	2.959
VO_2	MoO_2	2	2.65
ReO_2	ReO_2 (orthorhombic)	3	2.61
MoO_2	MoO_2	4	2.50
WO_2	MoO_2	4	2.49
TcO_2	MoO_2	6	(2.48)
ReO_2	MoO_2	6	(2.49)

the monoclinic rhenium dioxide (2.48 Å). However, if no intermetallic bond is present, the repulsion between the highly charged metal atoms would lead to metal-metal distances of octahedra sharing edges considerably longer than the ideal geometrical value (the normal oxygen-oxygen distance). This effect has actually been observed in several molybdenum and wolfram oxides, where distances of about 3.25 Å frequently occur [4]. Bonds are thus likely to be present also between the metal atoms of the strings of orthorhombic rhenium dioxide. Considering the fact that in this compound every metal atom is bound to two neighbours and the number of valence electrons per bond is thus only half that present in the MoO_2-type rhenium dioxide, the bond distance in the former compound fits in nicely in the qualitative relation between bond distance and number of valence electrons pointed out in a previous communication [13] (*cf.* Table 3).

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REFERENCES

1. Meisel, K. *Z. anorg. Chem.* **217** (1932) 121.
2. Zachariasen, W. H. *A. C. A. Program and Abstracts of Winter Meeting* (1951) F-4. *(Also private communication.)*
3. Wilhelmi, K.-A. *Acta Chem. Scand.* **8** (1954) 693.
4. Magnéli, A. *Nova Acta Regiae Soc. Sci. Upsaliensis* [4] **14** (1950) No. 8.
5. *Inorganic Syntheses, Vol. III,* New York-Toronto-London 1950.
6. Hambling, P. G. *Acta Cryst.* **6** (1953) 98.
7. Biltz, W. *Z. anorg. Chem.* **214** (1933) 225.
8. Lu, C. S. *Rev. Sci. Instr.* **14** (1943) 331.
9. Magnéli, A. *Acta Cryst.* **9** (1956) 1038.
10. Pauling, L. and Sturdivant, J. H. *Z. Krist.* **68** (1928) 239.
11. Sturdivant, J. H. *Z. Krist.* **75** (1930) 88.
12. Pauling, L. *Chem. Eng. News* **25** (1947) 2970.
13. Magnéli, A. and Andersson, G. *Acta Chem. Scand.* **9** (1955) 1378.

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