217. *The Structures of Inorganic Oxy-acids : The Crystal Structure of Selenic Acid.*

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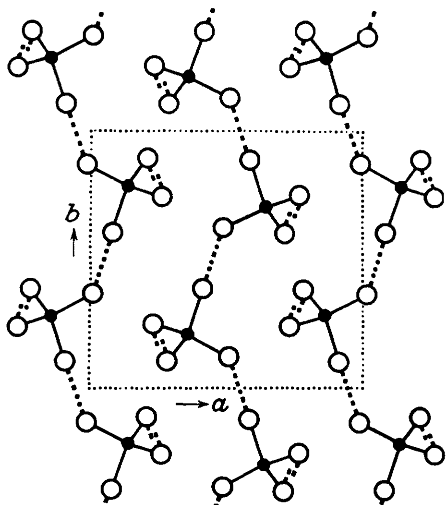
The crystal structure of anhydrous selenic acid, H_2SeO_4, has been determined. The crystals are orthorhombic : $a = 8{\cdot}52$, $b = 8{\cdot}17$, $c = 4{\cdot}61$ A., with 4 molecules in the unit cell. The space-group was taken as $P2_12_12_1$ though three very weak reflexions (700, 090, and 001) were observed on heavily-exposed photographs. The structure consists of tetrahedral SeO_4 groups (mean Se–O, 1·61 A.), each joined by four O–H–O bonds (lengths 2·61 and 2·68 A.) to four neighbouring groups to form puckered layers parallel to (100).

IN describing the crystal structure of the orthorhombic form of selenious acid, H_2SeO_3 (*J.*, 1949, 1282), we remarked that very little is known of the structures of crystalline oxy-acids H_mXO_n, the only other structure which had been determined being that of α-iodic acid (Rogers and Helmholz, *J. Amer. Chem. Soc.*, 1941, **63**, 278). When these acids are classified according to the value of the H : O ratio, $r_{H:O}$, they fall into four classes : (*a*), $r_{H:O} < \frac{1}{2}$, *e.g.*, HIO_3, $H_2S_2O_7$;

FIG. 1.

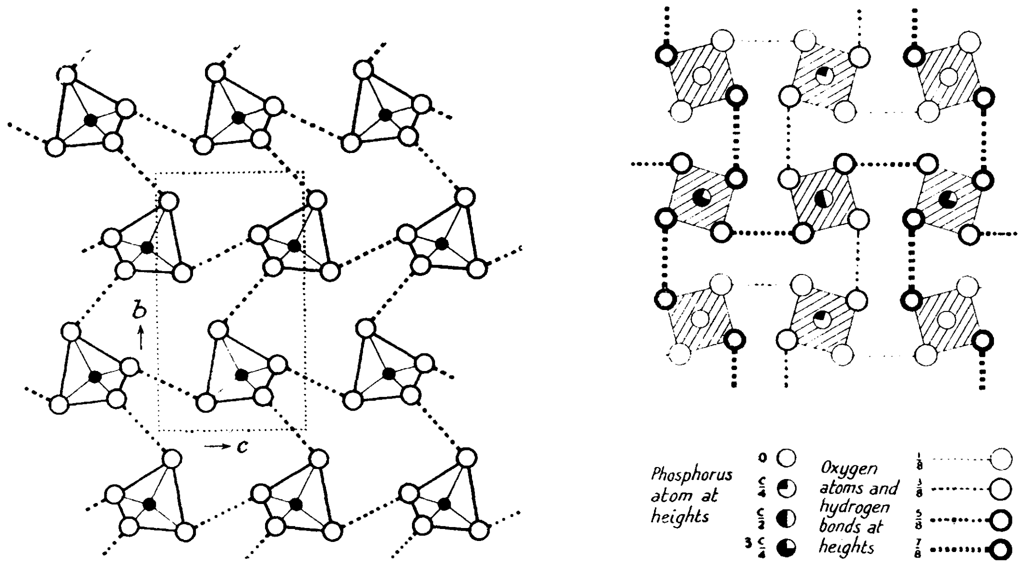


The crystal structure of selenic acid projected on (001). *The small black circles represent* Se *atoms. The puckered layers of* SeO_4 *groups linked by* O–H–O *bonds (heavy broken lines) are perpendicular to the plane of the paper. The pairs of short* O–H–O *bonds form links to oxygen atoms of* SeO_4 *groups situated above and below those shown.*

(*b*), $r_{H:O} = \frac{1}{2}$, *e.g.*, H_2SO_4, H_2SeO_4; (*c*) $1 > r_{H:O} > \frac{1}{2}$, *e.g.*, H_2SeO_3, H_3PO_4, and (*d*) $r_{H:O} = 1$, *e.g.*, H_3BO_3, H_6TeO_6. Since the hydrogen atoms link up the XO_n groups in these crystals by means of O–H–O bonds, as in " acid-salts " such as $NaHCO_3$ and KH_2PO_4, the ratio $r_{H:O}$ determines the type of hydrogen-bonded network. If $r_{H:O} = \frac{1}{2}$ there can be one O–H–O bond to each oxygen atom, as is found in crystals of KH_2PO_4 and $(NH_4)_2H_3IO_6$, and if $r_{H:O} = 1$ there can be two O–H–O bonds to each oxygen atom, as in crystalline H_3BO_3. In KH_2PO_4 the hydrogen-bonded network $[H_2PO_4]_n^{n-}$ is a three-dimensional framework, in the interstices of which the K^+ ions are situated. It was pointed out in the earlier paper that the structure of crystalline H_2SO_4 may be closely related to this $[H_2PO_4]_n^{n-}$ framework in KH_2PO_4 and isomorphous salts.

As an example of an oxy-acid H_2XO_4, selenic acid was chosen in preference to sulphuric acid, with which it is likely to be isomorphous, since it is solid at room temperature. Owing to their relatively high scattering power for *X*-rays, the selenium atoms can be readily located, but for the same reason the determination of the precise positions of the oxygen atoms is rendered more difficult. More accurate hydrogen-bond lengths could probably be obtained from a study of crystalline sulphuric acid. However, the crystal structure of anhydrous selenic acid has now been determined with sufficient accuracy to indicate without ambiguity the nature of the hydrogen-bonded network. Each tetrahedral SeO_4 group is linked by four O–H–O bonds to four neighbouring groups to form puckered layers which are viewed end-on in Fig. 1. (It is interesting that the orthorhombic form of selenious acid also has a layer structure.) A projection of the crystal structure of selenic acid normal to the plane of the layers is very similar to that of the $[H_2PO_4]_n^{n-}$ framework of KH_2PO_4, as is seen from Fig. 2. In the latter crystal,

FIG. 2.



(*a*) *Projection on* (100) *of one layer of the crystal structure of selenic acid.*

(*b*) *Projection on* (001) *of the structure of* KH_2PO_4.

however, this hydrogen-bonded framework extends indefinitely in three dimensions, in contrast to the layer structure of H_2SeO_4.

The Crystal Structure of Selenic Acid.

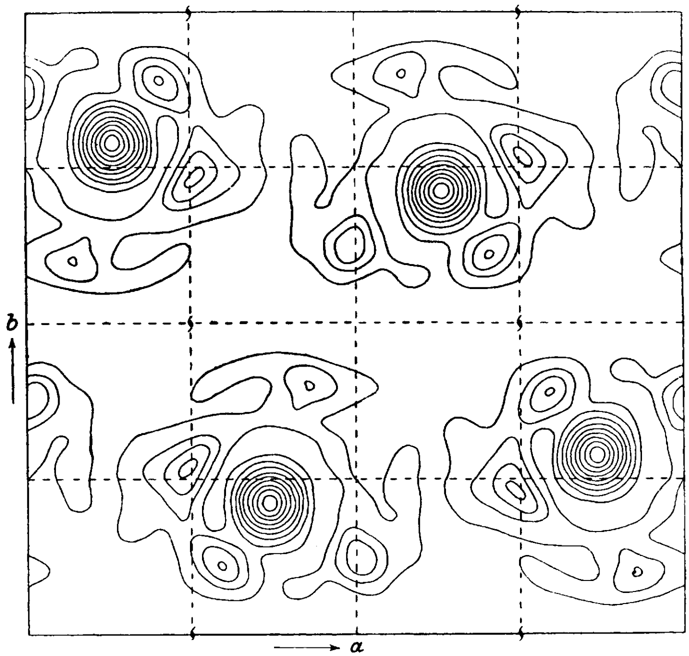
An aqueous solution of selenic acid was prepared by treating an aqueous suspension of silver selenite with the calculated quantity of bromine and filtering off the silver bromide. The anhydrous acid was obtained by distilling off the water under reduced pressure, the temperature being taken finally to 150°. It was not possible to grow suitable crystals from the molten anhydrous acid, and the method adopted was to allow a little moisture to enter the stoppered tube which was then warmed slightly. On cooling, needles elongated along the *c* axis were obtained. For the *X*-ray work needles (or portions of needles) were quickly transferred to thin-walled glass capillaries previously sealed at one end, the other end being sealed when the crystal had been suitably oriented.

Unit Cell and Space-group.—Oscillation photographs taken with the crystal rotating about the principal axes showed that the crystals are orthorhombic. Zero layer-line Weissenberg photographs were taken about the *a* and *b* axes, and zero and first layer-line photographs about the *c* axis, all with Cu-K_α radiation. The cell dimensions are: $a = 8{\cdot}52 \pm 0{\cdot}02$ A., $b = 8{\cdot}17 \pm 0{\cdot}02$ A., and $c = 4{\cdot}61 \pm 0{\cdot}01$ A., and this cell contains 4 molecules of H_2SeO_4 [density: calc., 3·00 g./c.c.; obs. (Landolt–Börnstein), 2·95 g./c.c.]. The systematic absences are the odd orders of *h*00, 0*k*0, and 00*l*, except that very weak reflexions 700, 090, and 001 were observed on photographs of very long exposure. These have been neglected, and the space-group taken as $P2_12_12$. Intensities were estimated visually by using the multiple film method and comparison with a time-calibrated scale of exposures, and they were converted into structure amplitudes by applying the appropriate correction factors.

Determination of Structure.—Apart from the hydrogen atoms (which cannot be located directly from the *X*-ray data), there are five sets of atoms (Se, O_1, O_2, O_3, and O_4) in four-fold general positions *xyz*, etc. The co-ordinates of the selenium atoms were determined first.

(a) *Selenium co-ordinates.* A close-packed arrangement of SeO_4 groups was considered probable, and would require *x* and *y* co-ordinates for Se of approximately $\frac{3}{8}$ and $\frac{1}{4}$, respectively. The intensities of the *h*00 and 0*k*0 reflexions were consistent with these values. The approximate value of z_{Se} and more accurate values of x_{Se} and y_{Se} were obtained from F^2-projections on (001) and (010). From the structure amplitudes of high-order reflexions and later Fourier projections the best Se co-ordinates were found to be: $x_{Se} = 0{\cdot}369$, $y_{Se} = 0{\cdot}212$, and $z_{Se} = 0{\cdot}563$.

FIG. 3.



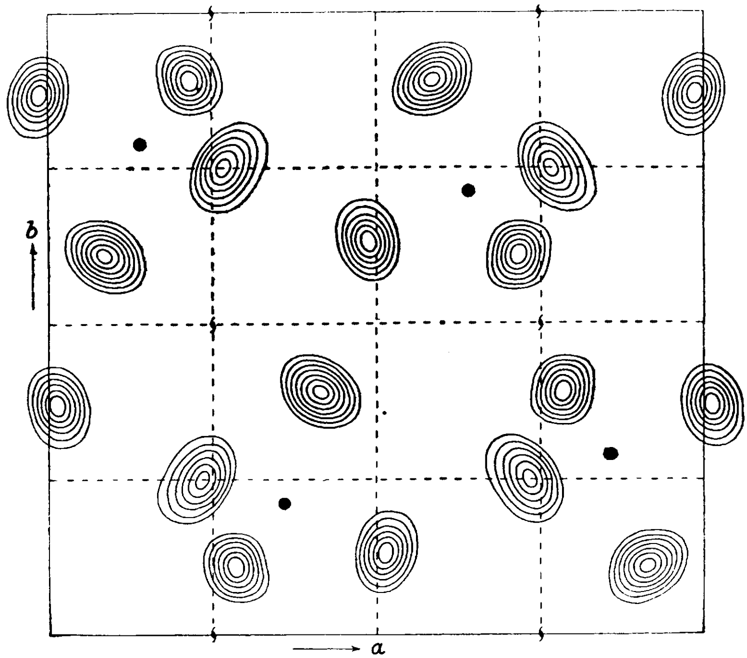
Electron-density projected on (001) *showing selenium atoms surrounded by four oxygen atoms.*

(b) *Oxygen* x *and* y *co-ordinates.* The structure was first projected along the *c* axis because (1) overlapping of atoms is less likely owing to the short length of this axis, and (2) errors due to absorption are smaller for (*hk*0) than for (*h*0*l*) or (0*kl*) reflexions when the crystals are needles elongated along the *c* axis. The origin for *c*-axis projections was taken at the point ($\frac{1}{4}$, 0, 0) about which the projection is centro-symmetrical. The signs of 57 structure amplitudes were determined, the selenium co-ordinates given above being used, and these terms were used for the first projection. Successive refinements were carried out with an artificial temperature factor, $e^{-2[(\sin\theta)/\lambda]^2}$ applied to $F_{obs.}$ to reduce errors due to the slow convergence of the series. The final projection of this set is shown in Fig. 3. The resolution and regularity of the oxygen peaks was not satisfactory, and a further synthesis was therefore computed by using the actual values of $F_{obs.}$ including values of F_{Se} for planes outside the range of the photograph having spacings down to 0·5 A. This appeared reasonable because the Se co-ordinates are known fairly accurately and because the oxygen scattering is negligible at high angles. The diffraction effects around the Se atoms which can be seen in Fig. 3 were considerably reduced in this projection, but the contours of the oxygen peaks were still rather irregular.

The final *x* and *y* co-ordinates were derived from projections for which the series was made much more rapidly convergent by using only that part of each observed F_{hk0} which was due to the oxygen atoms. The selenium contributions were calculated using the normal *f*-curve modified by a temperature factor $e^{-0 \cdot 5[(\sin\theta)/\lambda]^2}$ appropriate to this structure and were subtracted (algebraically) from the respective F_{hk0}'s which had been converted approximately into absolute values by comparison with calculated values. The resulting F_{hk0}'s should then correspond to the selenic acid structure from which the Se atoms have been removed. The projection obtained in this way is shown in Fig. 4.

(c) *Oxygen z co-ordinates.* The projections of the structure on (010) and (100) gave only approximate oxygen co-ordinates because of overlapping of the atoms and probably also because of inaccurate intensity data due to absorption. (Crystals used for [*a*] and [*b*] axis photographs were elongated along [*c*]; it was found impossible to cut equidimensional portions of crystals owing to cleavage(s) along the needle direction.) The oxygen *z* co-ordinates obtained from these projections were refined by line syntheses normal to (001), applying an artificial temperature factor $e^{-4[(\sin\theta)/\lambda]^2}$ to the values of $F_{obs.}$. For the calculation of phase angles the *z*

FIG. 4.



Electron-density projection [on (001)] showing oxygen atoms only. The small black circles indicate the positions of the selenium atoms.

co-ordinates of the oxygen atoms were taken as the means of the values obtained from the (010) and (100) projections. The final atomic co-ordinates, expressed as fractions of the cell edges, are :

	x/a.	*y/b.*	*z/c.*		*x/a.*	*y/b.*	*z/c.*		*x/a.*	*y/b.*	*z/c.*
Se	0·369	0·212	0·563	O_2 ...	0·285	0·108	0·321	O_4	0·415	0·390	0·411
O_1	0·513	0·128	0·714	O_3 ...	0·235	0·252	0·808				

The structure amplitudes calculated from these co-ordinates and incorporating a temperature factor $e^{-0 \cdot 5[(\sin\theta)/\lambda]^2}$ are listed in Tables I—III. The atomic *f* curves used were those of the International Tables (Vol. 2, p. 571) for Se and O atoms, the H atoms being neglected. For the *hk*0 reflexions the value of the function $\Sigma(F_{obs.} - F_{calc.})/\Sigma F_{obs.} = 0 \cdot 12$ and, for *hkl* reflexions, 0·16. It has not been calculated separately for *h*0*l* or 0*kl* reflexions for which the values of $F_{obs.}$ are less reliable owing to absorption. Values of $F_{obs.}$ which are seriously reduced owing to absorption are enclosed in parentheses in Tables II and III.

Description of the Structure.—The general nature of the structure has already been mentioned. The distances between oxygen atoms of different SeO_4 groups fall into two groups. Four of the O–O contacts of any SeO_4 groups (two of 2·61 A. and two of 2·68 A.) are much shorter than the rest, which are 2·95 A. or more. The number of these short O–O distances is the number of

TABLE I.

Observed and calculated structure amplitudes (hk0).

[Origin taken at (½, 0, 0.]

	$F_{obs.}$	$F_{calc.}$
020	66	−61
040	10	+10
060	14	−17
080	4	+ 4
0.10.0	17	+19
110	11	+15
120	21	−24
130	25	−26
140	28	+28
150	24	+25
160	23	−21
170	20	−22
180	13	+17
190	13	+17
1.10.0	10	−13
200	13	+10
210	53	−62
220	14	−14
230	20	+25
240	13	+14
250	11	−11
260	6	− 7
270	3	+ 1
280	<3	+ 1
290	14	+15
2.10.0	<2	− 2

	$F_{obs.}$	$F_{calc.}$
310	11	+ 9
320	16	−14
330	12	+10
340	25	+24
350	32	−35
360	28	−28
370	22	+21
380	22	+21
390	8	− 8
3.10.0	10	−10
400	31	−30
410	9	− 3
420	34	+31
430	2	0
440	25	−24
450	<3	+ 3
460	<3	0
470	<3	− 1
480	14	+15
490	4	+ 2

	$F_{obs.}$	$F_{calc.}$
510	14	−10
520	10	−10
530	29	+21
540	21	−21
550	31	−24
560	27	+27
570	25	+22
580	7	− 9
590	17	−17
600	6	− 2
610	42	+38
620	7	+ 5
630	34	−30
640	5	− 3
650	13	+13
660	4	− 5
670	5	+ 3
680	5	+ 4
710	4	+ 4
720	20	+16
730	12	−10
740	27	−20
750	13	+13
760	25	+21
770	8	−10
780	16	−19

	$F_{obs.}$	$F_{calc.}$
800	34	+33
810	10	+ 5
820	30	−28
830	18	−18
840	15	+16
850	9	+ 9
860	3	− 3
870	5	+ 6
910	6	+ 6
920	9	−10
930	16	−14
940	9	+ 8
950	20	+21
960	4	− 6
10.00	9	+ 4
10.10	21	−18
10.20	12	−10
10.30	16	+16
10.40	10	+11

TABLE II.

Observed and calculated structure amplitudes (hkl).

[Origin taken at (0, 0, 0).]

	$F_{obs.}$	$F_{calc.}$	α.
011	43	59	270°
021	15	17	0
031	15	19	90
041	15	15	180
051	8	8	270
061	9	9	0
071	<4	1	90
081	6	8	180
091	11	14	90
0.10.1	6	7	0
101	16	18	90
111	13	17	17
121	19	19	332
131	34	35	201
141	24	25	166
151	27	29	27
161	23	24	5
171	16	19	173
181	14	18	182
191	9	13	3
1.10.1	14	12	15
201	(33)	63	90
211	5	5	218
221	33	45	298
231	10	10	357
241	14	18	79
251	13	13	185
261	9	13	213
271	11	13	13
281	7	6	248
291	7	8	194
2.10.1	20	18	75

	$F_{obs.}$	$F_{calc.}$	α.
301	5	5	90°
311	9	9	168
321	13	10	72
331	22	19	356
341	25	27	215
351	24	24	185
361	21	24	356
371	22	22	13
381	12	15	35
391	15	16	201
3.10.1	9	8	329
401	6	4	270
411	41	43	98
421	14	10	139
431	29	30	273
441	15	11	329
451	17	12	65
461	16	12	181
471	4	2	123
481	15	12	4
491	13	12	261
501	9	8	270
511	15	11	278
521	22	17	152
531	11	9	346
541	28	23	333
551	23	22	173
561	22	22	172
571	14	15	358
581	21	19	7
591	8	9	144

	$F_{obs.}$	$F_{calc.}$	α.
601	30	30	270°
611	15	12	323
621	31	27	81
631	19	16	136
641	19	17	259
651	9	6	318
661	5	2	74
671	8	8	198
681	10	8	100
701	28	25	90
711	15	13	211
721	16	12	245
731	22	18	157
741	12	11	357
751	22	19	350
761	9	13	205
771	23	19	175
781	9	10	30
801	7	3	90
811	26	23	268
821	11	10	318
831	19	19	86
841	10	11	135
851	8	7	247
861	6	6	20
871	5	4	315
901	<4	1	90
911	12	7	59
921	12	13	352
931	10	9	141
941	19	16	179
951	8	8	356
10.01	21	20	90
10.11	9	6	69
10.21	20	19	269
10.31	10	8	284
10.41	12	14	80

TABLE III.

Observed and calculated structure amplitudes (h0l and 0kl).

[For $h0l$ origin is taken at (0, 0, ¼) and for $0kl$, at (0, ¼, 0).]

	$F_{obs.}$	$F_{calc.}$		$F_{obs.}$	$F_{calc.}$		$F_{obs.}$	$F_{calc.}$		$F_{obs.}$	$F_{calc.}$
002	14	−15	004	5	− 1	012	14	+12	014	10	+12
102	10	+ 7	104	22	−31	022	18	+20	024	2	+ 1
202	5	− 4	204	3	+ 2	032	(17)	+23	034	(14)	+20
302	16	+21	304	7	−10	042	(10)	+18	044	(<3)	+ 1
402	(22)	+43	404	4	+ 4	052	(17)	+22	054	(13)	+21
502	(17)	−31	504	(11)	+18	062	2	− 1	064	2	− 1
602	2	− 3	604	(<2)	+ 4	072	24	+20	074	22	+24
702	6	− 7	704	9	+11	082	12	−12			
802	16	−13	804	2	+ 2	092	20	+16	015	10	+12
902	17	+18							025	(9)	−16
10.02	7	+ 7	105	11	+18	013	11	−12	035	(8)	+13
			205	9	−11	023	18	−19	045	13	−16
103	15	−14	305	(10)	−18	033	(13)	−24	055	6	+ 8
203	9	−10	405	(<2)	− 5	043	(14)	−23			
303	22	+32	505	6	− 8	053	(6)	−12			
403	4	− 4				063	19	−12			
503	(8)	+13				073	3	+ 3			
603	(7)	+15				083	25	−24			
703	20	−20				093	3	+ 3			
803	14	− 9									
903	7	− 9									

hydrogen atoms in the crystal and they are therefore regarded as indicating O–H–O bonds. These link each SeO_4 group to four neighbouring groups to form puckered layers parallel to (100), as shown in Figs. 1 and 2. Including the three oxygen atoms of the same SeO_4 group, the numbers of neighbours up to a distance of 3·5 A. are as follows: O_1, 10; O_2, 12; O_3 and O_4, 11.

The interatomic distances and interbond angles within the SeO_4 group are:

Se–O_1	1·57 A.	O_1–O_2	2·66 A.	O_1–Se–O_2	116°
Se–O_2	1·57	O_1–O_3	2·61	O_1–Se–O_3	109
Se–O_3	1·64	O_1–O_4	2·68	O_1–Se–O_4	112
Se–O_4	1·66	O_2–O_3	2·66	O_2–Se–O_3	112
		O_2–O_4	2·59	O_2–Se–O_4	106
Mean	1·61	O_3–O_4	2·64	O_3–Se–O_4	106
		Mean	2·64	Mean	110°

The Se–O distance of 1·61 A. in SeO_4^{2-} may be compared with the values 1·73 A. and 1·78 A. in crystalline SeO_2 (McCullough, *J. Amer. Chem. Soc.*, 1937, **59**, 789), 1·72 A. in the orthorhombic form of H_2SeO_3 (Wells and Bailey, *loc. cit.*), and 1·61 A. in SeO_2 vapour (Palmer, *J. Amer. Chem. Soc.*, 1938, **60**, 1309). It is interesting that the bond length Se–O is the same in the SeO_2 molecule as in the SeO_4^{2-} ion of H_2SeO_4, whereas for 3-covalent Se in crystalline SeO_2 and H_2SeO_3 the distance is appreciably greater. In the case of sulphur the S–O distance is the same in the SO_2 molecule as in SO_4^{2-} (close to 1·45 A.) but also the same for 3-covalent sulphur in the $S_2O_5^{2-}$ ion (1·45 A.) (Zachariasen, *Physical Rev.*, 1932, **40**, 923). The value, 1·39 A., found in the SO_3^{2-} ion in Na_2SO_3 (Zachariasen and Buckley, *ibid.*, 1931, **37**, 1295) may be rather less accurate than the value from the carefully determined $K_2S_2O_5$ structure. This difference between sulphur and selenium is not unexpected, for there are many differences between the oxygen chemistries of these two elements; for example, whereas sulphur and tellurium form trioxides, selenium does not, and it is interesting that the next element in the same row of the Periodic Table, bromine, also does not form many types of oxy-compound formed by chlorine and iodine.

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