Compounds Formed between Hydrogen Peroxide and Sulphates, Selenates, and Tellurates in Aqueous Solution.

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The following compounds have been prepared by crystallisation from or by precipitation (on addition of ethyl alcohol) from aqueous solutions of hydrogen peroxide and the corresponding sulphate or selenate: $Na_2SO_4,0{\cdot}5H_2O_2,H_2O$; $(NH_4)_2SO_4,H_2O_2$; $Na_2SeO_4,0{\cdot}5H_2O_2,H_2O$; $(NH_4)_2SeO_4,H_2O_2$; and K_2SeO_4,H_2O_2—of which, the selenates are new. The formation of all these compounds and also of Na_2SO_4,H_2O_2 has been confirmed by phase-diagram studies at 20°. No evidence has been found for the existence of analogous lithium, rubidium, or cæsium compounds. The compounds reported are probably perhydrates.

The following compounds have been prepared by precipitation from aqueous solutions containing tellurates and hydrogen peroxide on addition of ethyl alcohol: $LiH_4TeO_{7\cdot5},2H_2O$; $LiH_4TeO_7,2H_2O$; $Na_2H_4TeO_8,0{\cdot}5H_2O$; $Na_2H_4TeO_{7\cdot5},0{\cdot}5H_2O$; $K_2H_4TeO_{8\cdot5}$; and $K_2H_4TeO_8$. These may be peroxytellurates.

ATTEMPTS have been made by various workers to prepare peroxyselenic acid and the corresponding alkali salts. Brown reported the formation of potassium peroxyselenates by an electrolytic method (*J. Amer. Chem. Soc.*, 1901, **23**, 358), but Dennis and Koller (*ibid.*, 1919, **41**, 964) were unable to confirm this. Worsley and Baker (*J.*, 1923, **123**, 2874) stated that peroxyselenic acid was formed by the action of hydrogen peroxide on either selenium trioxide or chloroselenic acid which they prepared from the trioxide. Since other workers have failed to repeat the preparation of selenium trioxide reported by these authors, it seems unlikely that a preparation of peroxyselenate was in fact achieved.

The preparation of potassium peroxyselenates by electrolytic methods under conditions most favourable to the formation of peroxy-compounds (*e.g.*, high current density, low temperature, presence of fluoride, etc.) was tried, but without success. The amount of oxygen evolved at the anode indicated that the whole of the current was utilised for the decomposition of water.

Compounds containing active oxygen and selenate have been prepared, however, and these seem to be similar to the compounds $Na_2SO_4,H_2O,\frac{1}{2}H_2O_2$ and $(NH_4)_2SO_4,H_2O_2$ reported by Willstätter (*Ber.*, 1903, **36**, 1828) whose work has been confirmed in the present studies which have included some phase-diagram studies. Tellurates containing active oxygen have also been obtained and some, at least, of these appear to be true peroxytellurates.

EXPERIMENTAL

Preparation of Compounds containing Active Oxygen.—Three methods of preparation have been used:

(1) A solution of the appropriate sulphate or selenate in 30% hydrogen peroxide was allowed to crystallise over concentrated sulphuric acid in a desiccator.

(2) A solution of selenate or tellurate in 30% hydrogen peroxide was treated with alcohol to cause precipitation.

(3) A solution of alkali-metal tellurate (2 g.) in 80% hydrogen peroxide (15—20 c.c.) was treated with excess of alcohol and set aside (an oil was obtained in the case of potassium and sodium tellurates, whereas lithium tellurate yielded a fine precipitate). The supernatant clear liquid was decanted, fresh alcohol was added, and the whole set aside until (in the case of the potassium and sodium compounds) a solid material was obtained (usually after 12—18 hr.). The solid was powdered, suspended in alcohol, filtered, washed repeatedly first with alcohol, then with ether until the filtrate was free from hydrogen peroxide, and dried in a vacuum over phosphoric oxide.

Analysis.—The active oxygen was determined by titrating the acidified solution with standard potassium permanganate.

Ammonia (in the ammonium compounds) was determined by distillation with sodium hydroxide: ammonia evolved was absorbed in standard sulphuric acid (known volume) and estimated by back-titration. For the estimation of selenium the method recommended by Dennis and Koller (*loc. cit.*) was used: selenium is precipitated by adding hydrazine hydrate solution to a hydrochloric acid solution of the sample at 60°. Tellurium was likewise determined gravimetrically as the element.

Sulphates containing Active Oxygen (*Perhydrates*).—Willstätter's reports (*loc. cit.*) of the formation of $Na_2SO_4,H_2O,0{\cdot}5H_2O_2$ and $(NH_4)_2SO_4,H_2O_2$ have been confirmed. Attempts to prepare analogous compounds from the sulphates of lithium, potassium, rubidium, and cæsium were unsuccessful.

FIG. 1. *The system,* Na_2SO_4–H_2O_2–H_2O, *at* 20°.

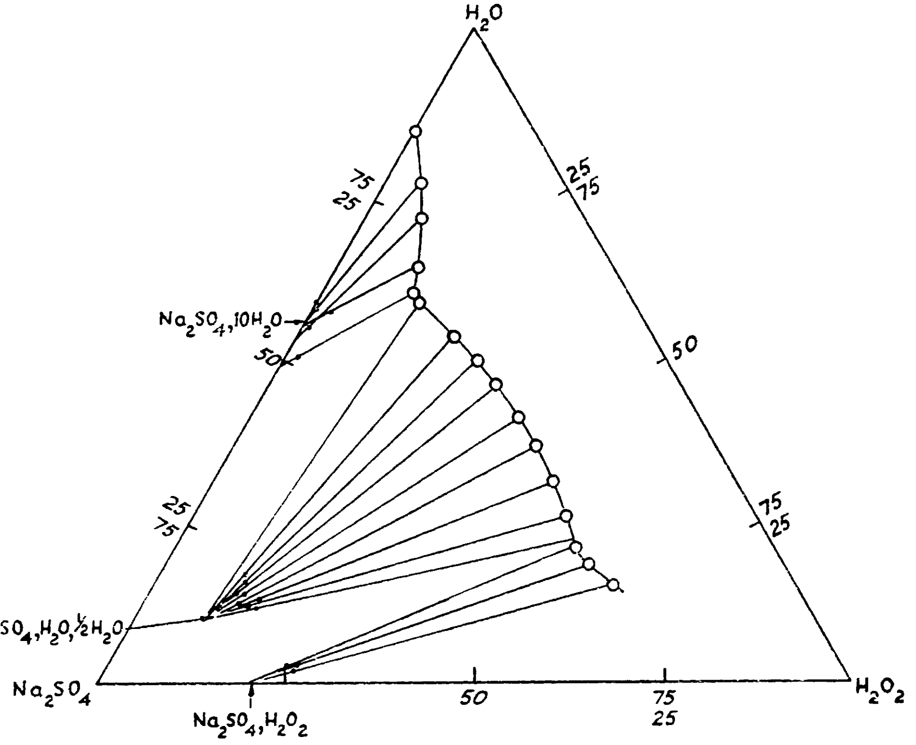


TABLE 1. *Selenates containing active oxygen.*

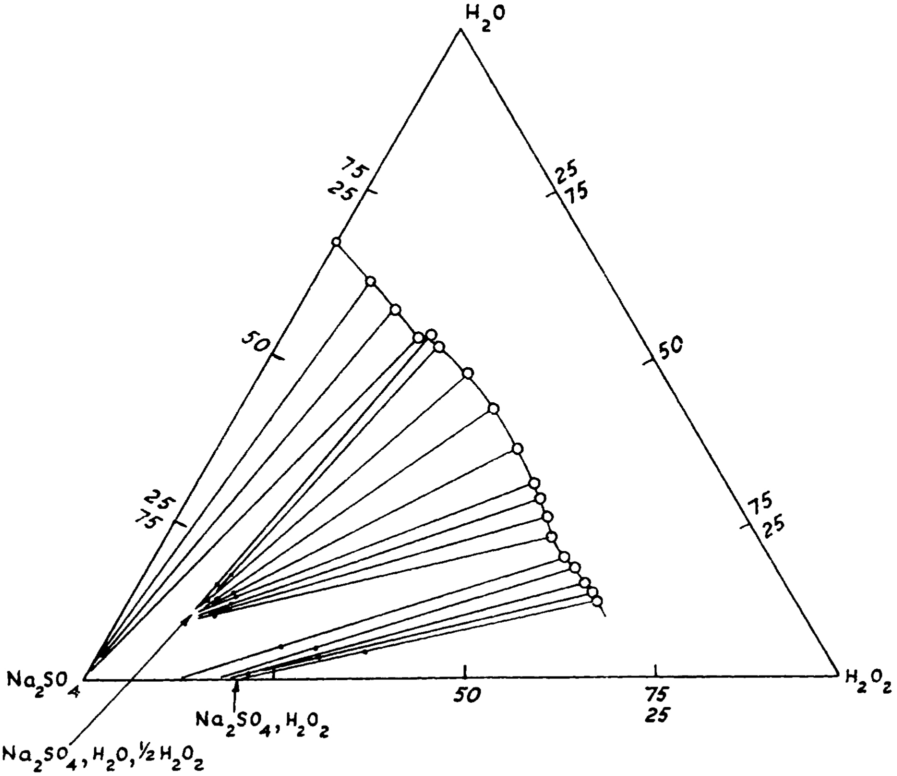
	Method of prep.	No. of samples analysed	O_a (%) †	Se (%)	Na, K, or NH_3 (%)	Wt. loss at 110° (%)
(*a*)	1	3	3·55	35·23	20·15 *	15·69
	2	2	3·55	35·08	20·02 *	15·70
	$Na_2SeO_4,0{\cdot}5H_2O_2,H_2O$ requires		3·58	35·28	20·55	15·65
(*b*)	1	3	6·22	30·91	30·13 *	13·39
	2	2	6·21	30·82	30·21 *	13·43
	K_2SeO_4,H_2O_2 requires		6·27	30·94	30·65	13·23
(*c*)	1	3	7·45	36·98	15·63	16·03
	$(NH_4)_2SeO_4,H_2O_2$ requires		7·51	37·08	15·97	15·97

* Only one sample analysed. † O_a = active oxygen.

Selenates containing Active Oxygen.—The analytical results for the sodium, potassium, and ammonium compounds are given in Table 1. These indicate the formation of: $Na_2SeO_4,H_2O,0{\cdot}5H_2O_2$; K_2SeO_4,H_2O_2; and $(NH_4)_2SeO_4,H_2O_2$. These are colourless crystalline solids, which lose all their active oxygen at 110°, yielding a residue of the type M_2SeO_4. The aqueous solutions of these compounds oxidise ferrous to ferric salts, liberate iodine from neutral solutions of potassium iodide (in acid solutions, selenates also liberate iodine from acidified solutions of potassium iodide), produce a blue colour with chromic acid, and decolorise acidified solutions of potassium permanganate. Hydrogen peroxide can be extracted from the solutions of these substances and, by repeated extraction with ether, all the active oxygen can be removed in this way. No corresponding compounds could be prepared from the selenates of lithium, rubidium, and cæsium by the methods described.

Tellurates containing Active Oxygen.—The analytical results for the lithium, sodium, and potassium compounds are given in Table 2. These indicate the formation of products

FIG. 2. *The system,* Na_2SO_4–H_2O_2–H_2O, *at* 35°.



of probable composition: $Li_2H_4TeO_{7.5},2H_2O$; $Li_2H_4TeO_7,2H_2O$; $Na_2H_4TeO_8,0{\cdot}5H_2O$; $Na_2H_4TeO_{7.5},0{\cdot}5H_2O$; $K_2H_4TeO_{8.5}$; and $K_2H_4TeO_8$. Indications were obtained that potassium compounds with still higher active-oxygen contents might be formed. However, no

TABLE 2. *Tellurates containing active oxygen.*

	Method of prep.	No. of samples analysed	$M_2H_4TeO_6$ (%) *	O_a (%) †	H_2O (%)
(*a*)	3	5	78·4	7·94	13·6
	$Li_2H_4TeO_{7.5},2H_2O$ requires		80·05	7·96	11·95
(*b*)	2	3	81·3	5·80	12·83
	$Li_2H_4TeO_7,2H_2O$ requires		82·24	5·45	12·27
(*c*)	3	5	86·8	10·18	3·22
	$Na_2H_4TeO_8,0{\cdot}5H_2O$ requires		86·98	10·17	2·86
(*d*)	2	5	87·37	8·12	4·51
	$Na_2H_4TeO_{7.5},0{\cdot}5H_2O$ requires		89·22	7·83	2·94
(*e*)	3	10	86·90	11·57	1·53
	$K_2H_4TeO_{8.5}$ requires		88·42	11·57	0
(*f*)	2	8	88·98	9·95	1·08
	$K_2H_4TeO_8$ requires		90·55	9·48	0

* Derived from % Te found. † O_a = active oxygen.

evidence was obtained of the compound $K_2TeO_5,2H_2O$ previously reported (Montignie, *Z. anorg. Chem.*, 1945, **253**, 90).

The lithium compounds are white powders whereas the sodium and potassium compounds

FIG. 3. *The system,* $(NH_4)_2SO_4$–H_2O_2–H_2O *at* 20°.

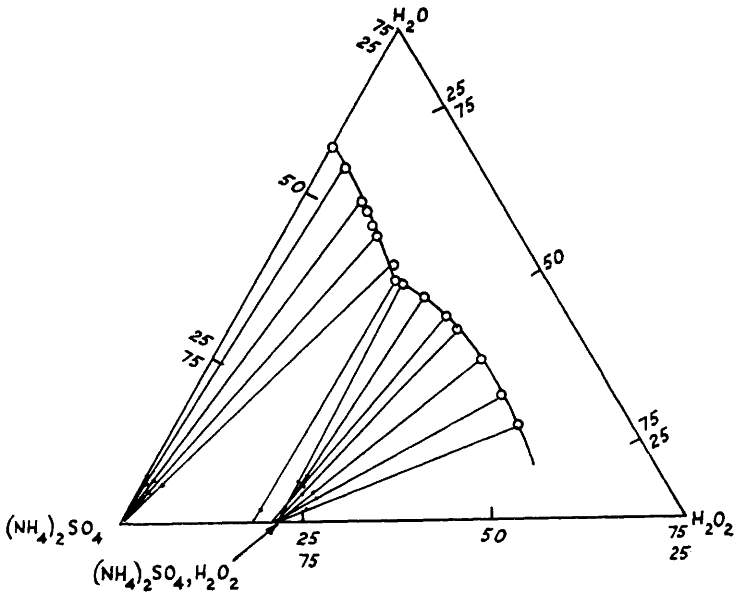
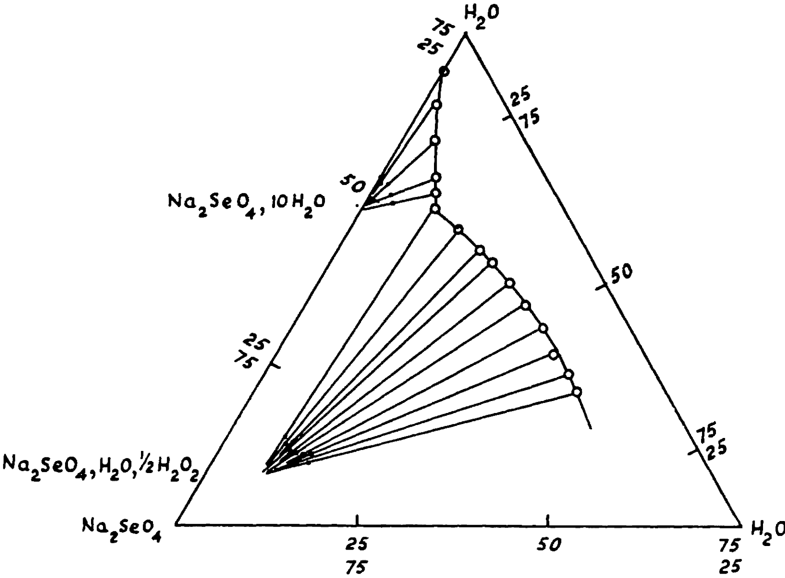


FIG. 4. *The system,* Na_2SeO_4–H_2O_2–H_2O *at* 20°



are crystalline. The active oxygen is lost on keeping or heating (below 100°). The compounds are more soluble in water than the corresponding tellurates and in general the solubility increases with the active oxygen content. The aqueous solutions of these compounds have oxidising properties similar to those of aqueous hydrogen peroxide. Ether extracts hydrogen peroxide from the solutions, but not from the dry substances (when the ether is also dry). The sodium and potassium compounds gave at 110° a residue of composition approximating closely to $M_2H_4TeO_6$.

Systems M_2SO_4–H_2O_2–H_2O *and* M_2SeO_4–H_2O_2–H_2O.—A limited study of the system Na_2SO_4–H_2O_2–H_2O has been made by previous workers and the existence of the compound $Na_2SO_4,H_2O,0{\cdot}5H_2O_2$ reported, but the experimental data are not sufficient to enable the phase diagram to be constructed (F. Münzberg, *Lotos*, 1928, **76**, 351). Otherwise no study of these systems appears to have been made.

To avoid appreciable decomposition of the hydrogen peroxide, the temperature selected for the studies of the systems was 20°. In addition the system Na_2SO_4–H_2O_2–H_2O was studied at 35°.

Alkali sulphate or selenate (anhydrous) was dissolved in aqueous hydrogen peroxide of various concentrations (0—85%) and the saturated solution was transferred to tubes containing a small amount of finely powdered alkali sulphate or selenate. The tube was stoppered and placed in a thermostat at 20° ± 0·1°. After 3—4 days a sample of the liquid phase was analysed and this was repeated several hours later. If the two analyses gave identical results, it was assumed that equilibrium had been reached and the solid and the liquid phase were separated by filtration and analysed.

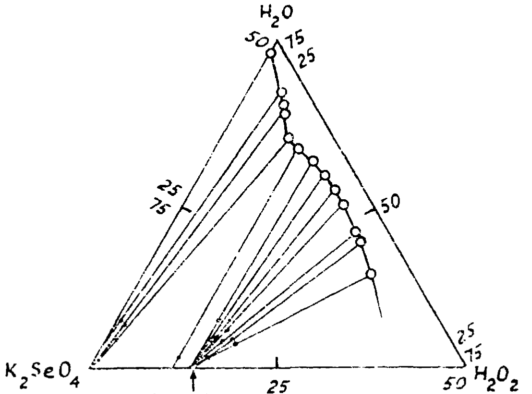


Fig. 5.
The system, K_2SeO_4–H_2O_2–H_2O *at* 20°.

Table 3. *The system lithium sulphate–hydrogen peroxide–water at* 20°.

Liquid phase		Moist solid phase		
Li_2SO_4 (%)	H_2O_2 (%)	Li_2SO_4 (%)	H_2O_2 (%)	Solid phase
25·20	0·00	81·6	0·00	Li_2SO_4,H_2O
22·04	7·70	83·9	0·61	
20·58	12·50	82·1	0·80	
18·59	17·42	77·2	2·98	
16·74	22·58	84·3	0·98	
13·77	29·17	82·8	1·78	
9·30	44·31	80·6	4·13	
6·98	52·86	78·4	5·99	
6·49	55·55	74·5	8·13	
4·07	68·0	81·2	3·71	
3·58	71·0	79·5	6·06	
2·30	80·8	81·5	4·73	
1·96	84·8	78·1	7·23	

Table 4. *The system sodium sulphate–hydrogen peroxide–water at* 20°.

Liquid phase		Moist solid phase	
Na_2SO_4 (%)	H_2O_2 (%)	Na_2SO_4 (%)	H_2O_2 (%)
15·75	0·00	41·5	0·00
19·21	4·82	42·2	0·67
21·61	7·32	44·7	1·05
25·95	10·78	40·7	2·63
28·89	12·07	48·4	1·85
28·51	13·38	79·3	9·13
26·17	20·88	71·9	11·25
25·13	25·45	72·5	11·84
24·40	30·69	74·7	11·60
23·89	35·51	74·0	12·54
23·93	40·10	75·4	12·58
24·23	44·99	72·3	14·75
25·19	49·08	74·3	14·05
25·95	52·4	73·6	14·98
26·64	52·6	73·7	23·58
26·63	53·6	73·6	23·62
26·36	56·0	72·4	24·99
25·01	59·9	73·4	24·61
24·62	60·8	76·1	22·98

The moist solid samples were dissolved in water, and aliquot portions of the solutions so obtained and of the liquid-phase samples were used for the analyses. Hydrogen peroxide was determined by titration with standard potassium permanganate. The sulphate or selenate was determined by carefully evaporating a portion to dryness and weighing the residue left after heating to constant weight at 110°.

System Li_2SO_4–H_2O_2–H_2O *at* 20°.—The results which are given in Table **3** indicate that the stable solid phase over the whole range of hydrogen peroxide concentration studied is Li_2SO_4,H_2O. Again no evidence was found for compounds containing active oxygen.

System Na_2SO_4–H_2O–H_2O *at* 20°.—The results which are given in Table **4** and Fig. 1 show the formation of three solid phases, $Na_2SO_4,10H_2O$; $Na_2SO_4,H_2O,0{\cdot}5H_2O_2$; and Na_2SO_4,H_2O_2, the last of which is now reported for the first time. The fact that the tie-lines indicating the region of stability of $Na_2SO_4,10H_2O$ do not meet very sharply may be attributed to the formation of solid solutions with lower hydrates or with perhydrates.

System Na_2SO_4–H_2O_2–H_2O *at* 35°.—The results which are given in Table **5** and Fig. 2 again show the formation of three solid phases, Na_2SO_4; $Na_2SO_4,H_2O,0{\cdot}5H_2O_2$; and Na_2SO_4,H_2O_2, and provide further confirmation of the existence of the last compound.

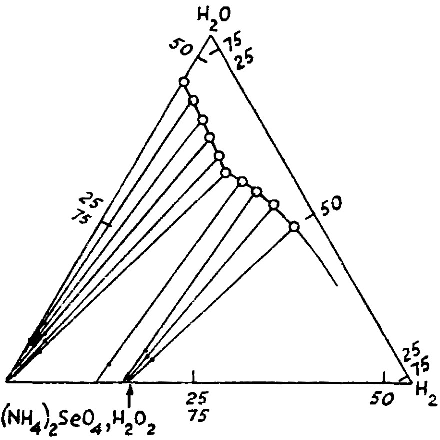


Fig. 6.
The system, $(NH_4)_2SeO_4$–H_2O_2–H_2O *at* 20°.

System K_2SO_4–H_2O_2–H_2O *at* 20°.—The results (Table **6**) indicate the separation of one solid phase only, namely, K_2SO_4. No evidence was found for compounds containing active oxygen.

System $(NH_4)_2SO_4$–H_2O_2–H_2O *at* 20°.—The results (Table **7**, Fig. 3) show the solid phases to be $(NH_4)_2SO_4$ and $(NH_4)_2SO_4,H_2O_2$.

System Li_2SeO_4–H_2O_2–H_2O *at* 20°.—The results (Table **8**) indicate the formation of Li_2SeO_4 and Li_2SeO_4,H_2O, but not of compounds containing active oxygen.

TABLE 5. *The system sodium sulphate–hydrogen peroxide–water at* 35°.

Liquid phase		Moist solid phase	
Na_2SO_4 (%)	H_2O_2 (%)	Na_2SO_4 (%)	H_2O_2 (%)
33·06	0·00	91·2	0·00
31·54	7·54	93·0	0·90
30·54	12·77	85·0	2·81
29·43	18·11	88·3	2·99
27·99	19·52	74·8	10·47
27·54	21·76	76·3	10·41
26·65	23·89	72·4	11·62
26·07	27·29	77·3	10·76
25·61	33·25	76·3	11·32
25·04	39·87	73·6	13·29
25·43	44·77	73·3	14·09
25·65	46·76	70·9	16·52
25·84	47·92	74·8	13·60
26·22	48·75	75·1	14·16
27·65	50·7	77·8	12·65
26·07	47·56	75·5	13·23
27·36	54·3	71·2	23·68
26·08	56·3	67·2	28·30
26·71	58·8	78·0	21·29
26·35	60·7	67·3	29·52
26·28	61·8	60·6	35·18

TABLE 6. *The system potassium sulphate–hydrogen peroxide–water at* 20°.

Liquid phase		Moist solid phase		
K_2SO_4 (%)	H_2O_2 (%)	K_2SO_4 (%)	H_2O_2 (%)	Solid phase
10·00	0·00	98·2	0·00	K_2SO_4
13·78	4·12	87·5	0·63	
16·78	8·35	91·4	1·00	
19·40	12·10	86·0	0·61	
23·12	15·57	89·7	2·00	
23·89	18·45	91·0	2·33	
24·83	20·11	93·6	1·89	
28·31	24·12	90·7	3·36	
31·41	28·17	95·7	1·81	
35·93	33·66	94·0	3·05	
41·09	39·29	93·0	4·75	
44·36	43·85	81·5	6·60	

System Na_2SeO_4–H_2O_2–H_2O *at* 20°.—The results (Table 9, Fig. 4) show the solid phases to be $Na_2SeO_4,10H_2O$ and $Na_2SeO_4,H_2O,0{\cdot}5H_2O_2$. No compound analogous to Na_2SO_4,H_2O_2 was found.

System K_2SeO_4–H_2O_2–H_2O *at* 20°.—In contrast to the corresponding potassium sulphate system, the existence of a compound containing active oxygen was established, namely, K_2SeO_4,H_2O_2 (Table 10, Fig. 5). The other solid phase found was K_2SeO_4.

System $(NH_4)_2SeO_4$–H_2O_2–H_2O *at* 20°.—This is similar to the corresponding ammonium sulphate system, and the solid phases found were $(NH_4)_2SeO_4$ and $(NH_4)_2SeO_4,H_2O_2$ (Table 11, Fig. 6).

TABLE 7. *The system ammonium sulphate–hydrogen peroxide–water at 20°.*

Liquid phase		Moist solid phase	
$(NH_4)_2SO_4$ (%)	H_2O_2 (%)	$(NH_4)_2SO_4$ (%)	H_2O_2 (%)
42·93	0·00	93·0	0·00
43·17	3·04	93·6	0·35
43·44	8·02	93·0	1·00
43·54	9·23	92·2	1·33
43·61	10·00	93·4	1·30
43·77	11·44	92·0	1·60
44·00	12·73	94·5	1·30
44·35	14·79	93·3	1·69
44·22	17·03	91·5	2·70
44·94	18·74	80·9	17·44
44·50	19·85	73·3	20·24
43·85	22·29	72·5	20·87
42·88	23·71	72·0	21·09
41·43	27·90	73·4	21·61
40·81	30·20	74·0	21·94
40·28	35·63	72·3	23·30
40·02	41·37	75·4	24·27
40·32	42·18	76·0	22·55
40·40	45·62	74·6	23·54

TABLE 8. *The system lithium selenate–hydrogen peroxide–water at 20°.*

Liquid phase		Moist solid phase		
Li_2SeO_4 (%)	H_2O_2 (%)	Li_2SeO_4 (%)	H_2O_2 (%)	Solid phase
40·64	0·00	85·0	0·00	Li_2SeO_4,H_2O
38·29	4·03	81·0	0·77	
35·42	9·61	85·3	0·83	
33·42	13·15	87·3	0·72	
29·86	19·88	83·0	2·55	
27·77	24·29	85·8	1·36	
22·59	35·56	87·1	1·77	
19·68	43·08	86·8	2·44	
17·36	46·62	80·0	5·40	
15·29	51·1	77·3	13·36	Li_2SeO_4
14·96	52·9	87·1	7·75	
12·61	58·9	78·1	14·06	
10·42	64·4	82·7	11·43	
8·26	71·5	85·7	11·05	

TABLE 9. *The system sodium selenate–hydrogen peroxide–water at 20°.*

Liquid phase		Moist solid phase	
Na_2SeO_4 (%)	H_2O_2 (%)	Na_2SeO_4 (%)	H_2O_2 (%)
30·11	0·00	46·42	0·00
33·79	1·15	47·03	0·30
36·59	4·19	45·71	1·51
39·63	7·10	46·42	3·00
40·27	8·28	46·49	3·62
41·88	9·24	78·6	7·88
40·08	14·36	79·3	8·50
39·04	18·54	78·1	9·39
38·50	21·03	79·4	9·15
37·51	24·91	79·8	9·32
36·85	28·82	78·4	10·29
36·53	32·73	77·7	10·07
37·12	36·14	76·7	12·27
36·64	39·99	79·5	11·05
37·35	40·99	79·0	11·49
36·89	42·55	77·8	12·62
39·71	46·47	73·1	17·58

TABLE 10. *The system potassium selenate–hydrogen peroxide–water at 20°.*

Liquid phase		Moist solid phase	
K_2SeO_4 (%)	H_2O_2 (%)	K_2SeO_4 (%)	H_2O_2 (%)
52·1	0·00	94·3	0·00
53·7	4·20	92·3	0·70
54·3	5·20	94·0	0·65
54·8	6·01	92·6	1·00
55·9	8·56	91·4	1·60
56·4	8·93	94·7	1·13
56·2	10·81	87·8	10·98
55·0	13·60	82·2	13·36
54·5	16·19	81·3	13·83
54·5	18·49	79·6	14·46
54·2	20·98	79·4	14·97
54·5	24·82	80·8	15·29
54·9	26·11	79·5	16·31
55·9	30·00	79·0	17·43

TABLE 11. *The system ammonium selenate–hydrogen peroxide–water at 20°.*

Liquid phase		Moist solid phase	
$(NH_4)_2SeO_4$ (%)	H_2O_2 (%)	$(NH_4)_2SeO_4$ (%)	H_2O_2 (%)
54·1	0·00	93·7	0·00
54·5	2·62	90·6	0·80
54·7	5·26	92·0	0·98
54·7	7·96	91·5	1·50
54·8	10·71	92·0	1·85
55·7	12·87	93·5	1·79
54·0	15·57	85·1	12·45
52·5	18·66	79·3	16·18
52·5	19·23	80·5	16·21
51·6	21·79	79·7	16·61
50·5	25·98	79·7	18·24

Systems containing Tellurates.—Attempts to extend these studies to systems containing tellurates were unsuccessful. The solubilities of lithium and sodium tellurates in hydrogen peroxide solutions were found to be greater than in pure water. Sodium and potassium tellurates were in fact highly soluble in aqueous hydrogen peroxide, to give pale yellow viscous solutions from which no solid material crystallised.

DISCUSSION

Sulphates and Selenates containing Active Oxygen.—Compounds of this class have been found in the cases of the sulphates and selenates of sodium and ammonium and of potassium selenate, and are of two types: (1) $M_2SO_4,0{\cdot}5H_2O_2,H_2O$ or $M_2SeO_4,0{\cdot}5H_2O_2,H_2O$ ($M = Na$); (2) M_2SO_4,H_2O_2 ($M = Na$ or NH_4) or M_2SeO_4,H_2O_2 ($M = K$ or NH_4)—the possibility that Na_2SeO_4,H_2O_2 may be formed at higher hydrogen peroxide concentrations (Fig. 4) cannot be ruled out.

The phase diagrams for the corresponding sulphate and selenate systems are, in general, similar, apart from the differences of the solubilities of the two series of salts in aqueous hydrogen peroxide. The selenates are more soluble than the corresponding sulphates, particularly in the case of the potassium salts, for which the phase diagrams show the greatest difference.

Lithium sulphate and selenate differ from the sodium, potassium, and ammonium salts, not only in failing to form any compounds containing active oxygen, but also in showing a rapid fall in solubility with rise in hydrogen peroxide concentration. The sodium, potassium, and ammonium salts show a slight fall or rise in solubility only, or even a marked rise in solubility (K_2SO_4).

The sulphates of the second type listed above (M_2SO_4,H_2O_2) do not appear to be salts of Caro's acid (*e.g.*, M_2SO_5,H_2O) since according to Willstätter and Hauenstein (*Ber.*, 1909, **42**, 1839) this acid is monobasic only, giving salts $MHSO_5$. In fact the properties of the sulphates and selenates described in this work are consistent with their being perhydrates. If so, then the absence of similar rubidium and cæsium compounds is in line with the reluctance of these to crystallise with water (or presumably, hydrogen peroxide) of crystallisation. However, it is not possible on the basis of the evidence available to establish unambiguously the structures of these compounds.

Tellurates containing Active Oxygen.—The potassium compounds are anhydrous and the amount of water present in the sodium compounds is not sufficient to allow all the active oxygen to be present as hydrogen peroxide of crystallisation. Evidently these compounds are salts of true peroxytelluric acids. The similarity of the lithium compounds to those of potassium and sodium suggests that they are of the same class (*e.g.*, $[Li,H_2O]_2[H_4TeO_{7{\cdot}5}]$), although it is possible here to ascribe to them a perhydrate formula.

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