By Syed Husain and J. R. Partington.

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# Historical.

Electrolyis of orthophosphoric acid does not give rise to perphosphoric acids,<sup>1</sup>,<sup>2</sup>,<sup>3</sup> even in presence of hydrofluoric acid.<sup>4</sup> In presence of hydrogen peroxide, however, a small quantity of permonophosphoric acid is produced.<sup>3</sup>

By the action of 30 per cent. or stronger hydrogen peroxide on phosphorus pentoxide, meta- or pyro-phosphoric acid, permonophosphoric acid, H<sub>3</sub>PO<sub>5</sub> is produced; in the presence of an excess of pyrophosphoric acid a perphosphoric,  $H_4P_2O_8$  is also formed. The two acids resemble the corresponding persulphuric acids in their properties; the permonophosphoric acid is, however, a stronger oxidising agent than the Caro's acid.<sup>3</sup>

Siebold<sup>5</sup> claims to have prepared "perphosphoric acid" by the action of 31 per cent. hydrogen peroxide on phosphorus oxychloride and a "true sodium perphosphate" by neutralising the "perphosphoric acid" with This statement is now found to be incorrect. alcoholic sodium hydroxide.

Sodium phosphate cannot be oxidised electrolytically,<sup>4</sup> but several phosphates of sodium containing active oxygen have been prepared by the action of hydrogen peroxide. They are described as perphosphates in patent literature, but are really compounds of hydrogen peroxide. The NaPO<sub>4</sub> of Alvarez<sup>6</sup> is an indefinite mixture of sodium phosphate and sodium peroxide.<sup>7</sup> Aschkenasi and Rudenko have prepared several compounds containing active oxygen by dissolving the phosphate in hydrogen peroxide and afterwards (according to Aschkenasi) evaporating the solution at a mild temperature and a reduced pressure, or (according to Rudenko) precipitating the solution with alcohol or evaporating it on a water-bath. Thus the following compounds are described (see next page).

True potassium perphosphates were prepared in solution by electrolysing a concentrated solution of secondary potassium phosphate containing fluoride and a small quantity of chromate, between platinum electrodes at a low temperature with a low anodic current density.<sup>4</sup> Cautious evaporation of the electrolysed solution gave solid potassium perphosphate, K4P2O8.8

<sup>&</sup>lt;sup>1</sup> Hittorf, Pogg. Ann., 1853, **89**, 209. <sup>2</sup> Lucknow, Z. anat. Cnem., <sup>3</sup> Schmidlin and Massini, Ber., 1910, **43**, 1162. <sup>4</sup> Fichter and Müller, Helv. Chim. Acta, 1918, **1**, 304. <sup>6</sup> Chem. News, 1906, **94**, 269. <sup>2</sup> Lucknow, Z. anal. Chem., 1880, 19, 1.

<sup>&</sup>lt;sup>6</sup> D R.P., 279,306. <sup>7</sup> Rudenko, J. Russ. Physical Chem. Soc., 1912, 44, 1215.

<sup>8</sup> Fichter and Rius Y. Miro, Helv. Chim. Acta, 1919, 2, 3.

Phosphate o Sodium.	f Concentration of Active Oxygen (Per Cent.).	Author.				
Primary ort	ho- 2	Aschkenasi, D.R.P., 299300, 296796				
Secondary ,	, 10 $(Na_2HPO_4 \cdot H_2O_2)$ 2.8 $(Na_2HPO_4 \cdot H_2O_2)$	Rudenko, loc. cit., 1209				
** *	8.9	Chem. Werke vorm. H. Byk, D.R.P. 287588				
"	, 1.4 and 7	Aschkenasi, D.R.P., 299300				
· · · · ·	8.8	,, D.R.P., 310997 ,, D.R.P., 318219				
Tertiary ,	$, \qquad 8.95 (Na_3PO_4 \cdot 2H_2O_2 \cdot 4\frac{1}{2}H_2O)$	Petrenko, J. Russ. Physic. Chem. Soc., 1902, 34, 204; Rudenko, loc. cit., 1209				
,, ,	, 1.4 and 2.8	Aschkenasi, D.R.P., 299300				
Pyro-	, 13.7 10.65 (Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub> . 2.5 H <sub>2</sub> O <sub>2</sub> )	, D.R.P., 316997 Rudenko, loc. cit., 1214				
"	8.5	Chem. Werke vorm. H. Byk,				
**	12.75 (Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub> . 3H <sub>2</sub> O <sub>2</sub> )	Ges. f. chem. Industrie, D.R.P.,				
Meta	3	Rudenko, loc. cit., 1212				

A secondary potassium phosphate containing 7<sup>·1</sup> per cent. of active oxygen was obtained by the action of hydrogen peroxide.<sup>9</sup> In a manner analogous to potassium perphosphates, rubidium and ammonium perphosphates were prepared in solution by electrolysis.<sup>4</sup> By the action of hydrogen peroxide a secondary ammonium phosphate containing 5<sup>·6</sup> per cent. of active oxygen,<sup>7</sup> and a tertiary ammonium phosphate containing 12<sup>·65</sup> per cent. of active oxygen <sup>10</sup> were obtained. Primary barium phosphate containing 1<sup>·5</sup> per cent. of active oxygen was prepared by dissolving barium peroxide in phosphoric acid or by the action of hydrogen peroxide on primary barium phosphate.<sup>11</sup>

The literature of the subject is incomplete and true perphosphates have not been distinguished from phosphates with hydrogen peroxide of crystallisation. The subject, therefore, seemed to merit further investigation.

# Criteria for True Perphosphates.

As a result of the present work it was found that true perphosphates do not give any of the characteristic reactions of hydrogen peroxide with permanganic acid, chromic acid and ether, or titanic acid (as do the phosphates containing hydrogen peroxide of crystallisation). On the other hand, they oxidise acidified manganous salt solutions to permanganic acid, acidified aniline solution to nitrosobenzene, which is then slowly oxidised to nitrobenzene, and silver nitrate solution to a black precipitate, which gradually turns yellow. Ammonium perphosphates, however, do not give the last-mentioned reaction (analogy with ammonium persulphate). It is interesting to note that perphosphoric acids are obtained only by the action of hydrogen peroxide; while the action of the same reagent on phosphates gives rise to pseudo-perphosphates. True perphosphates are obtained only by electrolysis.

### Experimental.

The experimental work was divided into two parts: (a) the action of hydrogen peroxide on phosphates; (b) electrolytic oxidation of phosphates. Great care was taken to ensure the purity of all materials used.

<sup>9</sup> Chem. Werke vorm. H. Byk, D.R.P., 287,588.
<sup>10</sup> Petrenko, *J. Russ. Phys. Chem. Soc.*, 1902, 34, 204.
<sup>11</sup> Aschkenasi, D.R.P., 296,796.

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	Remarks.		- - - -	Completely decomposes in a month.	T asso 1.1 ner cent of active axvaen in	a days.	Very stable, no loss of active oxygen in	Violent reaction with rapid decomposi-	Loses or 6 per cent. of active oxygen in a fortnight	Loses o'47 per cent, of active oxygen in a week. Toss on heating corresponds	to loss of $1.5 H_2O_2 + O_3$ Loses o'8t per cent. of active oxygen in 375 weeks. Loss on heating corre- sronds to loss of $0.5 H_2O_3 + O_3$		Completely decomposes in a month. Loses 177 per cent. of active oxygen in	Loses 1'84 per cent. of active oxygen in TT days.	Loses 3'14 per cent, of active oxygen in a month.	L oses 6:05 ner cent of active oxvoen in	a fortnight. Loses 3'18 per cent, of active oxygen in	a fortnight.	Special methods were devised to estimate the active oxygen.	-Alkaline. NNeutral. cent. (e) Calculated, 8 o per cent.
	Probable Formula of Product.		1	Li <sub>3</sub> PO4.0'25 H <sub>2</sub> O2	Ы4 <sup>F</sup> 3O7 025 H2O3 VH DO 705 H2O3	50711 C2 1 . FO 18111	K2HP04.275 H202	1	$K_4P_2O_7$ . $3H_2O_2$	Rb <sub>2</sub> HPO <sub>4</sub> . 2.5 H <sub>2</sub> O <sub>2</sub>	Cs <sub>2</sub> HPO <sub>4</sub> . 1.5 H <sub>2</sub> O <sub>2</sub>	1	(NH4)2HPO4.075 H2O2 NaNH4HPO4.075 H2O2	$(NH_4)_2H_2P_2O_7 \cdot H_2O_2 \cdot 2H_2O_1$	$CaHPO_4. o.5 H_2O_2$		BaHPO I'S H.O.			I.—Insoluble. A.—Acid. B t. (d) Calculated, 19'04 per
	Loss on Heating	to 50° C. in vacuo.	1	1	1	]	1	1	1	(p) 06.81	8.4 (e)	1	11	1		!				Soluble. ] 24 per cen
ent.).	۹ ۹	2		1	1	1	1	I	1	48°19 (a)	63 <b>·</b> 54 (b)	1			11		48.08 (c)	-	48*24	† S9 ulated, 48
Product (Per C	4.	Calculated.	1	}	1		36.65	1	32.85 P205	57.00	£0.£z	}	58.45	50.35 P <sub>2</sub> O <sub>5</sub>	11	] ]	27.88	5		(c) Calc
sis of the Dry	PC	Determined.		1	ł	1	36.25	1	31.52 P <sub>2</sub> O <sub>5</sub>	56.90	22.75	1	66.85	50°87 P <sub>2</sub> O <sub>5</sub>	11		17.55	- + ^ ^		a, K, etc. 36 per cent.
Analy	xygen.	Calculated.		3.23	qo6.1	61.11	15.43	1	1.11	9E.11	5.82	1	7.38	2.67	5.23	1	77.7 8.72	Ç,	11	xample, N ilated, 64
	Active O	Determined.	90.0	3.67	1.84	07.11	15.75	lin	12.4	19.11	6.20	320.0	10.L	5.64	none 5:5	none	9.00 8.10	) + )	none 0'2	netal, for e (b) Calcu
olu-	H <sub>2</sub> 0 <sub>2</sub>	ction.	Α.	ല്	т	4	щ	'n.	ц.	'n.	ų	V	, m m	Α.	A.	Α.	¥ 4	-	ν.	the r
<u>م</u>		Rea	0 S	Ļ		<i>i</i>	ທີ	Ś	Ś	Ś	လိ	U.	່າວ່າ	s.	s' i	ŝ		:	<b>11</b>	sents per c
	Phosphate.		LiH <sub>2</sub> PO <sub>4</sub>	Li,PO, or5 H,O	Li <sub>4</sub> P <sub>2</sub> O <sub>7.2</sub> H <sub>2</sub> O	hh2r04	K2HPO4	$K_3PO_4$	$K_4P_2O_7$ . 3 $H_2O$	$Rb_2HPO_4$ . $H_2O$	Cs <sub>2</sub> HPO <sub>4</sub> . H <sub>2</sub> O	Od H HN	(NH4) <sup>3</sup> HPO4 NaNH4HPO4.4H2O	$(\mathrm{NH}_4)_2\mathrm{H}_2\mathrm{P}_2\mathrm{O}_7$	CaH4(PO4)2 CaHPO4	${\operatorname{SrH}}_4({\operatorname{PO}}_4)_2$	BaHPO.	Parts of	TIH <sub>2</sub> PO4 TI <sub>2</sub> HPO4 or TI <sub>2</sub> HPO4. 2 TIH2PO4	* R repre (a) Calculated, 48.55

# TABLE I.

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\* R represents the metal, for example, Na, K, etc. (a) Calculated, 48.55 per cent. (b) Calculated, 64.36 per cent.

# 1. The Action of Hydrogen Peroxide on Phosphorus Compounds.

*Phosphorus Oxychloride.*—Siebold's  $^5$  work was repeated, but his results could not be confirmed. The action of 30 per cent. hydrogen peroxide on phosphorus oxychloride at  $^\circ$  in quantities expressed by the equation,

$$H_2O_2 + 4H_2O + 2POCl_3 = H_4P_2O_8 + 6HCl_1$$

gives rise only to a mixture of phosphoric acid and free hydrogen peroxide. Much chlorine is evolved during the reaction, owing to the oxidation of the resulting hydrochloric acid by hydrogen peroxide.<sup>12</sup> When the mixture so obtained is neutralised with alcoholic sodium hydroxide, a white precipitate is produced, which gives the reactions of free hydrogen peroxide and is, therefore, not a true perphosphate.

Phosphates .- The action of hydrogen peroxide was investigated on



A large copper vessel, B, covered with felt contained ice and salt. A copper ring, H, fitted in a perforated porcelain disc, D, resting on a tripod stand, supported the cell in the bath. A platinum crucible, A (of 19'15 sq. cm. working surface when to c.c. electrolyte was used), served as anode, while a platinum wire was used as cathode. The electrolyte was agitated by a glass stirrer S, and its temperature was measured on the Thermometer, T. All glass articles in contact with the electrolyte were coated with paraffin to prevent the action of hydrofluoric acid. A milli-ammeter and a copper coulo-



meter were included in the circuit. A voltmeter measured the difference of potentia across the cell.

several phosphates. The phosphate in question was dissolved or suspended in 30 per cent. hydrogen peroxide, and the resulting mixture was evaporated to dryness at room temperature in a vacuum (about 5 mm. press.) over fused calcium chloride. The same results were obtained in the case of ammonium compounds when instead of calcium chloride sodium hydroxide was used as a drying agent.

The results are summarised in the table on p. 237.

It was found that agar agar or waterglass do not improve the stability of  $K_4P_2O_7$ ,  $3H_2O_2$  or of NaNH<sub>4</sub>HPO<sub>4</sub>. 0.75 H<sub>2</sub>O<sub>2</sub>.

*Properties.*—All these substances in the dry state evolve hydrogen peroxide on warming, and liberate iodine slowly from a neutral 30 per cent.

<sup>12</sup> See Aloy, etc., and Moissan, Traité de Chimie minerale, vol. I., p. 271.

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potassium iodide solution. In aqueous solution they decolorise permanganic acid, produce a blue coloration with chromic acid and ether and a yellow coloration with titanic acid. With silver nitrate solution they give a yellow precipitate or a white one if they are prepared from a pyrophosphate.

# 2. Electrolytic Oxidation.

Apparatus.—The apparatus used for electrolysis is shown in Fig. 1.

Method of Electrolysis.—Usually 10 c.c. of solution were placed in the crucible and electrolysed at about 0° C. with an anodic current density of nearly 0.0146 amp./cm.<sup>2</sup> for 3 to 5 hours. At the end of electrolysis the copper deposited in the coulometer was weighed. The electrolysed solution was diluted to 100 c.c., 10 c.c. of which were analysed each time by adding to 200 c.c. of acidified potassium iodide solution (2 g. of KI, 100 c.c. of H<sub>2</sub>O and 15 c.c. of H<sub>2</sub>SO<sub>4</sub> (1:2)). The iodine liberated *immediately* and that *after a day* were titrated with 0.1 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution with freshly prepared starch solution as indicator. Blank titrations were always made to check the results. The iodine-value of the chromate present was subtracted from the amount of iodine liberated immediately.

# Special Experiments.

#### Lithium.

Lithium did not give satisfactory results. The only soluble phosphate of lithium,  $\text{LiH}_2\text{PO}_4$  was electrolysed under different conditions, for example (a) with a little chromate and acid lithium fluoride (normal fluoride is insoluble) or without any fluoride, (b) with a porcelain diaphragm, and (c) with superimposition of an alternating current of high frequency (from an induction coil) on a direct current and a diaphragm. In all these experiments a precipitate consisting of tertiary lithium phosphate and lithium fluoride or of the former only immediately appeared at the cathode. The resistance of the cell increased with the increase in the amount of the precipitate, with the result that the current ceased to flow and the temperature went up.

### Sodium.

On account of its greater solubility  $(3\cdot 16 \text{ per cent.})$  than that of secondary sodium phosphate (about  $1\cdot 67$  per cent.) which had failed to give rise to perphosphates by electrolysis,<sup>4</sup> sodium pyrophosphate was electrolysed. A saturated solution of sodium pyrophosphate containing 1M sodium fluoride and  $0\cdot 0035$  g. of potassium chromate per 10 c.c. was electrolysed for 5 hours. The electrolysed solution was found to contain no active oxygen.

### Rubidium and Caesium

Electrolysis of concentrated solutions of secondary rubidium phosphate,  $Rb_2HPO_4$ .  $H_2O$  or secondary caesium phosphate,  $Cs_2HPO_4$ .  $H_2O$ , in the presence of about 0.35 g. of chromate and even without the addition of fluoride gives rise to perphosphates, if a low anodic current density (nearly 0.0146 amp./cm.<sup>2</sup>) is used.

*Properties.*—The freshly electrolysed solutions do not show any of the characteristic reactions of hydrogen peroxide with permanganic acid, chromic acid and ether or titanic acid. On the other hand, acidified manganous salt solutions give an intense pink coloration of permanganic acid immediately on warming or after half an hour in the cold. Aniline solution, acidified with dilute sulphuric acid, gives a green solution on

Electrolyte.	C.c. $\frac{N}{10} \times \text{Na}_2$ in 1 Am	Current Efficiency in:Percentage.			
	Immediately.	After 18 Hrs.	H3PO5.	H <sub>4</sub> P <sub>2</sub> O <sub>8</sub> .	Total.
10 c.c. of 2.91 $M$ Rb <sub>2</sub> HPO <sub>4</sub> . H <sub>2</sub> O +	65.01	45*93	17.43	12'32	29.75
5 c.c. of 2.88 $M Cs_2HPO_4$ . $H_2O + 0.0017$ g. of $K_2CrO_4$	32.35	41.75	17.30	22.33	39'63

# TABLE II.

warming, which gradually turns brown. Silver nitrate solution gives a black precipitate, which slowly turns yellow. Ferrous sulphate solution is oxidised in the cold. Manganous sulphate solution gives a brown precipitate, which dissolves to a pink solution in dilute sulphuric acid. Solutions of salts of cobalt and nickel give precipitates with evolution of ozonised oxygen. Iodine is liberated immediately from a neutral 30 per cent. potassium iodide solution.

Rubidium and caesium permonophosphate are very unstable and continuously evolve oxygen from the time of their formation, decomposing completely in about 8 hours. But the corresponding perphosphates are fairly stable. The freshly electrolysed solutions, after keeping for 24 hours, contained the same amount of perphosphate and showed all the reactions of the freshly electrolysed solutions, except that they did not liberate iodine immediately from a neutral or an acidified solution of potassium iodide.

By allowing electrolysed solutions to evaporate at ordinary temperature in a vacuum over concentrated sulphuric acid, solid products containing rubidium and caesium perphosphates were obtained, in an impure condition, which gave the same reactions as those shown by the solutions which had been kept for 24 hours. On account of their extreme solubility the rubidium and caesium perphosphates, however, could not be prepared in the pure condition.

### Ammonium.

The influence of various factors that govern the electrolytic oxidation of ammonium phosphates was thoroughly investigated with the object of increasing the current efficiency and ultimately isolating the solid ammonium perphosphate. Secondary ammonium phosphate was used throughout.

(i) The current efficiency gradually decreased with increase of anodic current density except in the case of experiment No. 6 (Table III.).

(ii) The current efficiency decreased and the total content of perphosphates increased with increasing duration of electrolysis except in the case of experiment No. 1 (Table IV.).

(iii) The current efficiency decreased with the rise of temperature (Table V.).

(iv) The current efficiency of perphosphate increased with increasing concentration of the phosphate, while that of permonophosphate increased to a maximum and then fell (Table VI.).

(v) Using 3 M secondary ammonium phosphate the current efficiency of perphosphate (Table VII.) rapidly increased with increasing concentration of ammonium fluoride, until it reached a maximum somewhere between 2 and 3 M, and then began to decrease gradually. The current efficiency of permonophosphate reached the maximum at about 4 M ammonium fluoride and then became almost constant. The total current efficiency was highest at about 3 M ammonium fluoride.

(vi) Using 4 M secondary ammonium phosphate (Table VIII.) the current efficiency of perphosphate was again highest at 3 M ammonium fluoride, while the current efficiency of permonophosphate and the total current efficiency gradually increased with the concentration of fluoride. The maximum yield of perphosphate obtained was higher than that in Table VII.

(vii) The current efficiency of perphosphate and the total current efficiency were highest at a concentration corresponding to 0.32 g. of ammonium chromate per lit., while the current efficiency of permonophosphate gradually increased with the concentration of the chromate. (See Table IX.).

#### TABLE III .- THE INFLUENCE OF ANODIC CURRENT DENSITY.

For small C.D. the platinum crucible, A, Fig. 1, served as anode; for higher C.D. a piece of platinum foil of 1 sq. inch area was used. Variations in C.D. were effected by diminishing the surface of the anode by covering it with a layer of marine glue.

The electrolyte contained 1 M secondary ammonium phosphate, 1.2 M ammonium fluoride and 0.32 g. of ammonium chromate (added as ammonium dichromate) per litre. 10 c.c. of this solution were electrolysed each time at about + 5° C. for an hour. The current intensity was varied between 0.21 and 0.33 amp.

Anodic	Coulometer	C.c. $\frac{N}{10} \times Na_2$	S <sub>2</sub> O <sub>3</sub> - Soln.	Current Efficiency (Per Cent.).			
Current Density in Amp./cm. <sup>2</sup> .	g. Cu.	Immediately.	On the Following Day.	Н <sub>3</sub> РО <b>5</b> .	H <sub>4</sub> P <sub>2</sub> O <sub>8</sub> .	Total.	
0'01097* 0'0149 0'0184 0'0263 0'0368 0'0682 0'7813 Pt wire	0'3959 0'4002 0'3868 0'4002 0'3781 0'3792 0'3645 0'3645	14'71 12'88 11'10 10'72 5'63 8'27 4'21 3'25	7:34 8:76 7:98 7:98 4:76 4:76 3:15 3:09	11-93 7-03 9-22 8-60 4-78 7-01 3-71 3-01	5.96 7.03 6.63 6.63 6.41 4.05 4.04 2.78 2.87	17 <sup>.</sup> 89 17 <sup>.</sup> 37 15 <sup>.</sup> 85 15 <sup>.</sup> 01 8 <sup>.</sup> 83 11 <sup>.</sup> 05 6 <sup>.</sup> 49 5 <sup>.</sup> 88	

TABLE IV .-- THE INFLUENCE OF DURATION OF ELECTROLYSIS.

Conditions as in Table III., the anodic C.D. being 0.01671 amp./cm.<sup>2</sup>, but the time was varied.

Time Coulo-		C.c. $\frac{N}{10} \times \text{Na}_2$	Curr	ent Efficie (Per Cent.)	тсу. ).	Content. G./Lit.			
in meter Min, g. Cu	meter g. Cu.	Immediately.	On the Following Day.	H3PO5.	H <sub>4</sub> P <sub>2</sub> O <sub>8</sub> .	Total.	H3PO5.	H <sub>4</sub> P <sub>2</sub> O <sub>8</sub> .	Total.
10	0.0204	1.7	1.24	9.2	8.36	17.26	0.060	1'494	2.463
15	0.0932	3.25	3.48	11.10	11.08	23.17	1.853	3.376	5.229
20	0.1500	4.79	3.73	12.73	9.92	22.65	2.730	3.018	6.348
30	0.1801	7.26	5.8	12.54	10.00	22.54	4.138	5.626	9.764
40	0.2378	10.07	6.83	13.0	9.22	22.82	5.740	6.625	12.365
Ġо	0.3012	11.73	7.2	10.42	6.4	16.82	6.686	6.984	13.670
120	0.7406	25.28	10.22	10.00	4.58	15.54	14.210	10.234	24.644
180	1.0020	28.48	14.7	8.37	4.32	12.69	16.234	14.259	30.493

\* Duration of electrolysis I hr. 40 min.

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# TABLE V.-THE INFLUENCE OF TEMPERATURE.

Conditions as in Table IV., the duration of electrolysis being r hour, but the temperature was varied. The electrolyte was practically frozen at  $-5^{\circ}$  C, therefore the experiments were started from o°.

Tomp	Coulomator	C.c. $\frac{N}{10} \times \text{Na}_2$	5 <sub>2</sub> O <sub>3</sub> — Soln.	Current Efficiency (Per Cent.).			
°C.	g. Cu.	Immediately.	On the Following Day.	Н <sub>3</sub> РО <b>5</b> .	H <sub>4</sub> P <sub>2</sub> O <sub>8</sub> .	Total.	
0 5 10 15 20 25	0*3546 0*3615 0*3621 0*3714 0*3548 0*3572	12°26 11°73 9°68 9°17 5°18 3°25	8.24 7.20 6.57 6.31 5.15 4.25	11*11 10*42 8*59 7*93 4*69 2*92	7*46 6*40 5*83 5*46 4*66 3*82	18·57 16·82 14·42 13·39 9·35 6·74	

TABLE VI.-THE INFLUENCE OF CONCENTRATION OF AMMONIUM PHOSPHATE.

Conditions as in Table V., the temperature being about  $+5^{\circ}$  C., but the concentration of ammonium phosphate was varied. Electrolyte alkaline in each case. More than 4M-ammonium phosphate could not be dissolved.

Concn. of Ammonium	Coulometer g. Cu.	C.c. $\frac{N}{10} \times \text{Na}_2$	S <sub>2</sub> O <sub>3</sub> - Soln.	Current Efficiency (Per Cent.).			
Phosphate (M).		Immediately.	On the Following Day.	H3PO5.	H <sub>4</sub> P <sub>2</sub> O <sub>8</sub> .	Total.	
т 3 4	0'3615 0'3710 0'3746	11.73 21.54 16.38	7:20 25:24 30:71	10·42 18·65 14•05	6·40 21·85 26·34	16·82 40·50 40·39	

### TABLE VII.—THE INFLUENCE OF CONCENTRATION OF AMMONIUM FLUORIDE ON 3 M SECONDARY AMMONIUM PHOSPHATE.

Ten c.c. of solution containing 3 M secondary ammonium phosphate and 0'0032 g, of ammonium chromate electrolysed each time with the required amount of ammonium fluoride at about  $+5^{\circ}$  C, with anodic C.D. of 0'01645 amp./cm.<sup>2</sup> for an hour.

Concn. of Ammonium Eluoride	Coulometer g. Cu.	C.c. $\frac{N}{10} \times \text{Na}_2$	S <sub>2</sub> O <sub>3</sub> - Soln.	Current Efficiency (Per Cent.).			
Fluoride (M).		Immediately.	On the Following Day.	Н <sub>3</sub> РО <sub>5</sub> .	H4P208.	Total.	
0 1·1 2·1 3·3 3·8 4·8 6·1	0'3714 0'3710 0'3422 0'3077 0'3747 0'3726 0'3694	0'93 21'54 25'66 34'16 36'22 35'95 35'19	9.53 25.24 29.88 31.68 27.30 28.08 24.73	0.80 18.65 24.09 29.84 31.05 31.00 30.60	8.26 21.85 28.05 27.67 23.40 24.21 21.50	9.06 40.50 52.14 57.51 54.45 55.21 52.10	

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TABLE VIII.—THE INFLUENCE OF CONCENTRATION OF AMMONIUM FLUORIDE ON 4 M Secondary Ammoninum Phosphate.

Ten c.c. of solution containing 4M secondary ammonium phosphate, 0.0032 g. of ammonium chromate and the requisite amount of fluoride electrolysed each time under the conditions mentioned in Table VII.

Concn. of	Coulometer	C.c. $\frac{N}{10} \times \text{Na}$	Current Efficiency (Per Cent.).			
Fluoride (M).	g. Cu.	Immediately.	On the Following Day.	Н <sub>3</sub> РО <sub>5</sub> .	H <sub>4</sub> P <sub>2</sub> O <sub>8</sub> .	Total.
1*3 3 4	0*3746 0*3753 0*3703	16*38 26*04 30*29	30'71 35'29 34'39	14.05 22.29 26.27	26 <b>·3</b> 4 30 <b>·</b> 20 2 <b>9·</b> 83	40'39 52'49 56'10

TABLE IX.—THE INFLUENCE OF CONCENTRATION OF AMMONIUM CHROMATE.

Ten c.c. of solution containing 4 M secondary ammonium phosphate and the requisite amount of ammonium chromate (in the form of ammonium dichromate solution, 5 c.c. of which corresponded to 0:0032 g. of ammonium chromate) electrolysed each time under the conditions mentioned in Table VII.

Concn. of Ammonium	Caulometer	C.c. $\frac{N}{10} \times Na_2$	<sub>2</sub> S <sub>2</sub> O <sub>3</sub> – Soln.	Current Efficiency (Per Cent.).			
Dichromate Solution (C.c.)	g. Cu.	Immediately.	On the Following Day.	H <sub>3</sub> PO <sub>5</sub> .	H <sub>4</sub> P <sub>2</sub> O <sub>8</sub> .	Total.	
2 5 10	0*3734 0*3714 0*3785	0.41 0.93 1.34	6·18 9·53 5·6	0'35 0'80 1'12	5°43 8°26 4°75	5•78 9•06 5 <sup>.8</sup> 7	

# Attempts to Prepare Solid Ammonium Perphosphate.

According to these investigations the most favourable conditions for the formation of ammonium perphosphate in solution are:  $4M (NH_4)_2 HPO_4$ ,  $3M NH_4F$ , 0.32g. of  $(NH_4)_2 CrO_4$  per lit., anodic current density about 0.0146 amp./cm.<sup>2</sup>, temperature 0° C., duration of electrolysis from the point of view of efficiency, about 10 minutes, but from the consideration of the yield, the longer the duration the greater the yield.

Ten c.c. of electrolyte of the above composition were electrolysed under the above conditions for 3 hours. The solution showed the same reactions as a freshly prepared solution of rubidium and caesium perphosphates. It did not give a black precipitate with silver nitrate solution, but a whitish one, which soon turned yellow with evolution of ozonised oxygen (cf. ammonium persulphate). The solution did not evolve bubbles of oxygen as do the corresponding solutions of rubidium and caesium, indicating that the smaller alkalinity of ammonium phosphate solutions favours the stability of the permonophosphate.

When the electrolysed solution was evaporated at room temperature in a vacuum over fused calcium chloride or sodium hydroxide, even the fourth crop of crystals consisted chiefly of phosphate, while the perphosphate concentrated in the mother liquor. After separating the crystals the

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residual mother liquor dried to a residue containing a little ammonium perphosphate mixed with phosphate, chromate, and fluoride. The dry residue did not liberate iodine immediately from a neutral or an acidified solution of potassium iodide, but gave all the other reactions of a freshly electrolysed solution.

Ammonium perphosphate did not crystallise out even when the electrolyte was kept saturated during electrolysis by keeping it in contact with solid ammonium phosphate contained in an ebonite tube pierced with a number of holes.

Precipitation of the freshly electrolysed solution did not give good results; 96 per cent. alcohol and silver nitrate solution precipitated both the phosphate and the perphosphate, while glacial or dilute acetic acid gave no precipitate. Barium carbonate did not precipitate the phosphate. Barium hydroxide precipitated all the impurities, phosphate, fluoride, and chromate, giving a filtrate containing active oxygen. The filtrate was freed from ammonia by a current of air and placing at ordinary temperature in a vacuum over concentrated sulphuric acid. A current of carbon dioxide was then passed and the precipitated barium carbonate filtered off. The resulting filtrate contained only traces of active oxygen. The perphosphate probably decomposed during this lengthy process.

# Thallium.

Ten c.c. of solution containing about 0.5 M thallium fluoride were saturated with secondary thallium phosphate; and the solution so obtained was electrolysed with a diaphragm of parchment paper (since thallium chromate is insoluble) at  $0^{\circ}$  C., with an anodic current density of 0.0125 amp./cm.<sup>2</sup>

In about 10 minutes spongy lumps of bluish white crystals of metallic thallium separated around the diaphragm and in the electrolyte. The solution originally alkaline reacted acid, and contained no active oxygen. Electrolysis of thallous sulphate gave similar results.<sup>13</sup>

# Conclusions and Summary.

1. Perphosphoric acids are not obtained by the action of 30 per cent. hydrogen peroxide at 0° C. on phosphorus oxychloride.

2. Most of the alkali and alkaline earth phosphates react with hydrogen peroxide, giving definite compounds containing hydrogen peroxide of crystallisation. Primary phosphates of lithium, ammonium, calcium, and strontium, and phosphates of thallium, however, do not react with hydrogen peroxide, while tertiary potassium phosphate decomposes it.

3. Apparently there is no relationship between water of crystallisation and hydrogen peroxide of crystallisation. Some phosphates containing no water of crystallisation, give compounds containing hydrogen peroxide of crystallisation.

4. There seems to be some relation between the alkalinity of the phosphate and the formation of compounds containing hydrogen peroxide of crystallisation. Acid-reacting phosphates, such as primary phosphates, do not react with hydrogen peroxide or else give very unstable compounds. Slightly acid-reacting phosphates like secondary phosphates of alkaline earths give unstable compounds. Alkaline phosphates, for example, secondary phosphates or pyrophosphates of alkalis give rather stable

<sup>13</sup> Crookes, Proc. Roy. Soc., 1862, 12, 153; Chem. News, 1863, 7, 290; J.C.S. (2), 1864, 2, 132.

compounds, while strongly alkaline phosphates, like tertiary potassium phosphate decompose hydrogen peroxide.

5. Electrolysis of orthophosphoric acid or of phosphates of lithium, sodium, and thallium, does not give rise to perphosphates, while secondary phosphates of potassium, rubidium, caesium, and ammonium produce on electrolysis two perphosphates in solution, namely permonophosphate and perphosphate.

Electrolysis was carried out with a low anodic and a high cathodic current density, at a low temperature, in the presence of a little chromate to prevent cathodic reduction. In the case of rubidium and caesium, perphosphates may be obtained even without the addition of fluoride, but potassium and ammonium do not give perphosphates even with such addition.

6. Ammonium perphosphates can be obtained in solution with an increased current efficiency of over 57 per cent., by using a 4 M solution of secondary ammonium phosphate, containing 3 M ammonium fluoride and 0.32g. of ammonium chromate per lit., at 0° C., with an anodic current density of about 0.0146 amp./cm.<sup>2</sup>

7. The current efficiency for production of perphosphate by electrolysis of alkali phosphate without the addition of fluoride shows an interesting relation to the atomic volume of the alkali metal. Hydrogen, lithium, and sodium do not give rise to perphosphates. Potassium does not produce perphosphates except in the presence of fluoride, but with the increase of atomic volume the tendency towards perphosphate-formation increases. Thus, rubidium gives a current efficiency of  $12\cdot32$  per cent. and caesium a current efficiency of  $22\cdot33$  per cent.

8. As a result of a comparative study of the two sets of products, one obtained by electrolysis and the other by the action of hydrogen peroxide on the same phosphate, it is established that the compounds obtained by electrolysis are *true perphosphates*, while those prepared by the action of hydrogen peroxide are *products containing hydrogen peroxide of crystallisation*.

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