

experimental investigation of this question, with other allied matters, the subject of a future communication.

III. "On Perchloric Acid and its Hydrates." By HENRY ENFIELD ROSCOE, B.A., Ph.D., Professor of Chemistry in Owens College, Manchester. Communicated by Professor A. W. WILLIAMSON. Received December 12, 1861.

Stadion* in the year 1816 showed that perchlorate of potassium contains 45·92 per cent. of oxygen, and that its composition is therefore represented by the formula $\text{ClO}_4 \text{K}$ (requiring 46·17 per cent. of oxygen). Mitscherlich† and Serullas‡ in 1830, and Marignac§ in 1841, confirmed this result, their experiments respectively showing that the salt in question contains 46·06, 46·20, and 46·17 per cent. of oxygen.

Upon these determinations is based nearly all the knowledge we possess of the quantitative relations of perchloric acid. The anhydride, $\text{Cl}_2 \text{O}_7$, has not been isolated; no analyses of the hydrated acid itself have been published, and the composition of only one or two of its salts has been ascertained. Our acquaintance even with the general characters of this substance is also most limited; and we can only account for the neglect with which chemists have treated the highest and yet the most stable of the oxides of chlorine by the fact that the preparation of the acid in large quantity has hitherto been attended with great difficulties.

In the following communication I have to detail the results of experiments which I believe somewhat enlarge our views respecting the nature and properties of this interesting acid.

The first point to which attention was naturally directed, was the best mode of preparing the pure aqueous perchloric acid in quantity. After trial of a great number of methods, the following modification of that recommended by Serullas was adopted as yielding the best results. A large quantity of a saturated solution of hydrofluosilicic acid was prepared by heating dry sand and fluor-spar with more than the equivalent quantity of twice-rectified oil of vitriol in large stone-ware bottles, and leading the gaseous fluoride of silicon with the usual

* Gilbert's Annalen, lii. pp. 197 and 339.

† Pogg. Ann. xxv. p. 287.

‡ Ann. de Ch. et de Phys. xlv. p. 270.

§ Ann. Ch. Pharm. xlv. p. 11.

precautions into water. After straining off the precipitated silica, the acid was boiled down with chlorate of potassium (and not perchlorate, as Serullas advises), added in such quantity that for every kilogramme of fluor-spar 600 grammes of chlorate was present. On heating the mixture, the liberated chloric acid undergoes quiet decomposition, chloric oxide, and probably other oxygen compounds of chlorine, escaping as gas, whilst aqueous perchloric acid remains in the liquid. After the mixture has cooled, the aqueous acid was decanted from the insoluble fluosilicate of potassium, and the clear liquid concentrated by boiling until the perchloric acid began to volatilize. The acid was then distilled, and freed from chlorine by perchlorate of silver, and from sulphuric acid by perchlorate of barium. According to this method, 4 kilogs. of chlorate of potassium yielded 500 grammes of pure concentrated aqueous perchloric acid.

The aqueous acid thus prepared is a colourless, heavy, oily liquid, in appearance undistinguishable from oil of vitriol; its composition and properties will be hereafter described.

From this substance I have succeeded in preparing two definite compounds. One of these is the liquid pure perchloric acid, $\text{Cl O}_4 \text{ H}$, an interesting body which was previously unknown; and the other is the monohydrated or crystallized acid, $\text{Cl O}_4 \text{ H} + \text{H}_2 \text{ O}$, originally discovered by Serullas, but obtained by him in such small quantities that he was unable to determine its composition.

If aqueous perchloric acid be distilled with four times its volume of oil of vitriol containing 98.5 per cent. of real acid, decomposition begins at a temperature of about 110° C. ; dense white fumes are evolved and escape, whilst a yellowish, mobile, easily condensible liquid is found in the receiver. If the distillation be continued, the temperature gradually rises to 200° C. , and a thick oily liquid distils over, which, on coming into contact with the more volatile liquid in the receiver, immediately unites with it, forming a white, solid, crystalline mass. Both the first and the last portions of the distillate thus prepared were found to contain sulphuric acid mechanically carried over, and were therefore unfit for analysis. In order to obtain the substances in a pure state, the crystallized acid thus prepared requires redistillation. Heated, however, to a temperature of 110° C. , the crystals themselves undergo a decomposition similar to that just described, a strongly fuming volatile liquid first distilling over, and the

oily acid appearing in the neck of the retort when the temperature rises to 203°C ., and producing crystals on coming in contact with the first distillate. These crystals are likewise formed when water is added to the volatile liquid ; and this is, in fact, the best mode of preparing them in the pure state.

1. *Perchloric Acid*, ClO_4H .

Pure perchloric acid may be obtained in quantity by the process above described, or, more easily, according to the following method. Perchlorate of potassium is distilled together with four equivalents of strong sulphuric acid, until the drops of distillate no longer solidify on falling into the receiver ; in this way 100 grammes of perchlorate yield 14 grammes of crystallized perchloric acid containing traces of sulphuric acid. The impure crystals are then melted, placed in a small bulb-retort, and gently heated. Ebullition commences at 110°C ., and the decomposition continues for some time without further aid of heat ; dense white fumes, accompanied by small quantities of chlorine, issue from the mouth of the apparatus, and a mobile, easily condensible, heavy liquid is found in the receiver. This liquid is pure perchloric acid, ClO_4H , which, if the distillation has been conducted slowly, is perfectly colourless, but often has a slightly yellow colour, owing to the presence of lower oxides of chlorine. As soon as the first appearance of crystals in the neck of the retort is noticed, the distillation is stopped. The liquid distillate should then be at once sealed up in a bulb with long capillary ends, out of which any wished-for quantity may be obtained at pleasure. The greatest care is necessary in working with this body, owing to its explosive and corrosive properties.

The composition of the liquid thus prepared was determined in two ways : in the first place, by the estimation of the quantity of the potassium salt which a given weight of the acid yielded, as also of the quantity of chlorine, oxygen, and potassium which this salt contained ; and secondly, by estimation of the quantity of barium needed to form a neutral salt with a given weight of the acid. As the acid on exposure to the air absorbs moisture with the greatest avidity, producing the crystals, it is necessary that the acid for analysis should be quickly sealed up in weighed bulbs.

Analysis No. 1.—0.7840 gram. of pure perchloric acid, prepared as

last described, was mixed with water and neutralized by an excess of pure carbonate of potassium prepared from the tartrate. Acetic acid was then added to the acid reaction, and the whole evaporated to dryness on the water-bath. Treated with absolute alcohol, the insoluble* perchlorate was thrown upon a weighed filter, and completely freed from soluble acetate by washing with absolute alcohol. The weight of perchlorate of potassium obtained was 1.080 grm.; hence the liquid contained 0.7837 grm. of $\text{ClO}_4 \text{H}$, or 99.93 per cent. Of this potassium-salt, 0.9915 grm. lost, on heating in a long test-tube with pure peroxide of iron, 0.457 grm.; and the chlorine in the residual chloride of potassium required 0.7683 grm. of pure silver for complete precipitation.

Analysis No. 2.—A portion of acid prepared on another occasion gave the following results. Weight of acid taken 1.2185 grm.; weight of dry potassium-salt obtained 1.6785 grm.: of this salt 0.9660 grm., heated with peroxide of iron, lost 0.4440 grm., and the residual chloride required 0.7440 grm. of pure silver for complete precipitation. 0.3165 grm. of the same perchlorate yielded, on treatment with strong sulphuric acid, 0.2010 grm. of sulphate of potassium. Hence the liquid contained 1.2179 grm., or 99.95 per cent. of $\text{ClO}_4 \text{H}$.

Analysis No. 3.—0.3155 grm. of pure acid was diluted with water and treated with an excess of freshly precipitated carbonate of barium. On filtering and washing, the barium in the filtrate was estimated as sulphate, of which salt 0.3660 grm. was obtained, showing that the substance contained 0.3157 grm., or 100.06 per cent. of $\text{ClO}_4 \text{H}$.

Composition of Potassium-Salt obtained from acid.

			Found.	
			No. 1.	No. 2.
Cl	35.5	25.62	25.48	25.37
O ₄	64.0	46.17	46.09	46.24
H	39.0	28.21		28.51
	138.5	100.00		100.12

* It was found that 2 grms. of pure perchlorate of potassium, after washing with 100 cub. cent. of absolute alcohol containing a trace of acetate in solution, and then with 50 cub. cent. of pure alcohol, lost $\frac{8}{10}$ of a milligramme.

Perchloric acid is a heavy, colourless, volatile liquid, which does not solidify at temperatures above -35°C . At $15^{\circ}\cdot 5\text{C}$. the specific gravity of the liquid was found to be 1.782 as a mean of two determinations. The vapour of perchloric acid is colourless and transparent; but when brought into contact with the air, dense masses of white fumes of hydrated acid are given off, owing to rapid absorption of atmospheric moisture. Perchloric acid does not give up its oxygen to metals at the ordinary temperature as readily as nitric acid; but when heated with finely divided iron, copper, zinc, &c., the oxides of these metals are formed, with evolution of light and heat; sulphur and phosphorus are likewise at once converted into their highest oxides in presence of this acid. It is, however, when brought into contact with a carbonized material that the energy of the oxidizing action of perchloric acid becomes visible, as a single drop of this substance falling upon charcoal, paper, or wood, causes an explosive combustion which in violence does not fall far short of the detonation produced by the sudden decomposition of the chloride of nitrogen. Dropped into ether or alcohol, an explosion occurs violent enough to break in pieces the vessel containing the liquid. This latter decomposition may possibly be owing to the formation of the explosive body, described by Messrs. Hare and Boyle as the perchlorate of ethyl. Perchloric acid likewise combines with the greatest energy with water, causing a loud hissing noise, and forming either the crystallized or the oily acid, according to the relative quantities of water and acid present. In working with this substance the greatest care must be taken, as one drop falling upon the skin produces powerful cauterization, and leaves a wound which does not heal for weeks. Like nitric acid, NO_3H , which in many respects it closely resembles, perchloric acid cannot be distilled by itself under the ordinary atmospheric pressure without undergoing decomposition. The colourless liquid, when gently heated, begins to decompose at 75°C ., the temperature gradually rising to 92° , at which point it remains constant for some time, gives off dense white fumes, and quickly turns to a dark blackish-brown colour, large quantities of a yellow gas having the peculiar sweetish smell of chloric oxide being evolved. After some time drops of a dark-coloured liquid, resembling bromine in appearance, distil over, the decomposition continuing in the retort; this dark liquid contained 94.77 per cent. of ClO_4H . On continuing the distillation

the decomposition became more rapid, and a sharp explosion occurred; the receiver was broken to fragments, whilst the residual liquid in the retort became colourless, and, on cooling, solidified to a crystalline mass which contained 87·76 per cent. of ClO_4H . I propose to investigate the composition and mode of formation of this singular body at a future time; it may possibly prove to be the black explosive substance described by Millon* as produced by the action of organic matter on the so-called chloroperchloric acid. Perchloric acid likewise undergoes spontaneous decomposition at the ordinary atmospheric temperature, even when not exposed to light. The liquid, which when freshly prepared has a slight yellow colour, changes to a deep brown colour when kept in the dark for a few days; and after the lapse of about a fortnight the bulbs containing the acid are found to have exploded. Hence it is impossible to preserve pure perchloric acid for any length of time; it must be prepared when required from the crystallized acid.

2. *Perchloric Monohydrate*, $\text{ClO}_4\text{H} + \text{H}_2\text{O}$.

The first hydrate of perchloric acid is the solid crystalline substance discovered by Serullas, and supposed by some chemists to be the anhydride†.

It is best prepared in the pure state by carefully adding water to perchloric acid; great heat is thereby evolved, and the crystals which form on cooling generally possess a slight yellow colour, which rapidly disappears when they are exposed to sunlight.

By partially melting the crystals several times, and separating the liquefied portions, the residue was found to be in a fit state for analysis, as is seen by the close approximation of the experimental numbers to the calculated composition in the following determinations.

Analysis No. 1.—Weight of colourless twice recrystallized acid employed 0·6710 gram. Treated according to the method already described, this quantity of crystallized acid yielded 0·7820 gram. of perchlorate of potassium, corresponding to 0·6698 gram. $\text{ClO}_4\text{H} + \text{H}_2\text{O}$, or to 84·55 per cent. of ClO_4H . Of this potassium-salt 0·6360 gram. lost by heating 0·2935 gram., and required 0·4925 gram. of silver for complete precipitation.

* Ann. de Chim. et de Phys. sér. 3. t. vii. p. 333.

† Pelouze et Fremy, *Traité de Chimie*, "Acide Perchlorique," t. i. p. 418.

Analysis No. 2.—Another portion of crystallized acid, prepared and purified as above, was analysed with barium; 1·2345 grm. of acid yielded, according to the second method already described, 1·2155 grm. of sulphate of barium, corresponding to 1·2363 grm. of the monohydrate, or to 84·89 per cent. of $\text{ClO}_4\text{H} + \text{H}_2\text{O}$.

The following gives the results of the analyses:—

(a) *Composition of Crystallized or Monohydrated Perchloric Acid.*

		Calculated.	Found.	
			I.	II.
ClO ₄ H	100·5	84·80	84·55	84·89
H ₂ O	18·0	15·20		
	<u>118·5</u>	<u>100·00</u>		

(b) *Composition of the Potassium-Salt obtained from the crystallized acid*

		Calculated.	Found.
Cl	35·5	25·62	25·45
O_4	64·0	46·17	46·15
K	39·0	28·21	
	138·5	100·00	

The monohydrate of perchloric acid solidifies at the ordinary temperature to long silky needle-shaped crystals, which fume strongly in the air, most rapidly absorbing moisture, and immediately deliquescent on exposure. Placed in a thin bulb in a water-bath, the liquefied acid was found to freeze between $49^{\circ}\cdot 5$ and $50^{\circ}\cdot 0$ C., whilst the crystals melted between $50^{\circ}\cdot 0$ and $51^{\circ}\cdot 0$ C.; hence the melting- and freezing-points of this substance lie within a few tenths of 50° C. The specific gravity of the liquid monohydrate at 50° C. is 1·811; but the solid acid is considerably heavier, owing to the large contraction which the liquid undergoes on freezing. As has been described, the monohydrate splits up on heating into real perchloric acid and a less volatile aqueous acid; it therefore possesses no definite boiling-point. Heated to 110° C., the melted crystals enter into rapid decomposition, which, when once commenced, continues for some time, even when the thermometer sinks to 95° ; on further application of heat, the liquid becomes of a dark yellowish-brown colour, ebullition continues, and the temperature gradually

risers to 203°C ., at which point the mercury remains stationary, the colourless oily acid passing over unchanged.

Although not so violent in its action on organic matter as the pure acid, the fused monohydrate, when brought into contact with wood or paper, induces immediate combustion; and when dropped into water it combines with a hissing noise, forming the aqueous acid.

3. *Aqueous Perchloric Acid.*

There is certainly no other known acid in which the acid and the hydrates differ so widely from each other in their properties as is the case with perchloric acid,—the acid itself being a strongly fuming, volatile liquid, acting in a most violent manner on organic substances, and closely resembling nitric acid, whilst the monohydrate is a solid crystalline body, and the higher hydrates oily liquids having high boiling-points, being devoid of smell, and in outward appearance bearing a striking analogy to oil of vitriol.

When pure aqueous perchloric acid is concentrated by evaporation until white fumes are evolved, an acid is obtained on distillation which boils at a constant temperature (about 203°C .), and has a constant composition. The strength of such a residual acid was determined by volumetric analysis with a standard solution of soda; it was found to contain 71.6 per cent. ClO_4H . As a control analysis, 0.6550 gm. of the same acid was neutralized by carbonate of barium, and yielded 0.5435 gm. of sulphate of barium, corresponding to 71.57 per cent. HClO_4 . Of this acid 25 cubic centims. was placed in a retort and distilled until three-fourths of the liquid had passed over; analysis with soda and with barium showed that it contained 72.18 per cent. HClO_4 .

The residual acid boiling at 203°C . left in the retort after distilling the solid monohydrate was found to possess a composition identical with the foregoing. Thus 1.1385 gm. of such residual acid yielded 1.136 gm. of perchlorate of potassium, corresponding to 72.4 per cent. HClO_4 ; and 0.954 gm. of the same acid furnished 0.7995 gm. of sulphate of barium, or contained 72.28 per cent. HClO_4 . It is thus evident that an acid containing less HClO_4 than 72.3 per cent. loses water, whilst an acid stronger than this loses real acid on distillation; so that both liquids yield a residual acid possessing a constant composition of 72.3 per cent. HClO_4 , and

boiling at 203° C. This per-centage corresponds, however, to no definite hydrate of simple atomic composition; an acid having the formula $\text{H ClO}_4 + 2(\text{H}_2\text{O})$ containing 73.63 per cent. H ClO_4 . Aqueous perchloric acid follows, therefore, the same general relations respecting composition and boiling-point which I have shown hold good for so many aqueous acids*; namely, that the phenomena of constant composition and fixed boiling-point are in the above cases dependent mainly upon physical rather than upon chemical attractions. The specific gravity was found to be 1.709 at 11° C.

The reactions of aqueous perchloric acid have been sufficiently studied by other observers.

To the foregoing description of the properties of perchloric acid and its hydrates, I have to add the following analyses of a few of the salts of this acid which have hitherto not been examined. These analyses serve to confirm the fact that the estimation of perchloric acid by precipitation as potassium-salt in alcoholic solution is in accuracy second to few of the most exact methods of quantitative determination.

(1) *Perchlorate of Ammonium*, NH_4ClO_4 .

This compound is one of the very few non-deliquescent salts of perchloric acid. It is anhydrous and isomorphous, as Mitscherlich has shown with the potassium-salt. The ammonium was estimated as the double potassium-salt, and the perchloric acid as potassium-salt insoluble in absolute alcohol. Analysis gave:—

	Calculated.	Found.
NH_4 18.0	15.32	15.43
ClO_4 99.5	84.68	84.63
	<hr/> 117.5	<hr/> 100.06

(2) *Ammonio-perchlorate of Copper*, $2(\text{NH}_4)\text{O Cu ClO}_4$.

This salt is anhydrous, and was obtained in dark-blue crystals, which on exposure to air turn green, but do not deliquesce. It is best prepared by dissolving carbonate of copper in dilute perchloric acid, and adding an excess of ammonia. The crystals are readily obtained by pouring a layer of strong alcohol on to the surface of the

* Roscoe, Chem. Soc. Quart. Journ. vol. xiii. p. 146.

aqueous solution. The salt is decomposed on boiling the solution, half the ammonia being liberated, and oxide of copper precipitated: this decomposition serves as a mode of determining the constitution of the salt, which must be considered to be $\text{NH}_4\text{ClO}_4 + \text{NH}_4\text{CuO}$. The total quantity of ammonia contained in the salt was likewise directly determined; the perchloric acid being, as before, weighed as potassium-salt.

		Found.		
		I.	II.	III.
Cu	31.7	17.00	17.17
$2(\text{NH}_4)\text{O}$	52.0	27.98	28.30	
ClO_4	99.5	54.73	54.21
	<u>183.2</u>	<u>100.00</u>	<u>99.71</u>	

(3) *Ferrous Perchlorate*, $\text{FeClO}_4 + 3\text{H}_2\text{O}$.

This salt is obtained by dissolving metallic iron in aqueous perchloric acid; it is highly deliquescent, it does not lose water at 100°C ., and when heated above that temperature it is decomposed. The small greenish-white crystals obtained by concentrating the solution were dried *in vacuo* over sulphuric acid. Analysis gave:—

		Found.		
		I.	II.	III.
Fe	28.0	15.41	15.75	15.53
ClO_4	99.5	54.55	55.47	54.56
$3\text{H}_2\text{O}$	54.0			
	<u>181.5</u>	<u>100.00</u>		

(4) *Mercurous Perchlorate*, $\text{Hg}_2\text{ClO}_4 + 3\text{H}_2\text{O}$.

Mercurous perchlorate is a highly deliquescent salt, obtained by dissolving black oxide of mercury in dilute perchloric acid. It does not lose water either at 100°C ., or *in vacuo* over sulphuric acid.

		Found.	
		I.	II.
Hg_2	200.0	56.57	56.63
ClO_4	99.5		
$3\text{H}_2\text{O}$	54.0		
	<u>353.5</u>	<u>100.00</u>	

(5) *Perchlorate of Lead*, $2(\text{Pb ClO}_4) + 3\text{H}_2\text{O}$.

Perchlorate of lead is an extremely deliquescent salt; it is best prepared by dissolving carbonate of lead in perchloric acid. The salt may be dried *in vacuo* over sulphuric acid without losing water.

		Found.	
		I.	II.
2Pb 207·0	45·00	44·82
2ClO ₄ 199·0	43·26	44·74
3H ₂ O 54·0	11·74	42·22
	<u>460·0</u>	<u>100·00</u>	

I desire to acknowledge the able assistance I have received from M. Schorlemmer in carrying out the above experiments.

December 19, 1861.

In consequence of the lamented Death of His Royal Highness The Prince Consort, no Meeting took place.

January 9, 1862.

Major-General SABINE, President, in the Chair.

The President, on the part of the Council, submitted to the Meeting the following Address of Condolence to be presented to the Queen:—

WE, YOUR MAJESTY'S most dutiful and loyal subjects, the President, Council, and Fellows of the Royal Society of London for improving Natural Knowledge, desire humbly to offer to YOUR MAJESTY the sincere expression of our sorrow for the irreparable loss which YOUR MAJESTY and the nation have sustained by the death of HIS ROYAL HIGHNESS THE PRINCE CONSORT.

While we deeply share in the universal lamentation which this great calamity has called forth, we claim the mournful privilege of giving expression to our special grief for the loss of a Prince who, to his other high qualities and claims to the nation's esteem and gratitude, united a just appreciation of the importance to mankind