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# PERCHLORIC ACID

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## 1. INTRODUCTION

Perchloric acid $HClO_4$ differs substantially from other inorganic oxyacids in many respects, for example the volatility of anhydrous perchloric acid, its instability on storage, especially above room temperature, the difference in properties between the anhydrous acid and its hydrates.

Anhydrous perchloric acid contains more than 63% of available oxygen, *i.e.* oxygen which can be used in the oxidation of various reductants or liberated as gas.

This determines the value of perchloric acid as an oxidant, its oxidising properties being maintained on slight dilution of the acid with water. A diminution in the concentration of perchloric acid affects its redox potential far more rapidly than in the case of nitric acid.

Perchloric acid finds varied application both in industry and in the laboratory, for example in the electrolytic polishing of metals, as catalyst for hydrolysis or esterification and various rearrangements in organic compounds. It is used also, instead of or in addition to nitric and sulphuric acids, in wet combustion in quantitative organic analysis, to break down complicated minerals and ores in their quantitative analysis, etc.

Although perchloric acid has been known for more than 150 years, it has not yet been adequately investigated.

## 2. BRIEF HISTORICAL OUTLINE

Perchloric acid was discovered by Stadion in 1816.[1,2] On treating the product obtained by the cautious fusion of potassium chlorate with sulphuric acid, he found that the residue left after removal of excess of the acid, contained, in addition to potassium sulphate, the potassium salt of a new, hitherto unknown acid. Analysis of this salt showed its oxygen content to be 45.92%, its composition corresponding to the formula $KClO_4$.

Stadion found that this salt can be obtained also by the anodic oxidation of potassium chlorate, for which purpose he used a battery of twenty voltaic cells. On heating the new salt with three parts by weight of sulphuric acid containing 30% of water, he obtained in the distillate a fraction consisting of an aqueous solution of a new acid, which he termed "oxychloric" acid; later the name "perchloric acid" was applied to it. Stadion showed that it can be obtained also by the electrochemical oxidation in aqueous solution of chlorine dioxide, which he had discovered.

The preparation of perchloric acid by Stadion's method is seen to be based on the reactions

$$4KClO_3 = 3KClO_4 + KCl;$$

$$KClO_4 + H_2SO_4 + aq. = KHSO_4 + HClO_{4aq}.$$

Sérullas reported[3] that attempts to obtain perchloric acid by Stadion's method invariably terminated in explosions, which he attributed to the explosive decomposition, under the experimental conditions, of chloric acid formed from potassium chlorate by the action of sulphuric acid. Sérullas probably had not noticed that Stadion had treated the chlorate after fusion, *i.e.* actually the perchlorate obtained from the chlorate, with sulphuric acid. This suggestion is supported by the fact that, in another paper[4] and also in a German translation thereof[5], Sérullas reported his discovery of the conversion of chlorate into perchlorate on careful fusion.

Hence Sérullas assumed that in Stadion's method the perchloric acid is formed, not from the perchlorate by the action of sulphuric acid, but from chloric acid. It may be supposed that it was precisely this erroneous interpretation of Stadion's process that led Sérullas to develop a new method for obtaining perchloric acid. The method is based on the gradual decomposition of chloric acid when its solutions are concentrated by evaporation under any conditions. Decomposition of chloric acid occurs when its concentration reaches a critical value, above which the acid cannot exist. The process is completed by distilling off the water present in the system and then distilling over the perchloric acid in the form of an azeotrope.

Sérullas was also able to obtain a "solid perchloric acid"[6]. This was done on distilling a mixture of the constant-boiling perchloric acid (azeotrope) and sulphuric acid in the proportions 1 : 4–5 by volume. A mixture of the solid and liquid forms of perchloric acid passed into the distillate. Sérullas was unable to isolate the pure solid acid from this mixture, and hence did not establish its composition.

To Sérullas belongs the honour of introducing the use of perchloric acid for the quantitative determination of potassium in the presence of other cations[7]. This analytical method is based on the extremely low solubility of $KClO_4$ in alcohol.

The following rather clumsy procedure was suggested by Henry[8] for the preparation of perchloric and chloric acids. A solution of $ZnSiF_6$ is first obtained by the interaction of ZnO and $H_2SiF_6$, and this is then heated with $KClO_4$ or $KClO_3$ respectively to give $Zn(ClO_4)_2$ or $Zn(ClO_3)_2$ in solution, which with aqueous $Ba(OH)_2$ gives a solution of $Ba(ClO_4)_2$ or $Ba(ClO_3)_2$. Finally, the action of an equivalent amount of dilute sulphuric acid on these solutions yields aqueous perchloric or chloric acid.

Nativelle published[9] a more convenient recipe for obtaining perchloric acid by Stadion's method. Kolbe[10] reported the preparation of perchloric acid by the electrochemical oxidation of hydrochloric acid, and this possibility was confirmed a little later by Riche[11]. Subsequently, especially during recent years, this method of obtaining perchloric acid has formed the subject of many patents issued in various countries. At the present time it is used to produce perchloric acid industrially.

After Stadion and Sérullas the most important results were obtained by Roscoe[12–14], who found that perchloric acid obtained by the evaporation of dilute aqueous solutions until dense white fumes appeared had a constant boiling point of 203° and remained unchanged in composition on being distilled. He proved that the solid perchloric acid discovered by Sérullas was a monohydrate of the acid $HClO_4.H_2O$.

To Roscoe is due also to the credit of discovering anhydrous perchloric acid, which he obtained by distilling a mixture of the constant boiling perchloric acid and 98.5% sulphuric acid in the proportions 1 : 4 by volume. According to him, a mobile yellowish liquid begins to pass into the receiver at 110°, but on continued distillation the temperature gradually rises to 200°, and a thick oily liquid begins to enter the receiver, this giving a white crystalline mass on contact with the more volatile portion of the distillate.

It was established that the readily volatile mobile liquid was anhydrous perchloric acid; while the involatile oily

liquid was a constant-boiling acid of composition approximating to a dihydrate of the acid $HClO_4.2H_2O$. The anhydrous acid and the dihydrate react to give the monohydrate, a crystalline solid.

Hence formation of the monohydrate takes place according to the equation

$$HClO_4 + HClO_4 \cdot 2H_2O = 2HClO_4 \cdot H_2O \ .$$

Roscoe found that the reverse reaction takes place above 110°: *i.e.* the anhydrous acid and the dihydrate are formed from the monohydrate. He regarded this latter method of obtaining anhydrous perchloric acid as the better, since the monohydrate, being completely stable on storage, makes it possible to obtain the unstable anhydrous acid at any time.

The oxidation of ammonium perchlorate with a mixture of nitric and hydrochloric acids, reported by Schloesing [15], must also be mentioned. He suggested using the free perchloric acid obtained from the $NH_4ClO_4$, without isolating it from the solution, for the quantitative determination of potassium by Sérullas' method [7]. Later this reaction was employed by Willard [16] to obtain the azeotrope of perchloric acid from ammonium perchlorate.

Kreider [17] suggested obtaining the azeotrope by the double decomposition of sodium perchlorate and fuming hydrochloric acid:

$$NaClO_4 + HCl \rightleftarrows HClO_4 + NaCl.$$

The equilibrium is shifted to the right owing to the limited solubility of NaCl in this system. After removal of the bulk of the NaCl, the perchloric acid is obtained from the reaction as an aqueous solution, and freed from salts and water by distillation.

Vorländer and Schilling [18] found that, when a mixture of $KClO_4$ and 96–97% $H_2SO_4$ is heated in a vacuum, anhydrous perchloric acid at once distils over, not its hydrates as found by Roscoe and his predecessors, who had carried out the distillation of perchloric acid under atmospheric pressure. Michael and Conn [19] also suggested the use of a vacuum in the distillation.

Smith [20] suggested the use of oleum to remove water from the azeotrope and thus obtain the anhydrous acid. This resulted in a mixture of the latter with sulphuric acid, from which the perchloric acid was isolated by distilling it off in a vacuum. Zinov'ev [21] proposed to carry out this unsafe operation in a continuous-flow apparatus consisting essentially of a slightly inclined externally heated tube. The mixture to be separated is fed into one end of the tube, and from the other end the spent sulphuric acid flows out into a receiver, while the perchloric acid vapour escapes through an outlet in the middle of the tube into another, well cooled receiver. The perchloric acid distils off in a vacuum.

The distillation process is completely safe, since only a small quantity of the mixture undergoing separation is present in the hot zone of the apparatus, and also because it remains hot for only a few seconds, considerably less than the induction period for decomposition of the acid.

The anhydride of perchloric acid was first obtained by Michael and Conn [22].

## 3. FORMS OF PERCHLORIC ACID

Perchloric acid is the only oxyacid of chlorine which can exist in the anhydrous state, although it is unstable in this form. Even at room temperature, only a few hours after being prepared, it begins to decompose, at a rate which increases with time. Being extremely hygroscopic, perchloric acid vigorously adds on water to form several hydrates. The monohydrate $HClO_4.H_2O$ was discovered by Sérullas [6], but its composition was established by Roscoe [12], who obtained data indicating the existence of a dihydrate $HClO_4.2H_2O$ as well. The chief properties of the dihydrate were studied by van Wijk [23,24], who also discovered and characterised the higher hydrates of perchloric acid.

Fig. 1 shows the melting-point diagram constructed by van Wijk, and Fig. 2 the part corresponding to high water contents. The maxima in Fig. 1, corresponding to 50.0 and 33.3 mole% $HClO_4$, show the existence in the $HClO_4$–$H_2O$ system of a monohydrate and a dihydrate of perchloric acid, which are only slightly dissociated at their melting points (50° and -17.8° respectively, according to van Wijk).

At the higher water contents the diagram is very complicated (Fig. 2).

Steady crystallisation of the dihydrate (33.3 mole % $HClO_4$) at -17.8° is observed also with rather more dilute perchloric acid, but at an $HClO_4$ content of ~29 mole% the character of the crystallisation depends on the degree and conditions of cooling of the acid. This is evident simply from the fact that the lower part of the right-hand curve representing crystallisation of the dihydrate (Fig. 2) contains three eutectic points, two of which lie in the metastable region.

The hydrate $HClO_4 \cdot 2.5H_2O$ melts at -29.8°, which is very close to the eutectic point of this hydrate with the dihydrate. The temperature at which a eutectic mixture of the two hydrates solidifies is almost the same (-29.8°). The hydrate $HClO_4.3H_2O$ can exist in two forms, the $\beta$ form being metastable throughout its range of existence, and the $\alpha$ form being stable only over a very narrow range of compositions, 23.7–25.0 mole % $HClO_4$. Over the rest of the range the $\alpha$ form is metastable.

The $\alpha$-$HClO_4.3H_2O$ is formed from the $\beta$ form on cooling. The melting point of the $\alpha$ form of the trihydrate is -37°, and its eutectic with the dihydrate crystallises at -39.4°.

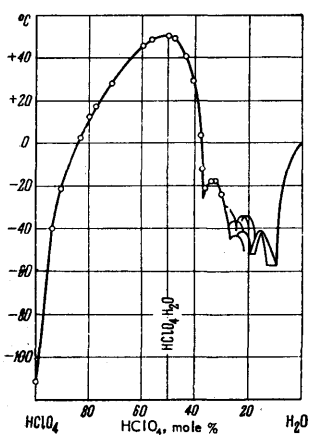



Fig. 1. Melting-point diagram for the perchloric acid–water system over the concentration range 0–100% $HClO_4$. [24]

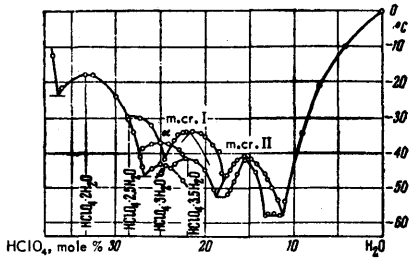



Fig. 2. Melting-point diagram of the perchloric acid–water system over the concentration range 0–36 mole % $HClO_4$.[24]

To the left of its maximum the curve for $\beta$-$HClO_4.3H_2O$ joins the dihydrate curve at the eutectic point having a crystallisation temperature of -46.5°, which is the final temperature of crystallisation of perchloric acid containing rather less than 29 mole% $HClO_4$. To the right of the extreme point of stable existence of the $\alpha$ form of the trihydrate its liquidus curve enters the region of mixed crystals I, in relation to which $\alpha$-$HClO_4.3H_2O$ is metastable.

The hydrate $HClO_4.3.5H_2O$ crystallises poorly, only after prolonged cooling, and always from the vitreous state. For this reason, van Wijk did not analyse this hydrate. For the same reason its melting point was not determined exactly (about -41°).

The liquidus curve of $HClO_4.3.5H_2O$ covers the range of compositions from 23.8 to 18.8 mole% $HClO_4$, where it intersects the liquidus of the mixed crystals II at -52.5°. The hydrate $HClO_4.3.5H_2O$ forms a eutectic with $\beta$-$HClO_4.3H_2O$ crystallising at -44.3°. This and also the fact that the hydrate $HClO_4.3.5H_2O$ remains in a metastable state below the curve for the mixed crystals I throughout its range of existence do not inspire complete confidence in the existence of the hydrate $HClO_4.3.5H_2O$, as van Wijk himself pointed out[24].

Van Wijk was unable to separate the mixed crystals I from the liquid phase, and so he was unable to analyse them. The liquidus of this phase extends from 24.6 to 17.7 mole% $HClO_4$, so that on the left-hand side this curve approaches from below the liquidus curve of the hydrate $\alpha$-$HClO_4.3H_2O$.

The mixed crystals II were also investigated very tentatively. Their liquidus extends from 17.7 to 11.6 mole% $HClO_4$. Kurnakov[25] noted the existence of berthollide phases in these mixed crystals.

When an acid containing less than 11.3 mole% $HClO_4$ is cooled, crystals of ice separate. The crystallisation curve for water intersects that for the mixed crystals II at -58.0°.

Thus according to van Wijk the hydrates of perchloric acid are characterised by the following melting points:

| | |
|---|---|
| $HClO_4.H_2O$ | 50° (according to Smith[26] 49.905°) |
| $HClO_4.2H_2O$ | −17.8° |
| $HClO_4.2.5H_2O$ | −29.8° |
| $HClO_4.3H_2O$: | |
| $\alpha$ form | −37° |
| $\beta$ form | −43.2° |
| $HClO_4.3.5H_2O$. | −41.4° |

## 4. PROPERTIES OF PERCHLORIC ACID HYDRATES

According to Berthelot[27], the heat of solution of anhydrous perchloric acid is $L_{600}^{13°} = 20.3$ kcal mole$^{-1}$. This value is inexact, since Berthelot did not work with the completely anhydrous acid. Krivtsov *et al.*[28] determined the heats of solution of perchloric acid over the concentration range 21–100 mole% $HClO_4$. They give a table and a graph showing the dependence of the heat of solution on the initial acid concentration (Fig. 3).

The heats of solution $L_{800}^{25°}$ of the anhydrous acid, the monohydrate, and the dihydrate are[28] 21.15 ± 0.04, 7.81 ± ± 0.04, and 5.43 ± 0.04 kcal mole$^{-1}$ respectively. Therefore the enthalpy of hydration of anhydrous perchloric acid to the monohydrate is $\Delta H_{25} = -13.34 \pm 0.07$ kcal mole$^{-1}$, and that to the dihydrate is -15.72 ± 0.07 kcal mole$^{-1}$.

The heat of fusion of the monohydrate of perchloric acid is[28] 2.48 ± 0.08 kcal mole$^{-1}$.

The density and the viscosity of perchloric acid up to 70% concentration have been studied by many investigators, beginning with Roscoe[12] and van Wijk[24], and including Reyher[29], van Emster[30], Brickwedde[31], Clark and Putmann[32], Garret and Woodruff[33], Simon and Weist[34], Simon and Richter[35], and also Smith and Goehler[26].

The density has been determined over the whole range of concentrations only by van Wijk[24] (at 20° and 50°) and by Zinov'ev and Babaeva[36] (at 20°, 55°, and 75°, Fig. 4).

As can be seen from Fig. 4, the density of perchloric acid increases on hydration, reaching a maximum with the monohydrate. Since this occurs in the liquid state, the high density of the monohydrate must be assumed to depend on peculiarities of its molecular structure. It must be noted in this connection that the volume of water in the monohydrate of perchloric acid, found as the difference in molar volume between the monohydrate and the anhydrous acid, is only ~7.5 compared with 12–15 cm$^3$ mole$^{-1}$ in the hydrates of other acids and various salts.

It must be borne in mind that no free water is present in concentrated perchloric acid. If the acid concentration exceeds 84.8%, the whole of the water is present as the

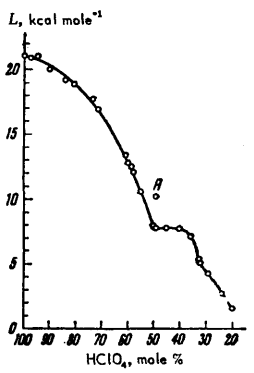



Fig. 3. Heat of solution in the perchloric acid–water system[28].

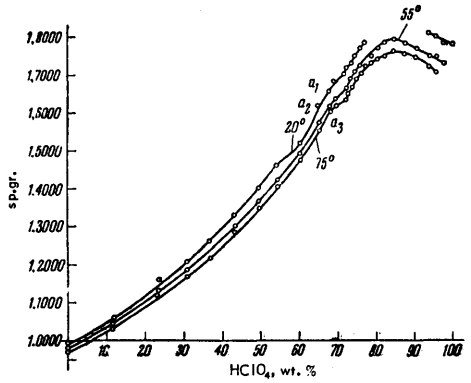



Fig. 4. Density isotherms (at 20°, 55°, and 75°) for the perchloric acid–water system [36].

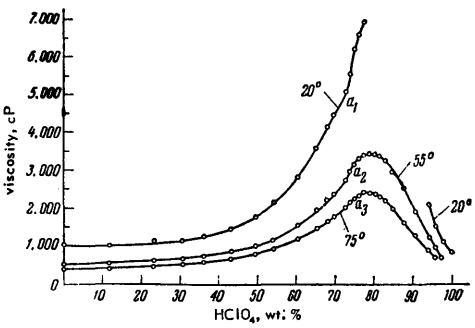



Fig. 5. Viscosity isotherms (at 20°, 55°, and 75°) for the perchloric acid–water system [36].

monohydrate, and such a specimen consists of the anhydrous acid and the monohydrate. When concentrated perchloric acid is strongly cooled, the monohydrate which it contains separates as a solid phase.

The viscosity of perchloric acid has been determined over the whole concentration range only by van Wijk [24], Simon and Weist [34], and Zinov'ev and Babaeva [36]. The graphs (Fig. 5) show that maximum viscosity occurs below the concentration than corresponding to the monohydrate. At 50° maximum viscosity occurs [35] with the 80% acid, at 55° with the 79% acid [36], and at 75° with 78% of perchloric acid [36]. The shift in maximum viscosity can be explained by an increasing degree of disproportionation of the monohydrate with rise in temperature:

$$2HClO_4 \cdot H_2O \rightleftarrows HClO_4 + HClO_4 \cdot 2H_2O.$$

## 5. MOLECULAR STRUCTURE OF PERCHLORIC ACID HYDRATES

The very considerable difference in properties between anhydrous perchloric acid and its monohydrate has led to a detailed study of their molecular structure.

Volmer [37] found that the X-ray diffraction pattern of crystals of the monohydrate was identical with that of ammonium perchlorate $NH_4ClO_4$. This led to the conclusion that the monohydrate, like the perchlorate, has an ionic structure, *i.e.* that it is oxonium perchlorate $H_3OClO_4$. Crystals of oxonium perchlorate have an orthorhombic structure with lattice constants $a = 9.065$, $b = 5.569$, and $c = 7.339$ Å.

Fonteyne [38], Simon [39], Redlich *et al.* [40], Simon and Weist [34], Millen and Vaal [41], and Mullhaupt and Hornig [42] investigated the Raman spectra of perchloric acid and found all the principal frequencies both of the perchlorate ion and of the pseudo-acid form of perchloric acid.

Richards and Smith [43] and at the same time, but independently, a Japanese group [44–46] employed proton magnetic resonance to study the structure of the monohydrate of perchloric acid. Lee and Carpenter [47] used an X-ray method for the same purpose, and Bethell and Sheppard [48] applied infrared spectroscopy.

The spectra of solutions containing less than 77% $HClO_4$ contain [34] lines at 460, 625, 928, and 1120 $cm^{-1}$. These frequencies coincide with the same lines in the Raman spectra of solutions of the salts. Hence the above frequencies are due to the perchlorate ion $ClO_4^-$, and at concentrations below 77% $HClO_4$ perchloric acid is entirely in the aci-form $H[ClO_4]$.

When the acid concentration is raised above 85% (the monohydrate contains 84.8% of $HClO_4$), new lines appear in the spectrum, their intensity increasing with increase in the acid concentration. At the same time the $ClO_4^-$ lines become less intense. Above a concentration of 99% the latter lines disappear, and only those of the pseudo-acid form of perchloric acid remain: 284, 424, 577, 740, 1001, and 1210 $cm^{-1}$, and also a line at 3300 $cm^{-1}$.

These results obtained by Simon and Weist were confirmed by later work. Thus Millen and Vaal [41] published a table of frequencies due to $ClO_4^-$, $H_3OClO_4$, and anhydrous $HClO_4$. The spectra were determined at -185°. The frequencies which they found differed little from those obtained earlier [34].

Mullhaupt and Hornig [42] obtained data showing that the spectrum of perchloric acid monohydrate contains two bands, one at 1500–1690 $cm^{-1}$ and the other at 2400–3600 $cm^{-1}$. These bands were assigned to the oxonium ion ($H_3O^+$).

Taylor and Vidale [49] published more exact data, assigning to the oxonium ion the frequencies 1175 ± 2, 1577 ± 5, 3100 ± 50, and 3285 ± 10 $cm^{-1}$ at 20°. Among those assigned by Simon and Weist [34] to the anhydrous acid was also 3300 $cm^{-1}$, as mentioned above. It follows from Taylor and Vidale's work that this frequency is due to the oxonium ion, which must therefore be present in anhydrous perchloric acid. This was established too by Richards and Smith [43], and also by the group of Japanese workers [44–46]. The oxonium ion was found to have a pyramidal structure, in which the O–H distances were 1.02 Å and the H–H distances 1.72 Å. Below -123° the oxonium ion is fixed in the lattice, but above this temperature it acquires an additional degree of freedom.

Lee and Carpenter [47] confirmed that the $ClO_4^-$ ion present in oxonium perchlorate is almost exactly tetrahedral, with a mean Cl–O distance of 1.42 Å. Each oxonium ion in the crystal lattice is surrounded by twelve oxygen atoms.

Rosolovskii and Zinov'ev [50] reported the occurrence of polymorphism in oxonium perchlorate. They established that the enantiotropic transition temperature is -24.9°. The high-temperature modification can exist in a supercooled

condition for a long time. The densities of the high-temperature and low-temperature modifications are $d_4^{25^\circ}$ = = 2.095 and 2.040 respectively. Zinov'ev and Babaeva reported[51] that the $H_3OClO_4$–$CH_3COOH$ system contains the compound $H_3OClO_4.2CH_3COOH$. Hence perchloric acid monohydrate (oxonium perchlorate) does not lose water of hydration in anhydrous acetic acid, and behaves as a chemical individual.

The molecular structure of perchloric acid hydrates containing two and more molecules of water has been studied by Michelsen[52]. The length of the Cl–O bond in the $ClO_4^-$ ion in the higher hydrates was determined from the X-ray distribution curve. Its mean value was found to be 1.49 Å, whence it follows that the distance between the oxygen atoms is 2.43 Å. Hydrogen bond formation was found to occur between molecules in melts of the hydrates.

Smith and Goehler[53] put forward the view that the dihydrate of perchloric acid is a monohydrate of oxonium perchlorate:

$$HClO_4 \cdot 2H_2O \longrightarrow H_3OClO_4 \cdot H_2O.$$

They extended this view to the other, higher hydrates. Hence

$$HClO_4 \cdot 2{,}5H_2O \longrightarrow H_3OClO_4 \cdot 1{,}5H_2O,$$
$$HClO_4 \cdot 3H_2O \longrightarrow H_3OClO_4 \cdot 2H_2O,$$
$$HClO_4 \cdot 3{,}5H_2O \longrightarrow H_3OClO_4 \cdot 2{,}5H_2O.$$

In their opinion, the difference between the $\alpha$ and $\beta$ forms of perchloric acid trihydrate is that one represents an ordinary trihydrate $HClO_4.3H_2O$, while the other form is the dihydrate of oxonium perchlorate $H_3OClO_4.2H_2O$. However, these workers gave no adequate grounds in support of this view.

## 6. VOLATILITY OF PERCHLORIC ACID

Anhydrous perchloric acid is very volatile, but it is impossible to distil it at atmospheric pressure owing to decomposition.

The distillation of both anhydrous perchloric acid and its hydrates was described in detail by van Wijk[24]. He found that on prolonged distillation the boiling point of the acid passes through a maximum, regardless of the initial concentration. If acid containing less than 72.4% $HClO_4$ is distilled, the distillate consists initially of water until the concentration of the liquid undergoing distillation reaches 72.4%. The vapour then has the same composition: *i.e.* ultimately an azeotrope of perchloric acid and water is obtained. The same occurs, *i.e.* an azeotrope is formed, when highly concentrated perchloric acid, for example the 100% acid, is distilled. In this case the vapour is a mixture of $HClO_4$ + $Cl_2O_7$, the boiling point of the acid gradually rising, while its concentration gradually falls, tending to the composition of the azeotrope.

Discussing his results on the distillation of perchloric acid, van Wijk concluded: "Concentrated perchloric acid must be regarded as a mixture of the anhydride of perchloric acid and water".

Since water which appears in the presence of 100% perchloric acid will pass into the monohydrate, the above conclusion of van Wijk must be restated: "Concentrated perchloric acid is a mixture containing the anhydride and the monohydrate of perchloric acid". In other words, concentrated perchloric acid is an equilibrium system:

$$3HClO_4 \rightleftarrows Cl_2O_7 + H_3OClO_4. \quad (1)$$

TABLE. Published data on the boiling point of perchloric acid.

| Pressure, mm Hg | B.p., °C | References |
|---|---|---|
| 11 | 19 | 19 |
| 15—20 | 14—17.3 | 30 |
| 18 | 16 | 24 |
| 56 | 39 | 18 |

No systematic investigation has yet been made of the variation of the vapour pressure of perchloric acid with temperature. Isolated data available in the literature are given in the Table.

Application of the Clausius–Clapeyron equation to these data enables an equation to be derived, relating the logarithm of the vapour pressure to the reciprocal of the absolute temperature:

$$\log P\,(\text{mm}) = -\frac{1923}{T} + 7.91. \quad (2)$$

Calculation based on this equation gives the boiling point of perchloric acid under atmospheric pressure as 109°, not 130°, as was found by Hantzsch[54], also by extrapolation. The value obtained for the heat of vaporisation is 8.80 kcal mole$^{-1}$, and for the Trouton constant 23.0.

It must be emphasised that the data in the Table give only a very rough characterisation of perchloric acid.

## 7. PERCHLORIC ACID AS AN ELECTROLYTE

Perchloric acid acts solely as a monobasic acid both in the anhydrous state and in the form of its hydrates, thus differing substantially from, for example, iodic acid, whose hydrates are polybasic acids.

On the basis of conductivity measurements on aqueous solutions of perchloric acid, Ostwald[55] included it among the strongest electrolytes. This has been confirmed many times by other workers. However, it cannot be regarded as sufficient to assess the strength of an acid from the electrical conductivity of its aqueous solutions. Many attempts have therefore been made to employ solvents other than water and also other methods to assess strong acids as electrolytes. One of these methods is based on the measurement of special functions giving an estimate of acidic properties, for example the Hammett function $H_0$ [56] or the similar function $J_0$ (otherwise symbolised as $C_0$ and $H_R$).

Lemaire and Lucas[57], Smith *et al.*[58], and Ludwig and Adams[59] have given values of the Hammett function for solutions of perchloric acid in acetic acid (anhydrous and containing up to 5% of water). It has been shown that in acetic acid perchloric acid behaves as a very strong electrolyte. The same conclusion was reached by Dahn *et al.*[60], who determined the function $J_0$ for solutions of perchloric acid in a mixed solvent (dioxane–water).

Deno *et al.*[61] determined the functions $H_0$ and $H_R$ for aqueous solutions of perchloric and nitric acids over the concentration range 0–60%. Perchloric acid was found to be a stronger electrolyte than nitric acid. A similar result was obtained by Bonner and Lockhart[62].

A common feature of all the measurements of $H_0$, $J_0$, etc. has been the not very high concentration of the samples of perchloric acid examined. Thus Hammett and Deyrup[56] confined their investigations to acid containing 64% $HClO_4$. Bonner and Lockhart[62] examined a higher concentration, 71.3%.

A comparative appraisal of perchloric and nitric acids as electrolytes was given by Redlich[63] on the basis of the Raman spectra and nuclear magnetic resonance. It was established that dissociation in the highly concentrated acid was due to the presence of water, according to the equation

$$H_2O+HClO_4 = H_3O^+ + ClO_4^- .$$

Hood *et al.*[64] showed that three species exist throughout the concentration range, including 100% perchloric acid, these being the pseudo-acid form $[O_3ClOH]$ and the ions $H_3O^+$ and $ClO_4^-$. This is the reason why perchloric acid conducts electricity at all concentrations.

Redlich points out[63] that nitric acid behaves differently: the acid having the composition $HNO_3.H_2O$ undergoes very little dissociation, and the more concentrated acid is practically undissociated. He explains such behaviour by not only the anhydrous acid but even the monohydrate being in the pseudo-acid form $[HNO_3.H_2O]$.

According to Simon and Weist's results[34], 100% nitric acid exists in the pseudo-acid form $[O_2NOH]$ only in the liquid state. Simon and Weist found that the Raman spectrum of the anhydrous acid in the solid state contains practically no $NO_2$ lines, but does contain a strong $NO_3$ line (at ~1050 $cm^{-1}$), and also a characteristic $NO_3$ line at 1400 $cm^{-1}$.

From nuclear magnetic resonance measurements, Redlich[63] obtained the following dissociation constants: $HClO_4$ 38, $HNO_3$ 22, and $CF_3COOH$ 1.8. According to old data, the dissociation constant of nitric acid is 21. It is evident from these results that perchloric acid is a stronger electrolyte than nitric acid.

## 8. PERCHLORIC ACID IN THE FORMATION OF ACIDIUM SALTS

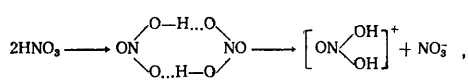
A study of the optical properties of acids made by Schäfer[65] showed that anhydrous nitric acid is similar to its esters but substantially different from its alkali-metal salts in optical properties, and that on dilution with water, nitric acid and its salts become identical in this respect.

This discovery was developed by Hantzsch and his coworkers[66–70], who showed that this property is not specific to nitric acid, but that similar relations are observed with other acids, except those which cannot be studied optically.

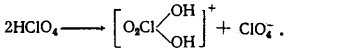
The results led Hantzsch to put forward a theory which postulates that acids exist in two forms, the so-called pseudo-acid form and the true or aci-form.

Measurements showed that nitric, sulphuric, and perchloric acids are able to conduct electricity even in the anhydrous state, *i.e.* in the pseudo-acid form. This indicates the presence of ions, and hence of salts, in anhydrous acids.

Hantzsch explained salt formation in terms of some of the molecules of the anhydrous acid reacting as proton-acceptors, obtaining their protons from the remaining molecules of the same acid, which act as proton-donors. According to this view, these acids undergo self-protonation, for example in the case of nitric acid



and in the case of perchloric acid



Hantzsch wrote the equation for perchloric acid by analogy, since this acid gives no absorption spectra in the ultraviolet, but does possess electrical conductivity.

He suggested[66] the following equations for a mixture of nitric and perchloric acids:

$$HNO_3 + HClO_4 = H_2NO_3^+ + ClO_4^-,$$
$$HNO_3 + 2HClO_4 = H_3NO_3^{2+} + 2ClO_4^- .$$

In support of these equations Hantzsch and Berger[68] reported that the conductance of the substance obtained in the first equation corresponds to a binary electrolyte, while the substance obtained in the second equation has a conductance corresponding to a ternary electrolyte. Furthermore, they found that, on electrolysis of these acidium salts, the nitric acid migrates to the cathode.

A paper by Hughes *et al.*[71] on the kinetics and mechanism of the nitration of aromatic compounds gives data indicating that the nitrating mixture contains high concentrations of $NO_2^+$. However, these workers postulate the existence also of the ion $H_2NO_3^+$ (mentioned by Hantzsch, but only as an intermediate stage), as follows from their equations

$$HNO_3 + H_2SO_4 \rightleftarrows H_2NO_3^+ + HSO_4^-,$$
$$H_2NO_3^+ \rightleftarrows NO_2^+ + H_2O .$$

Thus Hughes *et al.*[71] consider that the ion $H_2NO_3^+$ is unstable, and in $H_2SO_4$ medium readily passes into $NO_2^+$ by splitting off water. The same paper notes the possibility of the formation of $H_2NO_3^+$ even in the absence of sulphuric acid:

$$HNO_3 + HNO_3 \rightleftarrows H_2NO_3^+ + NO_3^-,$$
$$H_2NO_3^+ \rightleftarrows NO_2^+ + H_2O,$$
$$H_2O + HNO_3 = HNO_3 \cdot H_2O,$$

*i.e.* the self-protonation of nitric acid, as indicated by Hantzsch, is admitted.

In revising the results obtained by Hantzsch on acidium salts, Goddard *et al.*[72] prepared various acidium salts containing the $NO_2^+$ cation: $(NO_2^+)(ClO_4^-)$, $(NO_2^+)(HS_2O_7^-)$, $(NO_2^+)_2.(S_2O_7^{2-})$, etc.

The existence of the $NO_2^+$ cation in these salts was proved by numerous spectroscopic investigations by Goddard *et al.*[73], Ingold *et al.*[74,75], and Millen[76–78].

Gillespie made a series of investigations involving cryoscopic measurements on systems in concentrated sulphuric acid. In one of six papers on this topic[79] he gave results for solutions of ammonium perchlorate ($NH_4ClO_4$) and nitryl perchlorate ($NO_2ClO_4$) in sulphuric acid.

In contrast to the results discussed above and to be discussed below, Gillespie found that sulphuric acid is considerably stronger than perchloric acid, which is stronger than pyrosulphuric acid, *i.e.* that the strengths of these acids are in the order

$$H_2S_2O_7 < HClO_4 < H_2SO_4.$$

These views of Ingold, Goddard, and the other English workers differ from those of Hantzsch in assuming the existence, not of hydrated ions $H_2NO_3^+$, $H_3NO_3^{2+}$, etc., but of the ion $NO_2^+$ obtained from them by loss of water, in anhydrous acid systems capable of forming acidium salts. A second difference is that acidium salt formation is accompanied by the production of oxonium perchlorate, for example according to the equation

$$HNO_3 + 2HClO_4 = NO_2ClO_4 + H_3OClO_4.$$

Hantzsch's equations do not provide for the formation of oxonium perchlorate. The presence of $H_3OClO_4$ in the reaction mixtures was demonstrated experimentally by Ingold and others by extracting the oxonium perchlorate with nitromethane.

Simon and Weist[34], who made a thorough study of the Raman spectra of perchloric acid over the concentration range 41–100 wt.% $HClO_4$, found no frequencies which would indicate the existence of the $ClO_4^-$ ion in the 100% acid, whose spectrum showed only lines due to the pseudo-acid form of perchloric acid. On this basis they rejected[34] both Hantzsch's and Ingold's equations. According to Simon and Weist, the conductivity of anhydrous perchloric acid depends on the possible contamination of the acid with moisture during the experiments, the amount being so minute that the monohydrate $HClO_4.H_2O$ formed cannot be detected spectroscopically, although it gives rise to conductivity. However, these workers mentioned also another possible reason for conductivity, which is that perchloric acid decomposes very readily into $Cl_2O_7$ and water, resulting in the formation of oxonium perchlorate, which dissociates in the acid. As a result, Simon and Weist[34] regard Hantzsch's hypothesis of the self-protonation of perchloric acid as incorrect.

Even in mixtures with various acids, perchloric acid forms acidium salts not as a proton-acceptor but solely as a proton-donor. This indicates that it is a stronger electrolyte than the other acids. A possible exception to this principle is pyrosulphuric acid, which gives the compound $(ClO_3^+)(HS_2O_7^-)$, obtained by the interaction of anhydrous perchloric acid with sulphur trioxide[80]. However, this single indication of the possibility of perchloric acid acting as a proton-acceptor has not yet been confirmed by anyone. Furthermore, it contradicts Gillespie's sequence[79]

$$H_2S_2O_7 < HClO_4 < H_2SO_4.$$

In the $HNO_3$–$H_2SO_4$ system Usanovich[81] demonstrated the existence of the compounds $HNO_3.H_2SO_4$ and $HNO_3.2H_2SO_4$. According to Ref. 72, these compounds readily rearrange into acidium salts of pyrosulphuric acid, $[NO_2^+][HS_2O_7^-]$ and $(NO_2^+)_2[S_2O_7^{2-}]$.

Usanovich *et al.*[82] were unable, from a study of the conductivity of mixtures of $HClO_4 + H_2SO_4$ in different proportions, to establish the existence of a compound. Perchloric and sulphuric acids are obviously unable to form acidium salts. Nevertheless, the self-protonation of sulphuric acid, for example according to the equation

$$4H_2SO_4 = H_3SO_4^+ + HS_2O_7^- + H_2SO_4 \cdot H_2O$$

has been proved.

In spite of Gillespie's sequence[79], however, it may be supposed that the strengths of sulphuric and perchloric acids are of the same order of magnitude, while that of pyrosulphuric acid is probably somewhat higher.

It is of interest to examine how perchloric acid behaves towards considerably weaker acids.

Hantzsch and Langbein[69] reported that they had obtained the compound $CH_3COOH.HClO_4$, and Usanovich and Sumarokova[83] also found the compound $2CH_3COOH.HClO_4$ to be formed in this system.

In the $H_3PO_4$–$HClO_4$ system Simon and Weist[34] detected the existence at room temperature of a 1 : 1 crystalline compound melting at 41°. The Raman spectrum of the molten compound at 50° contains lines due to anhydrous phosphoric and perchloric acids and also to the perchlorate ion. These workers concluded from an analysis of the spectra that, of the two possible mechanisms for the process

$$H_3PO_4 + HClO_4 = P(OH)_4ClO_4 \qquad \text{(according to Hantzsch)}$$

and

$$H_3PO_4 + 2HClO_4 = PO(OH)_2^+ + H_3O^+ + 2ClO_4^- \qquad \text{(according to Ingold)},$$

Hantzsch's scheme is the more probable.

Usanovich and his collaborators investigated the systems $HClO_4$–$CH_2ClCOOH$,[84] $HClO_4$–$CHCl_2COOH$,[85] and $HClO_4$–$CCl_3COOH$.[86] They showed that $CH_2ClCOOH$ and $CHCl_2COOH$ form equimolecular compounds with perchloric acid, and also compounds in which the molar ratio of perchloric acid to substituted acetic acid is 1 : 2. But $CCl_3COOH$ and $H_2SO_4$ form no compounds with perchloric acid.

These facts show that the electrical conductivity of anhydrous perchloric acid depends, not on its self-protonation, but on the presence of $ClO_4^-$ ions formed spontaneously in the anhydrous acid and present as an integral part thereof. This is readily explained on the assumption that the composition of perchloric acid is represented by the equilibrium

$$3HClO_4 \rightleftarrows Cl_2O_7 + H_3OClO_4. \qquad (1)$$

As mentioned above, the behaviour of the acid on distillation leads to the same conclusion.

The presence of $Cl_2O_7$ in perchloric acid was proved by Missan and Sukhotin[87] from the polarisation curves. They found that the $Cl_2O_7$ content in the acid increases as the concentration of the latter approaches 100%.

## 9. CHLORINE HEPTOXIDE

### Preparation and Properties

Chlorine heptoxide was first obtained by Michael and Conn[22], who added perchloric acid slowly to phosphorus pentoxide cooled to -10°. After 24 h the resulting anhydride was distilled off under atmospheric pressure, and again distilled at 82°.

Meyer and Kesler[88] obtained chlorine heptoxide by the interaction of 3 parts of potassium perchlorate and 5 parts of chlorosulphonic acid at 75°. After purification by repeated vacuum distillation, a slightly coloured chlorine heptoxide of 98–99% purity was obtained in ~50% yield.

Goodeve and Powney[89] gradually added phosphorus pentoxide to perchloric acid which had been cooled to -78°. The mixture was allowed to reach room temperature, after which it was heated to 40°, and the resulting anhydride was distilled off under a vacuum, its vapour being led through phosphorus pentoxide and over active copper.

Zinov'ev and Rosolovskii[90] added anhydrous perchloric acid, allowing it to run in a thin film over the walls of the reaction vessel, on to phosphorus pentoxide dispersed on glass wool and cooled to -78°. The temperature of the reaction mixture was then raised to -38°, subsequently rising to -34°. The process was carried out at a pressure of 1–2 mm Hg, and the resulting chlorine heptoxide was distilled into a receiver cooled to -78°. The product obtained in this way was quite colourless, *i.e.* free from lower oxides of chlorine, and it contained also no perchloric acid, oxygen, or other contaminant. Later these workers[91] developed a method in which, instead of liquid perchloric acid, the vapour, formed from the liquid in a vacuum at room temperature, was fed to the phosphorus pentoxide.

Rosolovskii *et al.*[92] have also worked out an original method for obtaining chlorine heptoxide based on the reaction of oleum (for example 60%) with 70–75% perchloric acid. If the proportions of the reactants are chosen correctly, the oleum not only combines with the water of hydration but also removes the constitutional water from the perchloric acid. The resulting anhydride, being practically insoluble in sulphuric acid, separates as an upper layer on standing. It can be decanted from the sulphuric acid, and distilled.

These workers remark that all experiments with chlorine heptoxide require special care owing to its tendency to explode with great violence, the reason being unknown. In particular, the use of separating funnels with ground taps is excluded.

Chlorine heptoxide is a very mobile, heavy, colourless liquid which is immiscible with water. Therefore its interaction with water is slow. In spite of this, chlorine heptoxide fumes in air as a result of its reaction with moisture present in the latter, the monohydrate of perchloric acid being formed.

According to Goodeve and Marsh[93], the heat of solution of chlorine heptoxide in water is 50.0 ± 0.5 kcal mole$^{-1}$ (sufficient water to produce a 0.01 *N* $HClO_4$ solution). According to Rosolovskii *et al.*[94] the value at a final dilution of 1 mole of $Cl_2O_7$ in 1758 moles of $H_2O$ is 50.4 ± 0.3 kcal × × mole$^{-1}$. According to the same data, the heat of the reaction $Cl_2O_7 + H_2O = 2HClO_4$ is 8.1 kcal mole$^{-1}$.

Goodeve and Powney[89] reported the melting point and the boiling point of chlorine heptoxide as -91.5° and 80° respectively. They measured the vapour pressure at temperatures between -2.9° and 30.0°. From the results the following equation was deduced:

$$\log P(\text{mm}) = -\frac{1818}{T} + 8.03.$$

The heat of vaporisation of the anhydride calculated from Goodeve and Powney's data is 8.29 kcal mole$^{-1}$ and the Trouton constant 23.4. According to Michael and Conn, the boiling point of the anhydride is 82°. The vapour pressure at 0° calculated from the above equation is 23.7 mm Hg, which considerably exceeds the vapour pressure of perchloric acid at 0° (7.4 mm Hg, calculated from the equation given earlier for the acid:

$$\log P(\text{mm}) = -\frac{1923}{T} + 7.91).$$

The enthalpy of formation of chlorine heptoxide is, according to Goodeve and Marsh[93], $\Delta H_{17°} = -63.4 \pm 3$ kcal × × mole$^{-1}$, while that of perchloric acid is $\Delta H = 8.62$ kcal × × mole$^{-1}$ from the data of Vorob'ev *et al.*[95]

According to Zinov'ev and Rosolovskii[90], the melting point of chlorine heptoxide is -90 ± 2°, and the compound exists in two polymorphic modifications of enantiotropic type with a transition point at -100 ± 2°. They established[90] that above -23° chlorine heptoxide and carbon tetrachloride are miscible in all proportions.

The literature† contains only one mention of the density of chlorine heptoxide, a paper by Goodeve and Richardson[96] quoting the value $d_4^0 = 1.86$ found by Marsh.

The density of chlorine heptoxide according to Rosolovskii *et al.*[97] is shown in the following table:

| Temperature, °C | 20 | 10 | 0 | −10 | −20 | −30 | −40 | −50 |
|---|---|---|---|---|---|---|---|---|
| $d_4^t$ | 1.811 | 1.834 | 1.855 | 1.878 | 1.900 | 1.922 | 1.945 | 1.967 |

From these data the following equation was derived for the variation of density with temperature expressed in °K:

$$d_4^T = 2.4632 - 0.0022243\,T.$$

The viscosity of chlorine heptoxide was first determined by Zinov'ev and Rosolovskii[98], who obtained the following data:

| Temperature, °C | 20 | 10 | 0 | −10 | −20 | −30 |
|---|---|---|---|---|---|---|
| Viscosity, cP | 0.698 | 0.776 | 0.867 | 0.975 | 1.087 | 1.200 |

These data show that the viscosity of chlorine heptoxide is rather lower than that of anhydrous perchloric acid. Actually, the values at 20° are 0.698 and 0.859 cP[36] respectively.

## 10. MOLECULAR STRUCTURE OF PERCHLORIC ACID AND OF CHLORINE HEPTOXIDE

Simon[39] concluded from a study of the Raman spectrum that 100% perchloric acid in the liquid state contains only monomeric molecules, which are in the pseudo-acid form [$O_3ClOH$]. According to him, the $ClO_3$ group forms a trigonal pyramid, and the hydroxy-group is located on the extension of its height. This model belongs to the symmetry group $C_{3v}$.

Akishin *et al.*[99] used diffraction of fast electrons to study the molecular structure of the acid. They found that perchloric acid vapour consists of monomeric molecules, having the structure of a trigonal pyramid with the chlorine atom at its apex and the oxygen atoms at the corners of the triangular base. The OH group lies on the continuation of the height of the pyramid.

† Presumably "literature prior to 1960" is intended. (Ed. of Translation).

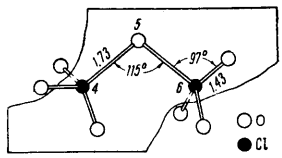



Fig. 6. Model of chlorine heptoxide molecule[99].

The chief parameters of the molecule are:

$$Cl=O \quad 1.42 \pm 0.01\ Å$$
$$Cl-O \quad 1.64 \pm 0.02\ Å$$
$$O-Cl-O \quad 100° \pm 2°.$$

The position of the hydrogen was not determined.

From a study of the Raman spectrum of a solution of chlorine heptoxide in carbon tetrachloride, Fonteyne concluded that the structure of the anhydride consists of two trigonal pyramids ($ClO_3$ atomic groupings) linked by an oxygen atom. The $ClO_3$ groups have symmetry $C_v$.

Akishin *et al.*[99] used diffraction of fast electrons to study the structure of chlorine heptoxide, and suggested the model illustrated in Fig. 6. In such a structure any oxygen atom of one $ClO_3$ group is situated between two oxygen atoms of another $ClO_3$ group, giving a minimum repulsion potential between unlinked oxygen atoms. The chief geometrical parameters of the molecule are as follows.

Distances: (Cl=O) 1.42±0.01 Å, (Cl—O′) 1.725±0.03 Å, ∠ClO′Cl = =115°±5°, ∠OClO′=97°±3°,

where O′ represents the oxygen atom linking the two trigonal pyramids. The length of the $Cl_2O_7$ molecular dipole is 0.15 Å, while the dipole moment is $\mu = 0.72 \pm 0.02\ D$.

The principal parameters of the $HClO_4$ and $Cl_2O_7$ molecules, namely the Cl=O distance and the OClO′ angle, are identical. However, the difference between the Cl—O distances in perchloric acid (1.64 Å) and in the anhydride (1.73 Å) considerably exceeds the experimental error in their determination.

Unlinked oxygen atoms in the $Cl_2O_7$ molecules are ~2.50 Å apart, which is less than the sum of the intermolecular radii (~2.80 Å), and this prevents free rotation of the $ClO_3$ group.

## 11. MELTING-POINT DIAGRAM OF THE $Cl_2O_7$–$H_2O$ SYSTEM

The complete melting-point diagram of perchloric acid over the concentration range 0–100% $HClO_4$ given by van Wijk[24] shows no line for the crystallisation of perchloric acid (Fig. 1). Consequently he observed neither a maximum which would correspond to $HClO_4$ nor a eutectic of the latter with the monohydrate $HClO_4.H_2O$, although he assumed that they did exist, but that the curve representing the crystallisation of perchloric acid was so short that the analytical methods available could not provide data from which it could be plotted. This point was checked experimentally by Zinov'ev and Rosolovskii[91], who studied fusibility in the $Cl_2O_7$–$H_2O$ system both thermographically and by visual observations over a range of temperatures (the visual polythermal method), their results being given in the form of a table and a diagram (Fig. 7). The points represented by circles were plotted from these results[91], while the triangles represent van Wijk's data[24]. The essential difference between the two set of results is that the lower portion of the crystallisation curve for the monohydrate, drawn by van Wijk on the basis of only two points, terminates in the point corresponding to -112° and precisely 100% $HClO_4$, *i.e.* 50 mole % $Cl_2O_7$. The lower portion of the curve representing crystallistion of the monohydrate of perchloric acid, plotted from seven experimental points[91], intersects the eutectic line at -100 ± 2° and 53 mole% $Cl_2O_7$ (*i.e.* a mixture of $HClO_4$ + $Cl_2O_7$).

But the diagram plotted from the later work[91] also shows no line for the crystallisation of anhydrous perchloric acid. One component of the eutectic (point *A* on Fig. 7) is the monohydrate of perchloric acid, while the nature of the other component was not entirely clear, since, when the content of the anhydride was increased from 53 to about 72 mole%, a drop in temperature resulted not in the separation of crystals but a breakdown in the homogeneity of the solutions, shown visually by the appearance of turbidity. This is entirely to be expected, since the monohydrate of the acid is an ionic substance, while the anhydride is a substance of low polarity (length of dipole ~0.15 Å); since homogeneity broke down above the melting point of the anhydride: the latter separates from the system as a liquid.

When the anhydride content of the mixture was increased, turbidity was found to appear at higher temperatures. This indicates a progressive diminution in the stability of the system with increase in concentration. But mixtures containing more than 72 mole% $Cl_2O_7$ deposited crystals on being cooled. Since the anhydride melts at -90°, the horizontal line on Fig. 7 at -90° ± 2° was regarded as corresponding to the crystallisation of chlorine heptoxide. Therefore, since separation into layers first occurs, and is followed by crystallisation of the anhydride, it was concluded that it is the anhydride which is the second component of the eutectic. Since, nevertheless, no points

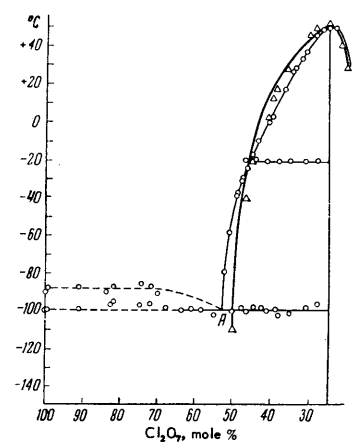



Fig. 7. Melting-point diagram for the chlorine heptoxide–water system[91]. Δ — van Wijk's data.

were obtained representing crystallisation over the range 53–72 mole%, this part of the diagram (Fig. 7) was shown as a broken line.

The horizontal straight line at -100 ± 2°, to the right and to the left of the point corresponding to 53 mole% $Cl_2O_7$, is a eutectic line. It was found that the polymorphic transition of chlorine heptoxide fortuitously also takes place at -100 ± 2°, [90] and the eutectic line and the polymorphic transition line have coalesced into one in Fig. 7.

Therefore the melting-point diagram constructed from the data in Ref. 91 also did not reveal the existence of $HClO_4$ in the $Cl_2O_7$–$H_2O$ system. The branch representing crystallisation of the monohydrate intersected the ordinate corresponding to 100% perchloric acid, and entered the region of compositions in which the anhydride content is 53 mole%. When acids containing somewhat less than 50 mole% $Cl_2O_7$ are cooled, it is not the anhydrous perchloric acid but its monohydrate which crystallises.

These peculiarities of perchloric acid were explained [91] by assuming that the very concentrated acid is not a chemical individual but represents a mixture characterised by the equilibrium $3HClO_4 \rightleftharpoons Cl_2O_7 + H_3OClO_4$ [Eqn. (1)], which is shifted far to the right, *i.e.* towards oxonium perchlorate at very low temperatures.

## 12. DENSITY OF $Cl_2O_7$–$HClO_4$ SYSTEMS

In order to check the soundness of equilibrium (1), Rosolovskii *et al.* [97] studied the dependence of several physical properties on composition, in particular the densities of $Cl_2O_7$ + $HClO_4$ mixtures, at various temperatures. The density was determined for mixtures over the composition range 100–43 mole% $Cl_2O_7$ at temperatures between 20° and -50°. These were the first data on the density of such mixtures. As mentioned above, there had been only one previous indication of the density of pure chlorine heptoxide (Marsh, private communication [95]): $d_4^{20} = 1.86$.

The densities of $Cl_2O_7$ + $HClO_4$ mixtures are presented in the paper [97] as a table and a series of isotherms (Fig. 8). The isotherms show that the density of the mixtures increases almost linearly from $HClO_4$ to $Cl_2O_7$. There are no singular points on the density isotherms between 50 mole% and 100% $Cl_2O_7$. There are practically no deviations from additivity. This all points to the absence of interaction between the components. As the concentration decreases from $HClO_4$, *i.e.* towards oxonium perchlorate, the density increases rapidly. The maximum density in the $Cl_2O_7$–$H_2O$ system occurs at $HClO_4.H_2O$. The composition $HClO_4$ corresponds to a sharp minimum on the 20° and 10° isotherms. As the temperature falls, the character of the minimum changes, and the singularity, which is clearly marked at higher temperatures, disappears.

It was concluded that these facts also support equilibrium (1), which as the temperature falls is displaced to the right, *i.e.* in the direction of the anhydride and the monohydrate of perchloric acid. Since both these compounds are denser than anhydrous perchloric acid, an increase in the content of $Cl_2O_7$ and $HClO_4.H_2O$ should be accompanied by an increase in density, which is actually the case.

The shift in equilibrium and consequent change in composition with decrease in temperature also explains the diminished sharpness of the minima on the density isotherms in Fig. 8.

## 13. VISCOSITY OF $Cl_2O_7$–$HClO_4$ SYSTEMS

No information was available in the literature on the viscosity of chlorine heptoxide or of anhydrous perchloric acid below 0° before the work of Zinov'ev and Rosolovskii [98]. Viscosity measurements have been made [98] on $Cl_2O_7$ + $HClO_4$ mixtures covering the range 100–42.8 mole% $Cl_2O_7$ at temperatures between 20° and -30°. Results are presented as a table and the six isotherms reproduced in Fig. 9. Each isotherm consists of two parts. With diminishing $Cl_2O_7$ content the left-hand portions of the isotherms rise slightly to ~54–52 mole% $Cl_2O_7$, after which the isotherms (the right-hand portions) begin to rise very steeply, breaking off at the boundary with the heterogeneous region (solid monohydrate of perchloric acid).

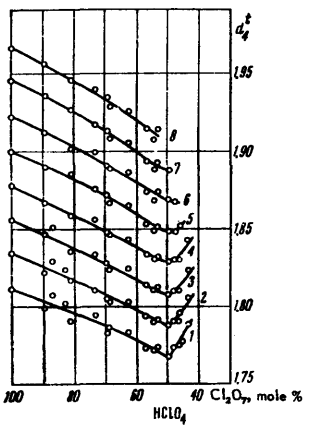



Fig. 8. Density in the chlorine heptoxide–anhydrous perchloric acid system [97]. Isotherms at:
1) 20°; 2) 10°; 3) 0°; 4) -10°; 5) -20°; 6) -30°; 7) -40°; 8) -50°.

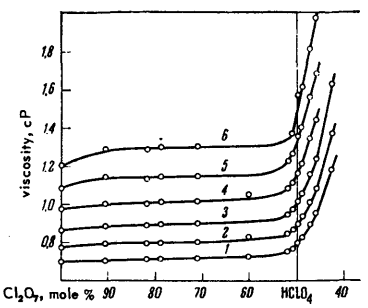



Fig. 9. Viscosity in the chlorine heptoxide–anhydrous perchloric acid system [98]. Isotherms at:
1) 20°; 2) 10°; 3) 0°; 4) -10°; 5) -20°; 6) -30°.

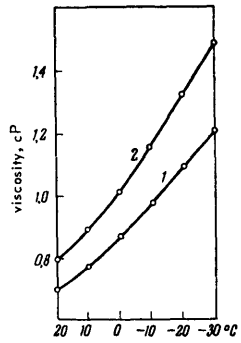



Fig. 10. Temperature variation of viscosity[98]: 1) chlorine heptoxide; 2) perchloric acid.

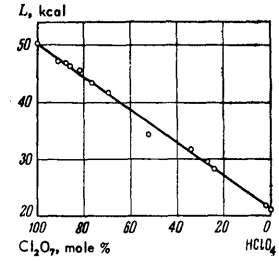



Fig. 11. Heats of solution in the chlorine heptoxide–anhydrous perchloric acid system[94].

The maximum viscosity, like the maximum density, occurs at a composition close to the monohydrate. As the temperature falls, the shape of the isotherm changes slightly, and over the range 55–100 mole% $Cl_2O_7$ the shape of the isotherms indicates the absence of interaction between $Cl_2O_7$ and $HClO_4$.

The inflection in the viscosity isotherms (Fig. 9) corresponding to formation of the compound $HClO_4$ is displaced somewhat towards the anhydride, especially at low temperatures. This shape of the isotherm supports equilibrium (1). Actually, since the viscosity of the monohydrate of perchloric acid is substantially grater than the viscosity of either the anhydrous acid or its anhydride, an increasing content of the monohydrate should result in an increase in viscosity. This is actually the case. The rise begins sooner in the viscosity isotherms (Fig. 9) the lower the temperature. This in turn indicates a shift in equilibrium (1) towards the monohydrate as the temperature is lowered.

Fig. 10 shows viscosity polytherms[98] for chlorine heptoxide and perchloric acid. They indicate that the increase in viscosity with fall in temperature is considerably greater with the acid than with the anhydride. This also points to a shift in equilibrium (1), with fall in temperature, towards oxonium perchlorate, increase in the concentration of which entails an increase in viscosity.

## 14. INTEGRAL HEATS OF SOLUTION IN THE $Cl_2O_7$–$HClO_4$ SYSTEM

Integral heats of solution in the $HClO_4$–$H_2O$ system have been indicated above[27,28]. Apart from this work, a paper published by Goodeve and Marsh[93] on the determination of the heat of solution of chlorine heptoxide gave a value of $50.0 \pm 0.5$ kcal mole$^{-1}$.

Rosolovskii *et al.*[94] have made a systematic investigation of the heats of solution of mixtures of perchloric acid and its anhydride. It was found that the acid passes into solution very rapidly (within 1–2 min), while the remaining anhydride dissolves with characteristic slowness, at a rate determined by the volume of the drops of anhydride, *i.e.* by the intensity of stirring. The results are tabulated in the paper[94] and are shown graphically in Fig. 11.

The additivity of the heats of solution suggests that $Cl_2O_7$ and $HClO_4$ do not interact, but give what may be regarded as true solutions. Absence of interaction is indicated also by the independent dissolution of the components of mixtures and the density and melting-point results for the $Cl_2O_7$–$HClO_4$ system. The heat of reaction was found to be

$$Cl_2O_7 + H_2O = 2HClO_4 + 8.1 \text{ kcal.}$$

The thermochemical data were also used to find the heat of the reaction

$$3HClO_4 = Cl_2O_7 + HClO_4 \cdot H_2O + 2.8 \text{ kcal.}$$

The positive heat of reaction in this case confirms the assumption that lowering the temperature shifts the equilibrium towards chlorine heptoxide and the monohydrate of perchloric acid. The content of $HClO_4$ in this mixture at about -100° is obviously so low that $HClO_4$ does not crystallise. For this reason the melting-point diagram does not contain a line representing crystallisation of the acid, as was stated above.

## 15. THERMAL STABILITY OF PERCHLORIC ACID

Anhydrous perchloric acid is unstable. A few hours after its preparation it already shows clear signs of decomposition, first becoming yellowish (owing to the lower oxides of chlorine which are formed), the colour then deepening, becoming darker, and finally almost black, and the acid becomes opaque. In this condition perchloric acid may explode.

At slightly elevated temperatures (not above 100°) perchloric acid passes through these stages considerably more rapidly, in periods measured in minutes, and at about 100° even in seconds. At all temperatures (up to 95°–99°), however, there is an interval during which decomposition of the perchloric acid has not yet occurred: *i.e.* the decomposition is preceded by an induction period. The kinetic curves for the decomposition are S-shaped, the isotherms for the rate of decomposition passing through a maximum. This and also the possibility of delaying the decomposition for some time by means of inhibitors give grounds for supposing that the thermal decomposition of perchloric acid takes place by a chain mechanism. If

decomposition occurs at a temperature not exceeding 100°, the residue contains the monohydrate, present in the theoretical quantity based on Eqn. (1).

Zinov'ev and Babaeva [101] cite data showing that the decomposition of perchloric acid begins with the formation and subsequent decomposition of chlorine heptoxide. The following stages in the decomposition may be noted.

1. Vigorous evolution of a small amount of oxygen (10–15 $cm^3 g^{-1}$ of acid) within a short period of time (1–2 min). The yield of oxygen varies from one specimen to another. It is obviously oxygen dissolved in the acid which is being evolved.

2. A second stage during which only slight changes are taking place in the acid, the initially colourless acid becoming coloured, accompanied by slight oxygen evolution (at a constant rate, since the isotherm is linear). The volume of oxygen evolved during this stage does not exceed 10–12% of the total quantity of oxygen obtained from a given weight of the acid.

3. The following stage of decomposition is characterised by the high rate and considerable complexity of the reactions which develop. The rate of decomposition of the acid at this stage increases rapidly with time, tending to a maximum.

4. The stage of decomposition after the maximum rate has been passed, tending to die away.

In the presence of inhibitors the duration of the second stage increases several hundred times, and the portions of the isotherms corresponding to this stage become more distinct and completely linear. This implies that the reaction is of zero order during this stage, while the activation energy is ~33 kcal $mole^{-1}$, [101] which coincides with the activation energy found by Figini *et al.* [102] ($E = 32 \pm 1.5$ kcal × × $mole^{-1}$) for the decomposition of chlorine heptoxide. Since this agreement is hardly fortuitous, and also as uncombined $Cl_2O_7$ is always present in perchloric acid, Zinov'ev and Babaeva concluded that the decomposition of perchloric acid begins with that of $Cl_2O_7$ formed from the acid.

The decomposition of chlorine heptoxide is assumed [102] to involve the intermediate formation of free radicals: $Cl_2O_7 = ClO_3 + ClO_4$, followed by very complicated and not yet elucidated reactions in which they take part. The following end-products of the decomposition of perchloric acid can be regarded as firmly established provided that the temperature does not exceed 100°: perchloric acid monohydrate $HClO_4.H_2O$, chlorine dioxide $ClO_2$, and elemental chlorine $Cl_2$. A probable decomposition product is $Cl_2O_6$.

The water formed in the reaction combines completely with still undecomposed perchloric acid, which is the reason for the formation of the monohydrate.

Above 110°, according to Roscoe [12], the monohydrate begins to decompose too. This has been confirmed by Zinov'ev and Tsentsiper [103].

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The above account of perchloric acid indicates that it differs substantially from other inorganic acids. The most remarkable fact is that perchloric acid is not chemically unique, but exists under all conditions as a component of a mixture of $HClO_4 + Cl_2O_7 + H_3OClO_4$. The composition of this mixture varies considerably with change in conditions, especially temperature, and at very low temperatures, in particular, $Cl_2O_7$ and $H_3OClO_4$ predominate to a very great extent over $HClO_4$.

Another peculiarity of perchloric acid is that, of all the forms in which it exists, only the monohydrate, better described as oxonium perchlorate $H_3OClO_4$, satisfies the requirements of an individual chemical species. In the $Cl_2O_7$–$H_2O$ system such requirements are met also by chlorine heptoxide.

The very different volatility of the various forms of perchloric acid is of considerable interest. Anhydrous perchloric acid is extremely volatile, but at atmospheric pressure it cannot be distilled without decomposition. Its distillation is readily achieved only at reduced pressure. The monohydrate of perchloric acid does not distil without decomposition either at atmospheric pressure or in a vacuum, but an azeotrope, whose composition is close to a dihydrate of the acid, can be distilled almost without decomposition even at atmospheric pressure (evaporation of the azeotrope from a dish takes place without any signs of decomposition, while distillation from a flask fitted with a condenser is accompanied by slight decomposition).

A substantial increase in density must be noted on passing from the anhydrous acid to its monohydrate, and the viscosity of the latter is several times greater than that of the anhydrous acid.

It is remarkable that the viscosity of the anhydrous acid is less than that of water under the same conditions.

Perchloric acid is among those acids which contain so-called available oxygen. It has a higher content of the latter (63.7%) than have other acids (nitric, chloric, etc.), but its oxidising power is very greatly dependent on its water content. Thus the $ClO_4^-$ ion exhibits no oxidising properties in aqueous solution. Above 100°, however, free perchloric acid, in the form of the azeotrope, readily oxidises many metals, ores, and especially organic compounds. On passing from the dihydrate to the monohydrate, the oxidising activity of the perchloric acid increases considerably, the monohydrate readily oxidising various reducing agents even below 100°.

The oxidising activity of perchloric acid increases very sharply when its composition approaches 100% $HClO_4$. Such an acid instantly sets fire to all oxidisable organic compounds, and oxidises almost all metals in the most vigorous fashion (with the exception of noble metals and those which can be passivated by oxidation), the heats of reaction usually being sufficient for the instantaneous decomposition of the acid, accompanied by a powerful explosion.

Colourless perchloric acid, *i.e.* an acid containing no lower oxides of chlorine, does not explode out of contact with reductants, and is therefore safe when handled carefully.

In spite of the great amount of work done on perchloric acid, its properties have not yet been adequately determined. This applies primarily to the dependence of vapour pressure on temperature, and then to the way in which the stability of the acid varies with temperature and other conditions. In this connection the problem of the stabilisation of perchloric acid still remains unsolved, its instability being a serious obstacle not only to its wide industrial use but also to its employment in laboratory experiments.

In spite of the work of many investigators, the nature of perchloric acid requires further study. In particular, it must be made clear why perchloric acid behaves as a mixture and how the properties of this mixture vary with the external conditions, especially with temperature.

Much work has been done on perchloric acid salts (perchlorates), but the diverse properties of these salts and mixtures thereof have been altogether insufficiently studied; it is even true that not all possible perchlorates have been prepared, which applies especially to those of the rare metals.


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