PERCHLORIC ACID

G. S. Pearson

Rocket Propulsion Establishment, Westcott, Aylesbury, Buckinghamshire, England

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I. Introduction

Perchloric acid is very widely used in industry and in the laboratory, but only in the last decade has its chemistry been at all closely examined.

In 1906 Van Wyk (*203*) suggested that the anhydrous acid did not exist alone but was always associated with chlorine heptoxide and perchloric acid monohydrate in an equilibrium represented by Eq. (1):

$$3HClO_4 \leftrightharpoons Cl_2O_7 + HClO_4{\cdot}H_2O \qquad (1)$$

This suggestion has still not been established, and in the present review the evidence for and against it will be discussed.

Perchloric acid, $HClO_4$, is one of the strongest acids and contains more oxygen (63.7%) than any other common acid. However, its oxidizing power depends very markedly on both concentration and temperature. For example, the anhydrous acid at room temperature reacts very vigorously, and in many cases explosively, with all reducing agents, whereas the dihydrate (73.6% by weight of acid*) has little oxidizing power at room temperature but becomes a powerful oxidizer above 100°C. The perchlorate ion itself shows no oxidizing properties in solution.

II. *Preparation*

A. ANHYDROUS ACID

Several methods have recently been described for the preparation of anhydrous perchloric acid. All involve the dehydration of the constant boiling point acid (72.4% by weight) or of more dilute acid by oleum, phosphorus pentoxide, or magnesium perchlorate. The purity of the final product must be considered in each case, since an excess of the dehydrating agent results in the formation of chlorine heptoxide (*150*).

The preparation of anhydrous acid by a simple laboratory method was described by Smith (*172*). In this method, 3, 4, or 5 volumes of 20% fuming sulfuric acid were slowly added to 1 volume of 72% perchloric acid cooled in an ice bath. The anhydrous acid was obtained by distillation of the mixture at 1 mm Hg or less, at 20°–25°C; the distillate was collected in a receiver cooled by dry ice. Gradual increase of the temperature to 75°C results in a 75% yield of the anhydrous acid. No analysis of the product was reported other than by addition of the theoretical quantity of 72% acid, which resulted in the crystallization of the monohydrate. A test for the presence of sulfuric acid was negative.

The product from this method can contain quite large quantities of chlorine heptoxide, as was shown by Levy (*98*), who obtained anhydrous

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* Unless otherwise stated, all acid percentages in this review are by weight.

acid containing up to 50% chlorine heptoxide. Analysis for the chlorine heptoxide was made by determining the number of moles of vapor, n_g, from the pressure, volume, and temperature, and the number of moles, n_a, of titratable acid. It follows that since

$$n_g = n_{Cl_2O_7} + n_{HClO_4}$$

and

$$n_a = 2n_{Cl_2O_7} + n_{HClO_4}$$

then

$$n_{Cl_2O_7} = n_a - n_g \tag{2}$$

and

$$n_{HClO_4} = 2n_g - n_a \tag{3}$$

The presence of the chlorine heptoxide was confirmed by infrared spectrometry. Pure samples of the anhydrous acid were obtained by converting the product from the oleum–72% acid distillation to the monohydrate by addition of the stoichiometric amount of 72% acid. The monohydrate was then distilled (no more than 5% of any one sample being used to ensure the absence of water) to give pure samples of anhydrous acid. Both analysis and the infrared spectra showed that chlorine heptoxide was absent.

Smith's process has been used on a microscopic scale by Sibbett *et al.* (*164*, *165*). The ratio of oleum (20%) to perchloric acid (72%) was 3:1, the temperature was not raised above room temperature, and a pressure of 2×10^{-4} mm Hg was used. The anhydrous acid vapor was passed over a drying bed of magnesium perchlorate. Tests of the product for sulfate and chloride ions were negative. The only impurity was believed to be water, although no analysis was made for chlorine heptoxide. However, it is unlikely that chlorine heptoxide was present in large quantities, since the oleum/acid ratio was low and the infrared spectra did not have the characteristic peaks of chlorine heptoxide.

A continuous process for the preparation of the anhydrous acid has been described by Zinov'ev (*220*), who stressed the importance of careful control of the oleum/acid ratio in order to avoid contamination of the product by chlorine heptoxide. It was suggested that the correct ratio should be found by trial and error. No details were given of the analytical method.

More recently, Smith (*173*) has described a preparation using magnesium perchlorate (containing about 5% water) and the 72% acid in a ratio of 5:1. A yield of 85% was reported. Chlorine heptoxide was found to be a minor impurity, which occurred in greater amount if the reaction mixture was not distilled immediately after its preparation. Its presence was shown by the fact that when the anhydrous acid was diluted to form the monohydrate the chlorine heptoxide did not react until 72–96 hours later. It was recommended that, if the anhydrous acid was not to be used immediately, it should be converted to the monohydrate and then reconverted to the anhydrous acid by distillation when required.

Mascherpa (*115*) has described a preparation from 95% sulfuric acid and 65% perchloric acid in a ratio of 3:1 by distillation at 70 or 100 mm Hg, using a falling film rectification column. A 75% yield of average concentration 99.98% was obtained, but no details were given of the product analysis.

The preparation of a pure sample for thermochemical work was described by Trowbridge and Westrum (*196*), who used Smith's method for the preparation using oleum. Fractional fusion data indicated a maximum impurity of 2.5 mole %, which was presumed to be the monohydrate. Conductometric titrations performed after the thermochemical experiments for acid and perchlorate content agreed, but indicated only 95% by weight, confirming the visual observation that the sample had partly decomposed in the calorimeter. Attempts to identify the contaminant by infrared spectrometry were unsuccessful. Other preparations of anhydrous perchloric acid by dehydration under reduced pressure have been described by Taketa (*190*) and Kakiuchi *et al.* (*87*).

It must be concluded that anhydrous perchloric acid prepared by direct dehydration of the 72% acid will probably contain some chlorine heptoxide. The chlorine heptoxide content can be minimized by (*i*) use of a small ratio (3:1) of dehydrating agent to acid, (*ii*) distillation at room temperature, and (*iii*) immediate distillation of the dehydrating agent–acid mixture. A pure sample of the anhydrous acid is best prepared by distillation of the monohydrate.

Solutions of anhydrous acid in halogenated hydrocarbons have recently been prepared (*90*) by addition of methylene or ethylene chloride to a mixture of 1 part by volume of 70% perchloric acid and 4 parts by volume of 25% fuming sulfuric acid. The monohydrate can be precipitated by passing moist air through the solution of the acid. Unsuccessful attempts have been made to prepare solutions of anhydrous perchloric acid in acetonitrile by reaction of barium perchlorate and sulfuric acid (*47*). Although barium sulfate is very insoluble in acetonitrile, such solutions continued to deposit a precipitate after equilibrium for 6 months. The hazards of acetonitrile solutions of perchloric acid have been described (*6*).

Smith (*172*, *173*) recommended that all ground-glass joints exposed to anhydrous perchloric acid vapor be lubricated with 72% perchloric acid. It was particularly stressed that silicone grease must not be used since it exploded with anhydrous perchloric acid. Hathaway (*70*) rejected the use of 72% perchloric acid since he found that joints sealed in this way would not hold a vacuum He used a minimum quantity of silicone grease and found that explosions did not occur so long as liquid acid was not allowed to pass over a disconnected joint.

Moreover, leaks in apparatus lubricated by 72% perchloric acid have resulted in anhydrous acid coming into contact with the operator's gloves with consequent spontaneous ignition (*108*). It was found that fluorocarbon grease carefully applied was quite safe (*108*), thus confirming the observation of Levy (*98*) that Kel-F fluorocarbon grease was resistant to attack.

All-glass systems using break seals and completely free from grease have been described (*98*, *164*, *192*).

B. HYDRATED ACID

Perchloric acid, 60% and 72%, is prepared on an industrial scale either by reacting sodium perchlorate with concentrated hydrochloric acid

$$NaClO_4 + HCl \rightarrow NaCl + HClO_4 \tag{4}$$

or by anodic oxidation of hydrochloric acid or a chlorate. Further details are given in the standard reference books; for example, see reference (*158*).

Details have recently been given (*65*) for the preparation of analytical grade perchloric acid from sodium perchlorate and hydrochloric acid. Magnesium perchlorate has been used as the dehydrating agent to produce 70–80% perchloric acid (*175*). Irradiation with light at 2537 Å has been used in a somewhat novel method of preparation (*153*). The mixture irradiated consists of a gaseous mixture of water, chlorine, and ozone at a pressure of about half an atmosphere. Hydrogen chloride can be substituted for the chlorine and most of the water, and the ozone can be diluted with oxygen.

C. DEUTEROPERCHLORIC ACID

Deuteroperchloric acid was first prepared as the constant boiling azeotrope (*189*). Deuterium sulfate was prepared by solution of sulfur trioxide in 99.25% D_2O, and then the sulfate was removed by addition of barium perchlorate, followed by centrifuging the precipitated barium sulfate. The deuteroperchloric acid (deuterium content 99 ± 0.3%) was purified by vacuum distillation, and the center fraction of the constant boiling mixture was collected. More concentrated deuteroperchloric acid was prepared by Giguère and Savoie (*54*) by distillation under reduced pressure at 65°C of a mixture of potassium perchlorate and deuterium sulfate (97%) in the ratio 1:5. The deuterium sulfate was prepared by condensation of sulfur trioxide onto a small amount of solid D_2O (99.7% deuterium) in a cold bath. The deuteroperchloric acid was distilled again to remove traces of deuterium sulfate. However, some contamination of the product by atmospheric moisture could not be avoided and, from the relative intensity of the OH bands in the deuteroperchloric acid spectra, the impurity was estimated to be about 15–20% $HClO_4$ in the $DClO_4$. The product was shown to be free from perchlorate ion, since the spectra had no indication of the strong perchlorate ion band at 940 cm^{-1}. Some chlorine heptoxide was present as an impurity.

The anhydrous acid was prepared by Smith and Diehl (*179*) by distillation of a mixture of anhydrous sodium perchlorate with a twofold excess of 98.2% deuterium sulfate at a pressure of 0.1–0.25 mm Hg and a temperature below 105°C. The anhydrous acid was obtained in 70% yield.

III. Perchloric Acid Hydrates

The classical study of the perchloric acid–water system was that carried out by Van Wyk in 1906 (*203*). He constructed a melting point curve which indicated the existence of five hydrates of perchloric acid: those containing 1 H_2O, 2 H_2O, 2.5 H_2O, 3 H_2O (α and β forms), and 3.5 H_2O.

Brickwedde (*23*) in 1949 repeated Van Wyk's observations for the range 0–70% by weight and obtained a curve of the same general shape as that of Van Wyk. However, the temperatures measured by Van Wyk lie outside the experimental error of Brickwedde's work in many cases. Brickwedde was unable to confirm the existence of the hydrates.

Very recently, Mascherpa *et al.* (*117*) have studied the perchloric acid system in the region 55–75% acid, and have shown that the four hydrates containing 2 H_2O, 2.5 H_2O, 3 H_2O, and 3.5 H_2O exist in this region.

A. QUARTER HYDRATE, $(HClO_4)_4 \cdot H_2O$

This was recently reported by Mascherpa (*116*) in a study of the region 85.8–100% acid. From a study of the liquid-solid equilibrium he concluded that the quarter hydrate existed in two allotropic forms with a transition temperature of $-100°C$ from the α to the β form, and a decomposition point of the α form at $-73.1°C$.

B. MONOHYDRATE, $HClO_4 \cdot H_2O$

This is the best established perchloric acid hydrate. It is a colorless crystalline compound melting at 49.905°C (*180*). Its X-ray structure was shown by Volmer (*208*) to be similar to that of ammonium perchlorate, NH_4ClO_4. This was later confirmed by proton magnetic resonance studies (*85, 86, 87, 184*), by Raman spectroscopy (*126, 127, 193*), by X-ray diffraction (*97, 130*), and by infrared spectroscopy (*16, 126, 156*). Taylor and Vidale (*193*) showed that the solid existed in two crystalline forms with a transition point at about $-30°C$.

Rosolovskii and Zinov'ev obtained a transition at −23.4°C by differential thermal analysis (*148*) and at −24.9°C by dilatometry (*225*). Mascherpa obtained −24.0°C by differential thermal analysis (*114*).

The crystal structure of both forms has been studied. The form stable at low temperature (*130*) belongs to the monoclinic space group $p2_1/n$ with parameters (in Å):

$$a = 7.541 \pm 0.0006$$
$$b = 9.373 \pm 0.011 \qquad \beta = 97°41' \pm 4'$$
$$c = 5.359 \pm 0.006$$

whereas the high temperature form (*97*) belongs to the orthorhombic P_{nma} space group with parameters (in Å):

$$a = 9.065 \pm 0.0008$$
$$b = 5.569 \pm 0.004$$
$$c = 7.339 \pm 0.004$$

C. DIHYDRATE, $HClO_4 \cdot 2H_2O$, AND OTHER HYDRATES, $HClO_4 \cdot 2.5H_2O$, $HClO_4 \cdot 3H_2O$, AND $HClO_4 \cdot 3.5H_2O$

These were all first proposed by Van Wyk (*203*) and have since been confirmed by Mascherpa *et al.* (*117*) (see tabulation below). However, Mascherpa was unable to detect the two forms, α and β, suggested by Van Wyk for the trihydrate.

Hydrate	M.P. (°C) (Van Wyk)	M.P. (°C) (Mascherpa)
$2H_2O$	−17.8	−20.65 ± 0.1
$2.5H_2O$	−32.1	−33.1 ± 0.1
	(α) −37	
$3H_2O$		−40.2 ± 0.1
	(β) −43.2	
$3.5H_2O$	−44.3	−45.9 ± 0.1

Evidence for the existence of these hydrates in solution has been obtained by Zinov'ev and Babaeva (*222*) as a result of their study of the specific gravity and viscosity of perchloric acid over a wide range of concentrations.

Evidence for the dihydrate was obtained by Smith and Richards (*185*) in a proton magnetic resonance study. The results indicated that the hydrate was $H_3OClO_4 \cdot H_2O$.

It may be concluded that the existence of the monohydrate is well established whereas that of the other hydrates is less fully substantiated.

IV. Structure

A. ANHYDROUS ACID

1. *Cryoscopic Evidence*

Van Wyk (*203*) suggested that it could exist only in equilibrium with the anhydride (Eq. 1):

$$3HClO_4 \leftrightarrows Cl_2O_7 + HClO_4 \cdot H_2O$$

and this has recently been supported by Zinov'ev and Rosolovskii (*225*). Data were obtained by thermal analysis and visual melting point studies for the chlorine heptoxide–water system in the range 25–100 mole %. The eutectic occurred at 53 mole % and -100 ± 2°C, whereas the melting point at 50 mole % was about −40°C. The components of the eutectic were believed to be the monohydrate, $HClO_4 \cdot H_2O$, and either chlorine heptoxide, Cl_2O_7, or a metastable compound such as $Cl_2O_7 \cdot 2HClO_4$. No evidence for a congruent melting point was reported. Mascherpa (*116*) has re-examined the region 84.8–100% acid, and found this region to be more complex than has previously been shown. A eutectic was found at −104°C between the quarter hydrate, $(HClO_4)_4 \cdot H_2O$, and another compound, perhaps the anhydrous acid. The melting point at 100% was about −100°C, well below that reported by the Russian workers.

Trowbridge and Westrum (*196*) obtained a melting point of −101°C from a careful thermodynamic study of the anhydrous acid. They discussed the results obtained by Zinov'ev and Rosolovskii (*225*), and concluded that the proposed eutectic at 53 mole % was in error, since such a eutectic would require the observed heat capacities to be nonlinear over the range −100° to −51°C. In view of the difficulty in analyzing high perchloric acid concentrations, it was possible that the error was in the titrimetric method used, where a 0.5% error would result in a 3% error in the concentration range near 50 mole % chlorine heptoxide. It was also suggested that fine structure, in the form of a hypothetical congruent melting point, may not have been detected. The presence of a congruent melting point for perchloric acid would suggest its stability and lack of disproportionation in the solid.

2. *Spectroscopic Evidence*

The infrared spectrum of gaseous perchloric acid was obtained by Sibbett and Lobato (*165*), using a 10-cm cell on a Beckman IR-5 spectrophotometer. Absorption maxima were obtained at 3500, 1360–980, and 750–690 cm^{-1}. After 3 hours the maximum at 3500 cm^{-1}, which was ascribed to O—H bonding, disappeared, and the other maxima, ascribed to O—Cl bonding, were modified. It was suggested that these changes were due to the reaction of perchloric acid with the lead sealing gasket between the sodium chloride windows and the cell body, and with the cell windows themselves.

A similar spectrum was obtained by Levy (*98*), who used a 10-cm cell on a Perkin-Elmer 13-U infrared spectrometer. Perchloric acid vapor obtained directly from the mixture of aqueous acid and fuming sulfuric acid had absorption maxima at 1300 and 1025 cm^{-1}. After a quarter of the acid had been distilled off from the reaction mixture, the cell was refilled and found to have absorption maxima at 1265–1200 cm^{-1} and 750–690 cm^{-1}, which agreed well with those reported by Sibbett and Lobato. The first spectrum was identical to that of chlorine heptoxide.

Shchukarev *et al.* (*160, 161*), using an 11.5-cm cell and a pressure of 18 mm, studied the infrared absorption spectra in the region 3700–2500 cm^{-1} and found an absorption peak at 3560 cm^{-1}. This band was also found in very dilute (0.001 M) solutions of perchloric acid in carbon tetrachloride, thus showing that perchloric acid is monomeric in the vapor phase. Freshly prepared liquid anhydrous acid had a band at 3390 cm^{-1} and this shift was attributed to hydrogen bonding. An estimate of 3 kcal $mole^{-1}$ was made for the energy of the hydrogen bonding.

More recently, Giguère and Savoie (*54*) made a detailed study of the infrared spectra of both anhydrous $HClO_4$ and $DClO_4$ in the vapor phase as well as in the liquid and solid phases. Their results are presented in Table I. From the shift in the O—H bond for the gas to liquid phase change, they estimated an energy of 3 kcal $mole^{-1}$ for the hydrogen bonding.

The Raman spectrum of solid perchloric acid has recently been measured by Dahl *et al.* (*40*), who obtained results in good agreement with those from infrared studies. In particular, they found no evidence of the very intense 921 cm^{-1} vibration of the monohydrate (*193*), or of the 501 and 695 cm^{-1} vibrations of chlorine heptoxide (*155*). This indicated that neither of these two species could be present in the solid in appreciable amount. It can be seen from Table I that the sample used by Simon and Weist (*168*) for their Raman spectra studies must have contained chlorine heptoxide since it had a band at 284 cm^{-1}.

The spectroscopic evidence is thus clearly in favor of perchloric acid existing as such in the anhydrous state, with no evidence for the existence of the equilibrium

$$3HClO_4 \rightleftharpoons Cl_2O_7 + HClO_4 \cdot H_2O$$

TABLE I
Raman and Infrared Spectra of Anhydrous Perchloric Acid

$HClO_4$								Cl_2O_7		$H_3O^+ClO_4^-$ (solid phase)	
Vapor phase			Solid phase			Liquid phase		Gas phase	Solid phase	+20°C	−10°C
		4750									
3500	3560	3560	3260	3336		3275	3350			3285	3320
		2450		3040						3100	2930
		1450		2329							
1360 to 980		1326	1315	1550	1312 to 1182	1315		1309	1294	1577	
		1303									
		1288									
		1263	1283					1271	1272		
		1200	1245	1243		1245					
										1175	
		1134	1200			1215	1210				
		1050	1033	1038	1032	1033	1031	1025	1034		
		1047								921	
750 to 690		725	740	738	738	743	740				
		721	760								
								696 680	695		
		632	603					600	612 595	627	
		579	585	585	585	582	577	571	565		
		560	566		572	571		559	554		
		526									
		519						521	510		
								506	501		

		430	428	436	425	440	424				
		413	371								
			346								
		318									
		307	478			480		472(?)	472	456	
							284	271	278		
References											
(*165*)	(*160, 161*)	(*54*)	(*54*)	(*40*)	(*120*)	(*54*)	(*168*)	(*155*)	(*155*)	(*193*)	(*160, 161*)

The interpretation of the spectroscopic evidence by Zinov'ev (*221*) in ascribing the 3560 cm^{-1} band to the hydronium ion, H_3O^+, is incorrect.

3. Other Evidence

Electron diffraction studies of both anhydrous perchloric acid vapor and chlorine heptoxide have been made by Akishin *et al.* (*3*). The results were in agreement with C_{3v} symmetry for perchloric acid in the vapor phase. Perchloric acid vapor was shown to be monomeric. The other evidence on the nature of anhydrous perchloric acid is chemical. Hathaway and Underhill (*70*) have shown that anhydrous ferric and ferrous chlorides react with anhydrous perchloric acid to yield hydrated perchlorates. Anhydrous nitric acid behaved in a similar way with a wider range of salts. Since nitric acid dissociates to the extent of about ½%, this can be regarded only as evidence that an equilibrium can occur, but its extent in the absence of anhydrous ferric or ferrous salts may be very small. It was also shown that anhydrous nitrates react to form hydrated perchlorates thus:

$$MNO_3 + 3HClO_4 \leftrightharpoons MClO_4 + NO_2ClO_4 + H_3OClO_4 \qquad (5$$

Since perchloric acid monohydrate is a product, it is conceivable that this could lose water to the metal perchlorate, resulting in formation of the hydrated perchlorate.

4. Conclusion

It is concluded that anhydrous perchloric acid certainly exists as such. The extent, if any, to which the equilibrium occurs is small. Further work is required to clarify this point and also the exact nature of the freezing point curve.

B. BOND LENGTHS, ANGLES, AND STRENGTHS

Giguère and Savoie (*54*) deduced, from empirical considerations, values of 1.70 and 1.45 Å for the bond lengths Cl—OH and Cl—O, respectively. Better values for these bond lengths (1.64 ± 0.02 Å and 1.42 ± 0.01 Å, respectively) were obtained by Akishin *et al.* (*3*), who also calculated a value of 100 ± 2° for the bond angle O—Cl—O. These may be compared with the corresponding values for chlorine heptoxide (*3*) of Cl—O = 1.42 ± 0.01 Å, Cl—OCl = 1.72 ± 0.034 Å, and an O—Cl—O angle of 97 ± 3°. Robinson (*144*) has collected data from the literature for the Cl—O stretching frequencies of seven oxychlorine compounds and ions. In a tetrahedral molecule of the type $XClO_3$, there should be one symmetric ClO_3 stretching frequency and two asymmetric stretching frequencies which are degenerate. In perchloric acid two asymmetric stretches have been observed and this is attributed to a loss of tetrahedral symmetry in the molecule, whereas in fluorine perchlorate and perchloryl fluoride only one bond has been observed (Table II). In a later paper Robinson (*145*) has compared calculated and experimental bond lengths (Table III).

TABLE II

Cl—O STRETCHING FREQUENCIES

Compound	Stretching frequencies (cm^{-1})	
	Symmetric	Asymmetric
Perchloric acid, $HOClO_3$	1050	1326 1263 } 1296
Fluorine perchlorate, $FOClO_3$	1049	1298
Perchloryl fluoride, $FClO_3$	1061	1315
Chlorine dioxide, ClO_2	943	1110
Chlorite ion, ClO_2^-	860	952
Chlorate ion, ClO_3^-	930 930 }	975 1087 }
Perchlorate ion, ClO_4^-	935	1110
Chlorine heptoxide, Cl_2O_7	1034 1057 } 1045	1260 1270 } 1275 1295

TABLE III

BOND LENGTHS FOR Cl—O COMPOUNDS

Compound	Force constant ($k \times 10^5$)	Bond order	Bond length	
			$r_{obs.}$	$r_{calc.}$
Cl_2O_7	9.32	1.62	1.424 ± 0.01	1.44
$HOClO_3$				
(Cl—O)	9.55	1.64	1.42	1.43
(Cl—OH)	3.79	1.05	1.64	1.66
ClO_4^-	8.20	1.50	1.46 ± 0.01 1.452 ± 0.005	1.47
$FOClO_3$	9.58	1.65	—	1.43
$FClO_3$	9.82	1.67	—	1.43

1. Perchlorate Ion Bond Length

Lee and Carpenter (*97*) obtained a mean Cl—O bond length of 1.42 ± 0.01 Å for H_3OClO_4, which was later revised by Truter (*197*) to 1.452 ± 0.005 Å.

More recently, Nordman (*130*) obtained values for the Cl—O bond lengths in the low temperature modification of perchloric acid monohydrate of 1.445 ± 0.006, 1.478 ± 0.005, 1.465 ± 0.007, and 1.468 ± 0.006 Å, in good agreement with the mean value of 1.46 Å suggested by Truter *et al.* (*198*). Values for the Cl—O bond length in perchlorates are presented in Table IV.

TABLE IV

Cl—O BOND LENGTHS IN THE PERCHLORATE ION

Compound	Bond length, (Å)	Reference
$LiClO_4$	1.44 ± 0.01	Prosen (*141*)
$LiClO_4 \cdot 3H_2O$	1.46 ± 0.02	Prosen (*141*)
$KClO_4$	1.43 ± 0.02	Prosen (*141*)
$KClO_4$	1.46 ± 0.05	Mani (*106*)
NH_4ClO_4	1.46 ± 0.03	Venkatesan (*207*)
$AgClO_4 \cdot C_6H_6$	1.44 ± 0.01	Smith and Rundle (*183*)
$AgClO_4 \cdot C_6H_6$	1.51 ± 0.01	Smith and Rundle (*183*)
H_3OClO_4	1.42 ± 0.01	Lee and Carpenter (*97*)
H_3OClO_4	1.452 ± 0.005	Truter (*197*)
NO_2ClO_4	1.464 ± 0.007	Truter *et al.* (*198*)
H_3OClO_4	1.445 ± 0.006	Nordman (*130*)
H_3OClO_4	1.478 ± 0.005	Nordman (*130*)
H_3OClO_4	1.465 ± 0.007	Nordman (*130*)
H_3OClO_4	1.468 ± 0.006	Nordman (*130*)

Infrared and Raman spectra of complex perchlorates have recently indicated that the coordinated perchlorate group may exhibit some covalent character (*62*, *71*) and thus be of lower symmetry than tetrahedral.

2. Bond Strengths

A value for the bond dissociation energy of the HO—ClO_3 bond was calculated by Levy (*98*, *99*) from the heats of formation available for gaseous perchloric acid, gaseous hydroxyl, and chlorine trioxide radicals. The value of 48.3 kcal mole^{-1} was in good agreement with Levy's experimental value of 45.1 kcal mole^{-1} for the activation energy of the rate-determining step in the thermal decomposition of perchloric acid vapor.

Heath and Majer (*72*), in a mass spectrometric study of the vapor of 72% perchloric acid, obtained a value for the HO—ClO_3 bond strength from measurement of the appearance potential of the ClO_3^+ ion:

$$A(ClO_3^+) = D(HO\text{—}ClO_3) + I(ClO_3) \tag{6}$$

The ionization potential of Dibeler *et al.* (*41*) for $I(ClO_3)$ was used to deduce a bond energy of 46 kcal mole^{-1}.

V. Thermochemical Data

Thermochemical data for perchloric acid are somewhat sparse. Only very recently have values been obtained for the specific heat and for the heats of evaporation and fusion of the anhydrous acid. The accuracy of much of the data on both the anhydrous and the diluted acid is uncertain.

A. SPECIFIC HEAT

The available values are presented in Table V. Only the value for the anhydrous acid is from a recent determination. No values are available for perchloric acid vapor.

TABLE V
SPECIFIC HEATS OF PERCHLORIC ACID

Moles H_2O/mole $HClO_4$	Specific heat (cal gm^{-1} deg C^{-1})	Reference
0.0	0.288	Trowbridge and Westrum (*196*)
3.085	0.501	Berthelot (*15*)
5.4	0.575	Berthelot (*15*)
9.59	0.6705	Berthelot (*15*)
46.35	0.893	Berthelot (*15*)
100	0.9466	Richards and Rowe (*142*)
590	0.993	Berthelot (*15*)

B. HEAT OF FUSION

The heat of fusion of the anhydrous acid was determined by Trowbridge and Westrum (*196*) to be 1657 cal mole^{-1} at the melting point, 171.13°K. A value for the heat of fusion of the monohydrate was deduced by Rosolovskii *et al.* (*147*) from measurements of the heat of solution at 25° and 48°C for solid monohydrate, and at 51°C for liquid monohydrate. This value of 2.46 ± 0.08 kcal mole^{-1} at 51°C was obtained by assuming the temperature coefficient of the heat of solution of solid monohydrate from 25° to 48°C to be valid from 48° to 51°C.

C. HEAT OF VAPORIZATION

The experimental data available for the vapor pressure of anhydrous perchloric acid until recently were sparse. Tauber and Eastham (*192*) have measured the pressure for the temperature range 0–20°C. Sibbett *et al.* (*164, 165*) have made the only study of the vapor pressure over an extended range. Their early experiments indicated a boiling point at 760 mm of 97.2°C (*165*), later corrected to 120.5°C (*164*). These data give a value for the heat of vaporization of 8.13 kcal mole^{-1}. The values quoted elsewhere in the literature for the heat of vaporization [8.80 kcal mole^{-1} by Zinov'ev (*221*), and 8.85 kcal mole^{-1} by Trowbridge and Westrum (*196*)] are based on the very scattered data in the early literature and are unreliable. The entropy change can be used to obtain another value of 7.60 kcal mole^{-1}, using the entropy of the vapor (*154*) and liquid (*196*) states at 298°K.

The data available for the constant boiling point mixture are somewhat scattered. Measurements of the vapor pressure of perchloric acid (72.4%) over the range 140°–203°C and 100–760 mm Hg yielded a good straight-line plot, and gave a heat of vaporization of 14.76 kcal mole^{-1} per mole of vapor produced (*36*). A vapor density determination (*39*) showed that the 72% acid did not associate in the vapor phase.

D. HEAT OF DILUTION

Heats of solution have been obtained under the differential experimental conditions indicated in Table VI for the systems $HClO_4,n_1H_2O$ diluted to $HClO_4,(n_1 + n_2)H_2O$.

TABLE VI
HEAT OF SOLUTION DATA:
$HClO_4,n_1H_2O$ Diluted to $HClO_4,(n_1 + n_2)H_2O$

n_1	$n_1 + n_2$	Reference
0–200	600	Berthelot (*15*)
2.31–55.5	110	Bidinosti and Biermann (*18*)
0–4	800	Krivtsov *et al.* (*93*)
5.0–500,000	∞	Vanderzee and Swanson (*204*)

A plot of the data suggests that those of Krivtsov *et al.* and of Vanderzee and Swanson, although not overlapping, appear to be consistent and are to be preferred to the other data. The heats of dilution of anhydrous and mono- and dihydrated perchloric acid at 298°K are −21.15, −7.8, and −5.43 ± 0.04 kcal mole^{-1}, respectively.

E. ENTROPY

The vibrational frequencies measured by Giguère and Savoie (*54*) were used by these authors in conjunction with probable values of the structural parameters to calculate the entropy of anhydrous perchloric acid in the gas phase at 298°K. The derived value is 70.7 cal deg^{-1} mole^{-1} (*53*), which is somewhat in error as the bond length for the Cl—OH bond was taken as 1.70 Å. This has been recalculated (*154*) to be 70.5 cal deg^{-1} mole^{-1} (using a Cl—OH bond length of 1.64 Å) (*3*).

The entropy of anhydrous perchloric acid in the liquid phase at 298°K was determined by Trowbridge and Westrum (*196*) to be 45.02 cal mole^{-1} deg^{-1}. Using a rather large value of the heat of vaporization, they calculated the entropy in the gas phase at 298°K to be 68.2 cal mole^{-1} deg^{-1}, and commented that the gas imperfection resulting from the intermolecular hydrogen bonding (estimated to be 3 kcal mole^{-1}) (*54*, *160*, *161*) would tend to increase the entropy to a certain extent.

F. Heat of Formation

1. *Perchloric Acid at Infinite Dilution*

Three methods have been used for the determination of the heat of formation of dilute perchloric acid: (*a*) measurement of the heat of solution of a perchlorate, (*b*) measurement of the heat of neutralization of the acid with a base, and (*c*) measurement of the heat of solution of chlorine heptoxide. The first two methods require an accurate value for the heat of formation of a perchlorate. The heat of formation of a perchlorate is found by measuring the heat of decomposition to the chloride and oxygen, e.g., for potassium perchlorate:

$$KClO_4 \rightarrow KCl + 2O_2; \qquad \Delta H_1 \tag{7}$$

Using the known heat of formaton of the chloride, the heat of formation of the perchlorate can be calculated.

Two values for ΔH_1 are currently available: -2.55 ± 0.18 kcal mole^{-1} was obtained by Vorob'ev *et al.* (*210*), whereas -0.96 ± 0.08 kcal mole^{-1} was obtained by Johnson and Gilliland (*83*). The discrepancy is considerable. Vorob'ev has discussed the two values (*170*) and concluded that his is the more reliable for the following reasons:

(*i*) Two calorimetric methods were used, yielding values of -2.5 and -2.6 kcal mole^{-1}.

(*ii*) ΔH_1 was measured for both sodium and potassium perchlorates. The results gave values for the heat of formation of aqueous perchloric acid of -29.82 and -29.73 kcal mole^{-1}.

(*iii*) A check was made for the possible decomposition to the oxide (*109*):

$$KClO_4 \rightarrow \tfrac{1}{2}K_2O + \tfrac{1}{2}Cl_2 + \tfrac{7}{4}O_2 \tag{8}$$

On the other hand, full experimental details are given by Johnson and Gilliland (*83*) but not by Vorob'ev *et al.* (*210*); hence, it is not possible to choose between these values. The National Bureau of Standards has recently made further experiments to check their value for the heat of decom-

TABLE VII
Heat of Formation at Infinite Dilution from Heat of Solution of Perchlorates

Property	Potassium perchlorate	Sodium perchlorate	Lithium perchlorate
Heat of solution	+12.115 ± 0.05 (*96*) +12.31 ± 0.06 (*21*) +12.14 ± 0.01 (*210*)	+3.326 ± 0.011 (*210*) +3.315 ± 0.007 (*204*)	−6.25 ± 0.03 (*111*) −6.296 ± 0.009 (*210*)
Mean value	+12.14	+3.320	−6.27
ΔH_f for perchloric acid at ∞ dilution	−31.28 (V: 29.73)	−30.97 (V: 30.08)	−30.77 (V: 29.70)

position of potassium perchlorate, using a slightly modified method, but no significant difference was found (*212*). In the present review the values obtained by Johnson and Gilliland, corrected for the latest values available for the heats of formation of potassium and sodium chlorides, will be used throughout. However, values based on the work of Vorob'ev will be quoted in parentheses with a V to indicate source.

a. Heat of Formation from Heat of Solution of Perchlorates. This method is based on the fact that at infinite dilution the perchlorate is made up of ClO_4^- and M^+ ions. When ΔH_f for M^+ is known, that for ClO_4^- can be calculated and is identical to the heat of formation of perchloric acid at infinite dilution. Values for the heat of formation of perchloric acid at infinite dilution derived from the heats of solution of potassium, sodium, and lithium perchlorates are presented in Table VII.

A slightly different treatment by Vorob'ev (*209*) gave a value of −29.46 kcal mole^{-1}.

b. Heat of Formation from Heats of Neutralization. The heat of formation of perchloric acid can be calculated from the heat of neutralization of perchloric acid with a base MOH, where the heats are known for the formation, solution, and dilution of the hydroxide (*151*, *213*) and the perchlorate. Thus, where

$$HClO_4,n_1H_2O + MOH,n_2H_2O = MClO_4,(n_1 + n_2)H_2O + H_2O; \quad \Delta H_2 \qquad (9)$$

$$M + \tfrac{1}{2}Cl_2 + 2O_2 = MClO_4(c); \quad \Delta H_3 \qquad (10)$$

$$MClO_4(c) = MClO_4,(n_1 + n_2)H_2O; \quad \Delta H_4 \qquad (11)$$

the heat of formation, ΔH_5, of perchloric acid in n_1H_2O is given by

$$\Delta H_5 = \Delta H_3 + \Delta H_4 + \Delta H_{f,H_2O} - \Delta H_{f,MOH\ in\ n_2H_2O} - \Delta H_2 \qquad (12)$$

The various values for ΔH_5 are shown in Table VIII.

TABLE VIII

HEAT OF FORMATION, ΔH_5, AT DILUTION

$HClO_4,n_1H_2O$, from Heat of Neutralization, ΔH_2

Base	ΔH_2 (kcal mole^{-1})	Reference	ΔH_5 (kcal mole^{-1})	n_1
KOH	−13.35	Vorob'ev *et al.* (*210*)	−31.54	4500
NaOH	−13.380	Bidinosti and Biermann (*18*)	−30.94	55.5
NaOH	−13.34	Hale *et al.* (*66*, *67*)	−30.99	∞
NaOH	−13.66	Vorob'ev *et al.* (*210*)	−30.94	465
NaOH	−13.336	Vanderzee and Swanson (*204*, *205*)	−30.99	∞
LiOH	−13.54	Markowitz *et al.* (*111*)	−30.81	225

c. Heat of Formation from Heat of Solution of Chlorine Heptoxide. The heat of solution of chlorine heptoxide

$$Cl_2O_7(l) + H_2O(l) + nH_2O = 2HClO_4,nH_2O \qquad (13)$$

is a direct approach to the heat of formation of dilute perchloric acid. The heat of solution, in 5500 and 1758 moles of water, respectively, was found to be −50.0 kcal mole^{-1} by Goodeve and Marsh (*60*), and −50.4 kcal mole^{-1} by Rosolovskii *et al.* (*147*). The mean value of −50.2 kcal mole^{-1} leads to a heat of formation of perchloric acid of −31.71 ± 1.65 kcal mole^{-1}.

A mean heat of formation of perchloric acid can be computed (the results from the comparatively inaccurate data on chlorine heptoxide being excluded) to be −31.03 kcal mole^{-1} (V: −29.93 kcal mole^{-1}). A best value for the heat of formation of dilute perchloric acid would be −30.48 kcal mole^{-1}.

2. Anhydrous Perchloric Acid

Since the heat of dilution of anhydrous acid (Section V,D) is −21.15 kcal mole^{-1}, the heat of formation of the anhydrous acid is −9.33 kcal mole^{-1}.

3. Heat of Formation of Perchloric Acid Vapor

Values can be obtained either by calculation from the heat of formation of dilute perchloric acid, or from experimental studies of the heat of dissociation of ammonium perchlorate.

Values for the heat of vaporization of ammonium perchlorate of 56.6 kcal mole^{-1} and 58 kcal mole^{-1} have been obtained by Powling and Smith (*140*) and by Inami *et al.* (*81*), respectively, assuming dissociation to occur as shown in Eq. (14):

$$NH_4ClO_4(c) \rightarrow NH_3(g) + HClO_4(g) \qquad (14)$$

Using the value of Gilliland and Johnson (*55*) of −70.67 kcal mole^{-1} for the heat of formation of ammonium perchlorate, the heat of formation of perchloric acid vapor is −3.07 and −1.67 kcal mole^{-1}, respectively. However, both of these studies were at considerably elevated temperatures and no correction has been made to obtain the heat of dissociation at 298°K.

Calculation using the heats of dilution and vaporization of anhydrous perchloric acid results in a value of −1.20 kcal mole^{-1} for the heat of formation of the vapor at 298°K.

A similar calculation can be made to give the heat of formation of the constant boiling mixture in the vapor phase at 298°K. This yields a value of −127.11 kcal mole^{-1} (*36*).

G. HEAT OF ADSORPTION

The heat of adsorption of anhydrous perchloric acid vapor on a Pyrex surface at 150°–260°C under pressures of up to half an atmosphere has been deduced by Sibbett and Geller (*164*) to be 9.7 kcal mole^{-1}. However, an alternative value of 15.85 kcal mole^{-1} appears to be possible (see discussion in Section VIII,B).

VI. Physical Properties

A. GENERAL

No attempt is made here to exhaustively review all the recent papers on the physical properties of perchloric acid. A literature source table is provided to indicate the properties and the concentration ranges studied (Table IX). For completeness, some old references have been included where these contain the only data available. Data for various physical properties of the 70–75% acid have recently been presented in graphical form (*68*). Some selected topics are briefly discussed below.

B. ACIDITY

Perchloric acid is one of the strongest acids known. Its solution in fluorosulfonic acid is one of the few cases where it is believed not to ionize to form the perchlorate ion (*217*). An ionization of the type

$$HClO_4 + 2HSO_3F \rightleftharpoons ClO_3^+ + 2SO_3F^- + H_3O^+ \qquad (15)$$

was proposed.

The H_0 scale of acidity has recently been redetermined and extended to cover the range 0–70% acid at 25°C (*218*). The H_0 scale decreases more rapidly than in aqueous sulfuric acid, since 79% perchloric acid has an indicator acidity equal to that of 98% sulfuric acid. It was conservatively estimated that an H_0 value of -16 would be reached for 100% perchloric acid. Perchloric acid is a much more efficient protonating medium than sulfuric acid. The activity coefficient has been measured for 3–10 *M* perchloric acid (*76*). The molarity activity coefficient for $H^+(H_2O)_4ClO_4^-$ was found to pass through a maximum near 8 *M* acid. This is in agreement with the observation (*80*) that perchloric acid extracts into ether with 4 moles of water. Later measurements of the activity coefficient indicate the existence of two more species, $HClO_4(H_2O)_3$ and $HClO_4(H_2O)_7$ (*77*). The dissociation constant for anhydrous perchloric acid could be reported only as >4, since the data did not extend to high enough concentrations. This may be compared with the estimate of the thermodynamic dissociation constant of 38 by Hood *et al.* (*78*), who concluded that perchloric acid was

TABLE IX
PHYSICAL PROPERTIES OF PERCHLORIC ACID

Property	Concentration range 0–72%	72%	72–100%	100%	100% and upward (i.e., Cl_2O_7-rich)
Acidity, H_0 scale	(*218*)	—	(*218*)	—	—
Activity coefficient	(*76, 146*)	—	—	—	—
Boiling point	—	(*36*)	—	(*115, 164, 165*)	—
Conductivity, electrical	(*23, 92*)	—	—	—	—
Density	(*92, 190, 222*)	—	(*190, 222*)	(*114, 115*)	(*149*)
Heat of fusion	—	—	—	(*54, 196*)	—
Heat of solution	(*204*)	—	(*93*)	—	(*147*)
Heat of vaporization	—	(*36*)	—	(*164, 165, 221*)	—
Ionization potential	—	(*72*)	—	—	—
Melting point	(*23, 117*)	—	—	(*116, 196*)	(*225*)
Osmotic coefficient	(*146*)	—	—	—	—
Parachor	—	—	—	(*190*)	—
Refractive index	(*181*)	—	—	—	—
Specific heat	(*15*)	—	—	(*196*)	—
Spectra					
Electron diffraction	—	—	—	(*3*)	—
Infrared	—	—	(*160, 161*)	(*54, 98, 165*)	—
Mass	(*72*)	—	—	—	—
Raman	—	—	—	(*40*)	—
Ultraviolet	(*74*)	—	—	—	—
Surface tension	(*129, 190*)	—	—	(*190*)	—
Sound, velocity of	(*1, 133*)	—	—	(*133*)	—
Transport numbers	(*10, 34, 64*)	—	—	—	—
Viscosity	(*92, 222*)	—	(*222*)	(*226*)	—

such a strong acid because the degree of dissociation was high even in highly concentrated solutions.

C. TRANSPORT NUMBERS

The transport numbers for the cation in perchloric acid was recently determined for the 0.1–5.1 *M* concentration range at 25°C (*64*). The results agreed well with those obtained earlier (*10, 34*).

VII. Chemical Properties

Anhydrous perchloric acid is an extremely powerful oxidizing agent. With most combustible materials there is an immediate explosive reaction in the cold. Gold and silver are oxidized in the cold; platinum is not attacked, but its presence results in rapid decomposition of the acid (*196*). Consequently, all handling of the acid should be in glass apparatus.

Sections A and B below discuss the nature of mixed acid systems and the explosion hazard concerned with the use of anhydrous acid. The system $HClO_4$–H_2O–H_2O_2 has recently been studied (*195*), but no compound containing hydrogen peroxide was detected.

Other chemical reactions are summarized by Schumacher (*158*), Mellor (*118*, *119*), and Burton and Praill (*30*).

A. Mixed Acid Systems

1. *Acetic Acid–Perchloric Acid System*

The ion association constants determined for perchloric acid in acetic acid at 25°C by potentiometric (*24*) and conductimetric (*186*) methods differ by a factor of 15. A value of 0.0644×10^{-6} has recently been obtained (*112*). Conduction with perchloric acid has been shown (*113*) to occur by a proton-jump mechanism in common with other solvated protons.

In the very concentrated system, perchloric acid monohydrate–anhydrous acetic acid, it has been shown that the perchloric acid retains its water of hydration (*223*).

2. *Sulfuric Acid–Perchloric Acid System*

Infrared absorption spectra of the perchloric–sulfuric and sulfuric–phosphoric acid systems have been studied (*162*) in the region 3700–750 cm^{-1}. The spectra indicate that chemical reaction occurs in the H_3PO_4–H_2SO_4 but not in the $HClO_4$–H_2SO_4 system, confirming the results of Usanovich (*202*) on the electrical conductivity and viscosity in the system H_2SO_4–$HClO_4$. However, simultaneously another group of Russian workers (*163*) studied the freezing point diagram of the ternary system Cl_2O_7–SO_3–H_2O, and observed the formation of an intermolecular compound, $H_2SO_4 \cdot 2HClO_4$.

3. *Nitrous Acid–Perchloric Acid System*

This system has been particularly studied in connection with the reactivity of nitrous acid in acidic media.

The proportion of nitrosonium ion present in solutions of sodium nitrate in concentrated perchloric acid was measured spectrophotometrically in 1956 (*169*), but no equilibrium constant was available until 1958 (*200*). Dilute solutions of nitrous acid in 50% perchloric acid were observed to decompose steadily with time. This was confirmed by later workers (*14*), who also studied the kinetics of the nitrite decomposition (*13*) and found the rate to be strongly dependent on the perchloric acid concentration. The maximum decomposition occurred at about 50% by weight where both nitrous acid and the nitrosonium ion exist in appreciable concentration. The reaction of sodium nitrite with perchloric acid has been briefly studied (*63*).

4. *Nitric Acid–Perchloric Acid System*

This system has been thoroughly examined by Goddard *et al.* (*57*) and Millen (*82*). They showed clearly that the reaction

$$HNO_3 + 2HClO_4 = NO_2^+ClO_4^- + H_3OClO_4^- \quad (16)$$

occurred on mixing the anhydrous acids at −40°C.

B. EXPLOSIVE NATURE

Anhydrous perchloric acid has long had a reputation of being explosive. Recently it has become clear that it is not, and that its earlier reputation arose from the preparation of impure samples containing chlorine heptoxide, which can explode violently on shock or sudden heating. Samples of the anhydrous acid on standing at room temperature rapidly become colored with chlorine oxides which are explosive. It must also be emphasized that contact of the anhydrous acid with many materials—especially organic ones—will result in explosion. The nonexplosive nature of carefully prepared anhydrous acid has been shown by Levy (*98*). However, samples of anhydrous acid in closed bottles can produce pressure bursts as a result of the formation of solid monohydrate around the stopper, which is thus effectively cemented in (see also Section VIII,A). Diluted perchloric acid (72% or below) is stable at room temperature, as was shown by Dietz (*44*) and Elliott and Brown (*45*). Its mixture with organic compounds can be very dangerous, especially so with acid anhydrides which have the effect of producing a solution of anhydrous perchloric acid (*107*). The dangers of mixtures with acetic anhydride used in electropolishing are reviewed by Schumacher (*158*). Mixtures with ethyl alcohol have a detonation velocity of 1600 m/sec (*95*), while other mixtures with organic compounds have been proposed as monopropellent fuels (*11*, *215*) and also as a means of producing explosions on surfaces (*48*). The paper by Elliott and Brown is a particularly useful survey of the explosive nature of various perchloric acid mixtures (*45*).

Ventilating systems for perchloric acid vapor must be carefully designed (*43*). The sealant in such systems must *not* be a litharge-glycerin cement, since this has resulted in fatalities (*201*). Portable scrubbers (*167*) and digestion units (*105*) have been described.

VIII. Thermal Decomposition

A. INTRODUCTION

Little information was available until recently on the thermal decomposition of perchloric acid in either the gas or liquid phase, although the unstable nature of the anhydrous acid was well known. Mellor (*118*) stated that the anhydrous acid exploded if an attempt was made to distill it at atmospheric pressure; at 72°C the acid darkened in color, at 92°C white fumes mixed with chlorine dioxide were evolved, and on further heating explosion occurred. It is now clear that anhydrous perchloric acid is not explosive when pure. The fact that earlier workers often found even freshly prepared samples to be explosive can be explained by the ease with which the anhydrous acid can be dehydrated to the anhydride chlorine heptoxide, which explodes violently on shock or sudden heating. This has been shown by Levy (*98*), who found that samples of perchloric acid vapor, from acid prepared in the usual way by dehydration of the dehydrate, could be exploded either by heating a spiral of wire in the vapor or by plunging the bulb containing the vapor into a hot bath. These samples of acid were shown to contain as much as 50% chlorine heptoxide. Pure samples of vapor, freed from the chlorine heptoxide, did not explode. It is thus clear that statements such as the one by Sibbett and Lobato (*165*), that the sample of acid passed over phosphorus pentoxide in order to remove all traces of water was unstable, can be explained by formation of the unstable chlorine heptoxide.

An outstanding feature of the perchloric acid system is the marked increase in stability with increasing dilution of the acid. The monohydrate is a crystalline solid (m.p. 49.9°C) (*180*) stable up to about 110°C (*199*), the 72.4% acid is a constant boiling mixture which is quite stable and decomposes only slightly when heated to its boiling point (203°C), whereas the anhydrous acid is unstable even at −78°C (*220*). It is suggested that this stability is associated with the formation of the perchlorate ion, i.e., the aci-form, and the inherent instability of the anhydrous acid with the covalent form.

B. GAS PHASE DECOMPOSITION

The thermal decomposition of anhydrous perchloric acid vapor was studied at 200°–220°C by Sibbett and Lobato (*165*). They showed that reaction proceeded according to the over-all equation

$$HClO_4 = \tfrac{1}{2}H_2O + \tfrac{1}{2}Cl_2 + \tfrac{7}{4}O_2 \qquad (17)$$

although a complete analysis was not obtained. The kinetics were found to be second order in the early stages of the reaction, changing to first order as the reaction proceeded. The reaction was shown to be heterogeneous at 200°–220°C.

Levy (*98*, *99*) confirmed that the over-all reaction yields chlorine, oxygen, and water for the temperature range 200°–439°C. Hydrogen chloride was not a product. The decomposition kinetics at 200°–350°C were determined in a static system using anhydrous perchloric acid, and at 350°–439°C in a flow system using 70% perchloric acid. Experiments at 294°C indicated that water had a moderate inhibiting effect: 2.53 moles of water per mole of acid decreased the first-order rate constant from 0.062 to 0.038 min^{-1}. This indicated that the presence of small amounts of water in the acid should not significantly affect the kinetics. Below 310°C a heterogeneous reaction was involved, whereas above this temperature the decomposition was homogeneous and first order. An Arrhenius plot of the data for the homogeneous reaction yielded the expression

$$k = 5.8 \times 10^{13} \exp(-45{,}100/RT)\ \text{sec}^{-1} \tag{18}$$

The first-order nature of the reaction and the magnitude of the activation energy suggest that the rate-determining reaction is

$$\text{HOClO}_3 \rightarrow \text{HO}\cdot + \text{ClO}_3 \tag{19}$$

followed by the fast reactions

$$\text{HO}\cdot + \text{HOClO}_3 \rightarrow \text{H}_2\text{O} + \text{ClO}_4 \tag{20}$$

$$\text{ClO}_4\cdot \rightarrow \tfrac{1}{2}\text{Cl}_2 + 2\text{O}_2 \tag{21}$$

$$\text{ClO}_3\cdot \rightarrow \tfrac{1}{2}\text{Cl}_2 + \tfrac{3}{2}\text{O}_2 \tag{22}$$

Although reactions (21) and (22) are written as single equations, it is likely that the decompositions of the ClO_3 and ClO_4 radicals are complex and involve formation and decomposition of lower chlorine exides.

Using the heats of formation of HClO_4(g) (−1.20 kcal mole^{-1}) (Section V,F), HO·(g) (9.37 kcal mole^{-1}) (*213*), and $\text{ClO}_3\cdot$(g) (37 kcal mole^{-1}) (*61*), a value of 47.6 kcal mole^{-1} can be calculated for the heat of reaction (*19*) at 298°K, which agrees well with the experimental activation energy of 45.1 kcal mole^{-1}.

The heterogeneous reaction which occurred below 310°C was found by Levy to have an activation energy of the order of 10 kcal mole^{-1}. More recently, Sibbett and co-workers (*166*) have studied this heterogeneous reaction at 150°–260°C. They proposed the following mechanism:

$$2\text{HClO}_4 \xrightarrow{k_2} \text{Cl}_2 + \tfrac{7}{2}\text{O}_2 + \text{H}_2\text{O} \tag{23}$$

$$HClO_4 + H_2O \rightarrow HClO_4 \cdot H_2O \tag{24}$$

$$HClO_4 \cdot H_2O \xrightarrow{k_1} \tfrac{1}{2}Cl_2 + \tfrac{3}{2}H_2O + \tfrac{7}{4}O_2 \tag{25}$$

Rate constants for the second-order reaction, k_2, and the first-order reaction, k_1, have been computed from the initial and final data obtained by following the rate of pressure change. A computer solution of the simultaneous differential equations representing the reaction scheme demonstrated that the observed pressure may be computed when the two rate constants are evaluated. Activation energies were calculated to be 8.9 and 21.3 kcal mole^{-1} for the second- and first-order steps, respectively. Both steps were shown to be surface-catalyzed with a linear dependence of the two rate constants on the surface-to-volume ratio at 200°C.

This research has been further described by Sibbett and Geller (*164*). The reaction was second order initially and then became first order. The amount of chlorine evolved was found to be directly proportional to the amount of decomposed acid at all times. Computer multiple-trial calculations showed that the reaction scheme best fitting the data was

$$2HClO_4 \xrightarrow{k_1} H_2O + Cl_2 + \tfrac{7}{2}O_2 \tag{26}$$

$$HClO_4 + H_2O \rightarrow HClO_4 \cdot H_2O \tag{27}$$

$$HClO_4 \cdot H_2O \xrightarrow{k_2} \tfrac{3}{2}H_2O + \tfrac{1}{2}Cl_2 + \tfrac{7}{4}O_2 \tag{28}$$

On the assumption that these reactions occurred on the glass surface (the data showed that most of the reaction, if not all, was heterogeneous), it followed that

$$\frac{-d[HClO_4]}{dt} = 2k_1[HClO_4]^2 + \frac{k_2[HClO_4][H_2O]}{1 + K_B[H_2O]} \tag{29}$$

where K_B is the equilibrium constant for the adsorption of some inhibiting species, presumed to be water, on the reactor surface. From consideration of Langmuir-Hinshelwood adsorption theory, it followed that reaction (26) occurs by a mechanism in which perchloric acid is weakly adsorbed and surface coverage is slight. Then the initial bimolecular process can be described by

$$V_1 = 2k'_1K^2[HClO_4]^2 \tag{30}$$

The experimental rate constant, k_1 is equal to k'_1K^2, where K is the equilibrium constant for the adsorption of perchloric acid on Pyrex. This requires that the observed activation energy

$$E_{a_1} = E_T - 2\lambda_{HClO_4} \tag{31}$$

where λ_{HClO_4} is the heat of adsorption of $HClO_4$, and E_T is "the true activation energy for the homogeneous gas phase decomposition of $HClO_4$."

Two alternative possibilities exist for the surface processes in reactions (27) and (28). Both $HClO_4$ and the inhibiting reaction product (assumed to be H_2O) can (1) compete for the same sites, or (2) be adsorbed on two different types of surface site. It was shown that for competitive adsorption

$$E_{a_2} = E_T - \lambda_{H_2O} \tag{32}$$

and for noncompetitive adsorption

$$E_{a_2} = E_T - \lambda_{H_2O} - \lambda_{HClO_4} \tag{33}$$

Sibbett and Geller earlier used the value of 32.8 kcal $mole^{-1}$, obtained by Zinov'ev and Babaeva (*224*) for the liquid phase decomposition, as the value of E_T in Eq. (31). This, with the experimental value of $E_{a_1} = 13.4$ kcal $mole^{-1}$, yielded a value of 9.7 kcal $mole^{-1}$ for the heat of adsorption of $HClO_4$.

Substitution of this value, along with $\lambda_{H_2O} = 13.3$ kcal $mole^{-1}$ for Pyrex glass and the experimental value for E_{a_2} of 20.5 kcal $mole^{-1}$, in Eqs. (32) and (33) leads to values for E_T of 33.8 and 43.4 kcal $mole^{-1}$, respectively. Hence it was concluded that the competitive adsorption process was more probable.

However, if the value obtained by Levy (*98*, *99*) of 45.1 kcal $mole^{-1}$ is used for E_T, it follows that $\lambda_{HClO_4} = 15.85$ kcal $mole^{-1}$. Substitution of this value in Eqs. (32) and (33) yields values for E_T of 33.8 and 49.65 kcal $mole^{-1}$, respectively. Consequently it might appear that the noncompetitive adsorption process is more probable.

Perchloric acid vapor (72% acid) has been introduced by Heath and Majer (*72*) into A.E.I. type M.S.2 mass spectrometer. They studied the heterogeneous decomposition of perchloric acid vapor on a hot platinum wire just outside the ionization box of the mass spectrometer. The results showed that the dominant mode of decomposition was into hydrogen chloride and oxygen:

$$HClO_4 \rightarrow HCl + 2O_2 \tag{34}$$

The equilibrium constants for the Deacon equilibrium (*36*)

$$2HCl + \tfrac{1}{2}O_2 \rightleftharpoons Cl_2 + H_2O \tag{35}$$

show that, at the temperatures and pressures used by Heath and Majer (estimated to be 950° and 1170°K), a preponderance of hydrogen chloride would be expected. The equilibrium constants at 450°–700°K (the temperature range used by Levy) show that production of chlorine should be dominant at these temperatures.

C. CHLORINE HEPTOXIDE THERMAL DECOMPOSITION

The gas phase decomposition was studied by Figini *et al.* (*46*) at pressures of 1.5–80 mm Hg and temperatures of 100°–120°C. The decomposition was found to be homogeneous and unimolecular, and to have an energy of activation of 32.9 ± 1.5 kcal mole^{-1}. The reaction was followed by the pressure rise, since analysis of the products showed the over-all decomposition to be

$$Cl_2O_7 \rightarrow Cl_2 + 3\tfrac{1}{2}O_2 \tag{36}$$

The effect of added chlorine and oxygen was studied. Both activated the decomposition but were about 4.5 times less active than pure heptoxide.

Experiments with added fluorine showed that the first stage is decomposition into ClO_3 and ClO_4 radicals:

$$Cl_2O_7 \rightarrow ClO_3 + ClO_4 \tag{37}$$

The liquid phase decomposition has very recently been studied by Babaeva (*7*) at temperatures of 60°–80°C. The isotherms of liberation of oxygen were very nearly straight lines. An activation energy of 32.1 kcal mole^{-1} was deduced for the zero-order process. Additions of trichloroacetic acid or carbon tetrachloride had no effect on the decomposition. However, additions of perchloric acid (1%) considerably modified the decomposition: the oxygen liberation rate increased, the oxygen liberation curves became S-shaped, and the whole decomposition was more rapid.

At 60°–80°C, the Cl_2O_7 became pale yellow but did not darken in color in the course of the experiment. However, at 50°C the color became more intense and this led to an acceleration of the reaction in the final stage. The oxygen liberation isotherm became S-shaped. In the next section, the liquid phase decomposition is compared and contrasted with that of liquid perchloric acid.

D. Liquid Phase Decomposition

Zinov'ev (*220*) in 1958 stated that, although anhydrous perchloric acid decomposed slowly at room temperature and even at −78°C, it also had an induction period when heated, and that it was because of this induction period that anhydrous perchloric acid could be distilled. An electrochemical study by Missan and Sukhotin (*122*) showed that 97% perchloric acid decomposed at room temperature to give oxygen, chlorine dioxide, and chlorine trioxide. They also found that highly concentrated perchloric acid contained chlorine heptoxide whose concentration increased rapidly as the perchloric acid concentration approached 100%. In view of the discussion in Section II, this observation confirms that chlorine heptoxide is an impurity in highly concentrated perchloric acid when the latter is not specially purified. The decomposition of the acid was reduced by addition of 1–2% chloral hydrate to the concentrated acid.

A series of papers on the thermal decomposition of liquid perchloric acid has been published by Zinov'ev and co-workers (*8*, *9*, *199*, *224*, *227*).

It was assumed that the over-all decomposition could be represented by the equation

$$HClO_4 \rightarrow \frac{1}{2}H_2O + \frac{1}{2}Cl_2 + \frac{7}{4}O_2$$

and the reaction was followed by measuring the volume of oxygen evolved. The actual reaction is considerably more complex, since chlorine oxides have been detected as intermediate products. The decomposition in the liquid phase was found to take place in three stages: an induction period, an active period in which the reaction rate rose sharply to a maximum, and a final period in which the reaction rate fell to zero. The final product was a yellowish liquid crystallizing at 47°–48°C and containing 85.3–86.0% perchloric acid. This corresponds to the monohydrate. The earlier papers studied the decomposition of the 83–100% acid over the temperature range 40°–95°C, with experiments at 110°–145°C for the 83% acid. Plots of the logarithm of the maximum rate of oxygen evolution against the reciprocal of the absolute temperature yielded a value of 22.2 kcal mole^{-1} for the activation energy of the second stage (*227*). A later value was 22.56 kcal mole^{-1} (*199*). The induction period was found to decrease with increase in temperature and increase in acid concentration. A detailed study of the induction period by Zinov'ev and Babaeva (*224*), who also studied the effect of inhibitors (trichloroacetic acid and carbon tetrachloride), led to a value of 32.6 kcal mole^{-1} for the activation energy of the induction period. This was obtained by plotting the logarithm of the induction period against the reciprocal of the absolute temperature. An identical activation energy was obtained with perchloric acid–chlorine heptoxide mixtures. The induction period study was extended (*9*) to six acid concentrations from 84.8 to 100%, and activation energies of 32.5 and 22.58 kcal mole^{-1} were obtained for the induction period and active period, respectively.

The mechanism by which the inhibitors act was not discussed (*224*), but it was apparent that the C—Cl bond is the effective agent since this is the common factor in the known inhibitors (chloral hydrate, trichloroacetic acid, and carbon tetrachloride).

More recently, kinetic curves have been obtained for the formation and consumption of chlorine, chlorine dioxide, and chlorine trioxide during the decomposition of anhydrous perchloric acid (*8*). The shape of the kinetic curves was complex and no detailed mechanism was suggested.

Tsentsiper (*199*) proposed that the decomposition was a chain process initiated by fission of the HO—ClO_3 bond. The sharp fall in the rate of decomposition with increase in dilution was ascribed to a decrease in the concentration of the pseudo (covalent) form, $HOClO_3$, and an increase in the concentration of the more stable aci-form, ClO_4—as indicated by Raman spectra.

However, Zinov'ev and Babaeva (*224*) suggested that the decomposition rate was determined by the formation and subsequent decomposition of chlorine heptoxide:

$$2HClO_4 \rightleftharpoons Cl_2O_7 + H_2O \qquad (38)$$

This reaction would be facilitated by the tendency of perchloric acid to hydrate:

$$HClO_4 + H_2O \rightarrow HClO_4{\cdot}H_2O \qquad (39)$$

This mechanism was based on three observations: (*i*) the activation energy for the decomposition was independent of the initial composition throughout the range from 84.8% perchloric acid through 100% acid to acid containing 35.4% chlorine heptoxide, (*ii*) the activation energy calculated for the induction period was close to that observed for the gas phase decomposition of chlorine heptoxide, and (*iii*) Missan and Sukhotin had detected chlorine heptoxide in highly concentrated perchloric acid (*122*). Zinov'ev and Babaeva therefore rejected the mechanism proposed by Tsentsiper.

However, recent work has thrown more light on this controversy. It is now clearly established that concentrated perchloric acid when not specially purified will contain chlorine heptoxide. The recent work by Babaeva (*7*) on chlorine heptoxide in the liquid state indicates that it does not decompose in the same way as the anhydrous acid, since (*i*) inhibitors for perchloric acid have no effect on chlorine heptoxide, and (*ii*) addition of 1% perchloric acid to chlorine heptoxide changes the whole character of the decomposition. The earlier finding of Zinov'ev and Babaeva (*224*), that additions of chlorine heptoxide to the acid do not affect the kinetics of decomposition save by reducing the induction period, when considered along with Babaeva's recent work, does not lend support to the idea of decomposition through the heptoxide.

In fact, the observed phenomena can be better explained by the alternative theory of Tsentsiper (*199*) along with the assumption that the dissociation

$$3HClO_4 \rightleftharpoons Cl_2O_7 + HClO_4{\cdot}H_2O$$

does not occur to a great extent. The effect of addition of chlorine heptoxide to the acid can then be explained as being due solely to the shift of this equilibrium to the left. The finding of Rosolovskii *et al.* (*147*), that the heat of reaction for the above equation, as written from left to right, is $\Delta H = -2.8$ kcal, also supports Tsentsiper's theory since increase in temperature will tend to shift the equilibrium to the left. Further, decomposition of 83% acid does not differ significantly from that of acid more concentrated than the monohydrate (84.8%); it is difficult to believe that chlorine heptoxide is present in 83% acid.

The sole evidence remaining to support the decomposition of anhydrous perchloric acid through chlorine heptoxide is that the numerical value of the activation energy deduced from the induction period (32.5 kcal $mole^{-1}$) is the same as that in the gas and liquid phase decomposition of chlorine heptoxide, as deduced from the pressure rise of products (32.9 and 32.1 kcal $mole^{-1}$, respectively). It would perhaps be more logical to compare the activation energies of the acid decomposition for the induction period with that of ammonium perchlorate also for the induction period (~32 kcal $mole^{-1}$) (*187*), or of guanidine perchlorate also for the induction period (~30.5 kcal $mole^{-1}$) (*56*).

IX. Radiation Chemistry

A. PHOTOCHEMICAL RADIATION

The optical density of perchloric acid is less than 0.1 in the 2300–2800 Å region (*131*), and the perchlorate ion absorbs light very slightly at 2000–8000 Å (*74*). This is in accord with the method for the preparation of perchloric acid in which a mixture of chlorine, ozone, and water vapor was photolyzed at 2537 Å (*153*). The photolysis by sunlight of a mixture of cerous and ceric perchlorates and of perchloric acid has been used to produce microquantities of hydrogen and oxygen (*73*). The perchlorate acted as a catalyst, and it is hoped that this process may eventually be of economic importance.

B. IONIZING RADIATION

Solutions of perchloric acid were found to be decomposed into chlorate and molecular oxygen by X-rays (*143*). In the presence of ferrous ions, an additional interaction occurred in which the ferrous salt was oxidized and chloride was produced.

The amount of chlorate formed by 200-kV X-rays was directly proportional to the perchloric acid concentration (*121*). Ceric salts had no effect on the chlorate formation, while ferrous salts resulted in the formation of an equivalent amount of chloride. Whereas irradiation of ferrous sulfate in solution in sulfuric acid liberated equivalent amounts of hydrogen and ferric salts, this was not the case in perchloric acid solutions where a less than equivalent amount of hydrogen was liberated (*143*). The discrepancy between the yields of hydrogen and the ferric salt became more marked as the acid concentration increased. It was thus shown that irradiation of perchloric acid solutions results in a "direct effect," i.e., the energy of the radiation excites the perchloric acid molecules. The irradiation of perchloric acid solutions at 77°K by γ-rays from a 1000-curie cobalt-60 source was found to produce substantial amounts of atomic hydrogen (*102*, *219*). The atomic hydrogen was detected by the paramagnetic resonance spectrometer, which also showed lines from other unpaired-electron species formed by the irradiation and trapped stably at 77°K. The atomic hydrogen disappeared on moderate warming of the acid by a second-order rate, and with an activation energy of several kcal mole^{-1}.

The yields of atomic hydrogen have recently been measured by the paramagnetic resonance method, along with the volumes of hydrogen and oxygen liberated on warming the irradiated acid (*101*). It was found that the yields were independent of whether the acid was in a glassy or crystalline state, unlike the case for phosphoric and sulfuric acids. The yields of atomic hydrogen, hydrogen, and oxygen increased steadily with the acid concentration up to a concentration of about 0.15 mole fraction, at which point (*a*) the atomic and molecular hydrogen yields showed a sudden decrease, (*b*) the molecular oxygen yield showed a sudden increase, and (*c*) an unidentified gaseous species was detected in a quantity increasing with acid concentration from 0.14 mole fraction. This unknown species was thought to be chlorine or a chlorine compound, since it colored yellow the liquid phase produced on warming. The yields of atomic hydrogen were greatly in excess of those of the molecular hydrogen liberated. This difference was ascribed to reaction of the hydrogen atoms with other unidentified species. The saturation of a 0.125 mole fraction solution of perchloric acid by irradiation gave a hydrogen atom concentration of 2.0×10^{19} atoms per gram—a factor of 10 greater than that from sulfuric acid. Nitric acid addition scavenged the hydrogen atoms but not to as great an extent as in sulfuric acid.

Tritiated samples of perchloric acid solutions (molar ratios of $HClO_4:H_2O = 1:7$, and of $HClO_4:H_2O:D_2O = 1:3:4$) have been studied by electron paramagnetic resonance (*94*). H and D atoms were readily produced, along with other unidentified species which colored the acid yellow. The change in H and D atom concentrations on warming was followed, and at about −150°C the H and D concentrations were found to decrease rapidly, while a new unidentified radical species appeared and rapidly increased in concentration.

The yields of molecular hydrogen from tritiated perchloric acid were in good agreement with the early work on γ-irradiated acid (*101*). However, the ratio of the yields of molecular and atomic hydrogen was twice as high in tritiated acid as in γ-irradiated acid at the same concentration. This may be accounted for by the different linear energy transfer of these types of radiation.

Irradiation of perchloric acid solutions at room temperature has been studied by Cottin (*32*), using radiation from three sources: γ-rays from 25- and 90-curie cobalt-60 sources, X-rays of 10 keV, and α particles from polonium. The yields of ClO_3^- and Cl^- were proportional to the concentration of the irradiated acid (0–4 *M*), and were independent of the presence of dissolved oxygen or the physical state. Other products were hydrogen, chlorine, oxygen, and chlorine dioxide. The experiments indicated that the chloride ion was probably formed simultaneously with the chlorate ion. Possible reactions were

$$ClO_4^- \rightsquigarrow ClO_3^- + O \tag{40}$$

and

$$ClO_4^- \rightsquigarrow Cl^- + 4O \tag{41}$$

although it was difficult to visualize a mechanism for the latter process. The energy required to decompose a perchlorate ion was 24.7 eV.

Bugaenko (*25–28*) has studied the effect of X-rays (up to 70 keV) on 2.5 *M* perchloric acid at 20° ± 1°C. The acid solutions were either saturated with hydrogen, nitrogen, or oxygen, or contained 0.008 *M* ferrous sulfate. No chlorine dioxide was formed, but chloride and chlorate ions and hydrogen peroxide were formed. Their accumulation curves were linear in all cases. Since the *G* value for perchlorate ion reduction was the same in all cases and was the same for 2.5 *M* sodium perchlorate, it was deduced that the perchlorate ion was reduced directly by the ionizing radiation. The following mechanism was suggested:

$$ClO_4^- \rightsquigarrow ClO_4^{-*} \tag{42}$$

or

$$ClO_4^- \rightsquigarrow ClO_4 + e \tag{43}$$

The excited perchlorate ions probably transferred their energy to neighboring molecules and probably also decomposed by

$$ClO_4^{-*} \rightarrow ClO_3^- + O \tag{44}$$

The perchlorate radicals decomposed by

$$ClO_4 \rightarrow ClO_2 + O_2 \tag{45}$$

which then reacted with hydroxyl radicals to form chlorate ions:

$$ClO_2 + OH \rightarrow ClO_3^- + H^+ \tag{46}$$

Chloride ions were produced by the scheme

$$ClO_3^- \xrightarrow{OH} ClO_2 \xrightarrow{H} ClO_2^- \xrightarrow{2H} ClO^- \xrightarrow{H_2O_2} Cl^- \tag{47}$$

In the presence of hydrogen the reaction

$$H_2 + OH \rightarrow H + H_2O \qquad (48)$$

occurred, resulting in an increased yield of chloride ion. Addition of ethyl alcohol and acetone resulted in a decrease in the yield of the reduction of the perchlorate ion. This was believed to be due to the reaction

$$ClO_4 + RH \rightarrow ClO_4^- + H^+ + R \qquad (49)$$

Very recently, Katakis and Allen (*88*) studied the radiolysis of perchloric acid in the absence and presence of radical scavengers over a range of acid concentrations. Irradiation was by γ-rays from a cobalt-60 source at a dose rate of 3.2×10^{20} ev/l min and by 33-MeV He^{++} ions from a cyclotron.

Radiolysis of 10^{-2} *M* perchloric acid indicated that the free radicals from the water radiolysis did not react with the perchlorate ion. In more concentrated solutions, the perchlorate ion decomposed by the direct action of the radiation, with a yield increasing directly with its concentration, while the yields of hydrogen and other water decomposition products decreased.

Up to 2.5 *M* perchloric acid, the yields of chlorate $G(ClO_3^-)$, and chloride ion $G(Cl^-)$, agreed with those obtained by Cottin (*32*), but above 2.5 *M* Cottin's yields were higher. This may have been due to differences in thermal reactions, which were not investigated but were believed to involve a reaction between chloride and chlorate ions giving products which rapidly oxidized the hydrogen peroxide. Addition of 10^{-2} *M* sodium chloride increased the chlorate yield, and below 3 *M* perchloric acid this became equal to the sum of $G(Cl^-)$ and $G(ClO_3^-)$ as measured in the absence of added chloride ion. This indicated that the chloride ion was mainly a secondary product in the radiolysis resulting from the attack of the chlorate ion by free radicals. The added chloride ion protected the chlorate from attack. This was verified by irradiation of chlorate ion in the presence and absence of chloride ion. The reaction involved was proposed to be

$$OH + ClO_3^- + H^+ \rightarrow H_2O + ClO_3 \qquad (50)$$

followed by decomposition or reduction of the chlorate radical to yield a chloride ion. The oxygen liberated along with the chlorate may emerge as oxygen, hydrogen peroxide, HO_2 or OH radicals, or O atoms.

Since the yields all vary linearly with the perchlorate ion concentration, the excited perchlorate ions did not react with other perchlorate ions but rather decomposed unimolecularly. Two possible reactions were

$$ClO_4^{-*} \rightarrow ClO_4 + e \qquad (51)$$

and

$$ClO_4^{-*} \rightarrow ClO_3^- + O$$

The results indicated that reaction (51) was very unlikely and the usual process was production of chlorate ions and oxygen atoms. Most of the oxygen atoms will probably be in the ground state, since Taube (*191*) has shown that oxygen atoms in the ^1D state react readily with water to form hydrogen peroxide, and can also reduce perchloric acid to chloric acid. This was confirmed because the hydrogen peroxide yield was decreased.

X. Perchloric Acid Flames

A. AMMONIUM PERCHLORATE COMBUSTION

Flames in which perchloric acid is used as the oxidizer have been studied recently because of the widespread use of ammonium perchlorate as oxidizer in composite propellants for rocket propulsion. It is believed that, at least under certain conditions, the monopropellent combustion of the ammonium perchlorate particles is the controlling factor in the burning rate of the propellant (*2*, *12*). There has been much discussion in the past decade on possible mechanisms of ammonium perchlorate decomposition. Those favored are

(*i*) Decomposition of the perchlorate ion (*20*).

(*ii*) Electron transfer (*19*, *51*):

$$NH_4^+ClO_4^- \rightleftharpoons NH_4 + ClO_4 \tag{52}$$

(*iii*) Proton transfer (*50*, *157*):

$$NH_4^+ClO_4^- \rightleftharpoons NH_3 + HClO_4 \tag{53}$$

Mechanism (*i*) seems unlikely since the activation energy for such a process in the crystal lattice would be too high. The bond dissociation energies for Cl—O and O—ClO are 63 and 57 kcal mole^{-1}, respectively (*33*), and the activation energy for the thermal decomposition of potassium perchlorate is 70 kcal mole^{-1} (*69*, *135*). The observed activation energy for ammonium perchlorate is about 30 kcal mole^{-1} and thus it is unlikely that Cl—O bond fission is important.

It has been suggested by Galway and Jacobs (*52*) that ammonium perchlorate is decomposed by an electron transfer mechanism below 300°C and by a proton transfer mechanism above 350°C, but Russell-Jones (*152*), working with Jacobs, has recently concluded that the same process is involved under all conditions, and this process was deduced to be effectively proton transfer although free protons are not involved. Russell-Jones obtained activation energies of 30.6 kcal mole^{-1} for sublimation. Previous discrepancies in the values obtained for the high temperature reaction were ascribed to the fact that gas phase reactions were limiting at high temperatures.

Evidence for the formation of free ammonia and perchloric acid continues to accumulate. Bircumshaw and Newman (*19*) showed that added perchloric acid reduced the induction period and added ammonia increased it, as would be expected if the formation of decomposition centers was associated with the production of free perchloric acid. The effect of the perchloric acid addition to ammonium perchlorate is minimized in an ammonia atmosphere at 200°–240°C (*20*). Later work (*110*) showed that, when calcium oxide is placed above the perchlorate in a tube in which sublimation is occurring, the amount of sublimate is considerably reduced presumably because of adsorption of the perchloric acid by the calcium oxide. A recent study of ammonium perchlorate, in which the salt was heated to a given temperature and then put into cold water and analyzed for possible acids, indicated that the first reaction step is dissociation into ammonia and perchloric acid (*132*). This was found to be first order with an activation energy of 21.5 kcal mole^{-1}.

Sublimation experiments on ammonium perchlorate at 300°C with analysis of the sublimate (*31*) have resulted in the suggested decomposition reaction

$$NH_4ClO_4 \rightarrow \tfrac{1}{6}(NH_3 + HClO_4) + \tfrac{5}{6}(HNO_3 + HCl + H_2O) \qquad (54)$$

Mack *et al.* (*103*) used methods of Knudsen's free flow and matrix isolation in the study of the gaseous species in equilibrium with crystalline ammonium perchlorate. The gaseous species effusing from a cell at 200°C were successfully trapped at liquid helium temperatures in a nitrogen matrix. Infrared spectra of these species studied over the range 4000–650 cm^{-1} showed that the only major species in the vapor are ammonia and perchloric acid. Confirmatory evidence has come from Inami *et al.* (*81*), who studied the dissociation pressure of ammonium perchlorate at 510°–620°K by passing helium through a porous bed of the perchlorate, and condensing the sublimate on a cold finger some 2 cm from the porous bed. The cold finger was held at 340° ± 10°K to prevent condensation of water. The sublimate was analyzed for NH_4^+, ClO_4^-, and Cl^-, and found to contain equimolar quantities of NH_4^+ and ClO_4^-. The results were interpreted in terms of an equilibrium dissociation

$$NH_4ClO_4(s) \rightleftharpoons NH_3(g) + HClO_4(g) \qquad (55)$$

which was effectively confirmed by addition of ammonia to the helium gas stream. The sublimate was then found to contain equimolar quantities of NH_4^+ and Cl^- and only traces of ClO_4^-. The heat of dissociation was calculated to be 58 ± 2 kcal mole^{-1}.

Powling (*138–140*) has studied the surface temperature of burning ammonium perchlorate at a range of pressures from 1/40 atmosphere up to 4 atmospheres. Since at a given pressure the surface temperature was independent of the burning rate, it was assumed that near equilibrium conditions exist between the solid and vapor. Consequently, a surface temperature-pressure plot should yield the heat of sublimation (or dissociation) of ammonium perchlorate. The value obtained, 57 kcal mole^{-1}, is in such close agreement with the calculated value, 58 kcal mole^{-1}, that this may be regarded as strong support for the dissociation reaction (*55*).

A mass spectrometric study (*72*), in which ammonium perchlorate was heated in a compartment adjoining the ion source of the mass spectrometer, showed spectra corresponding only to ammonia and perchloric acid. No trace of a parent peak corresponding to ammonium perchlorate was found.

B. PERCHLORIC ACID–AMMONIA REACTION

The vapor phase reaction of ammonia with perchloric acid has been studied briefly. Friedman and Levy (*49, 100*) made a preliminary investigation at 367°C. Separate streams of ammonia and perchloric acid in nitrogen were mixed, passed through a reaction vessel at a known temperature, absorbed, and analyzed. The main problem was the mixing of the two reactants in a time short compared to the residence time in the reaction vessel (ca. 2 sec). It was found that a greater percentage decomposition of perchloric acid occurred in the presence of the ammonia than would have occurred with the perchloric acid alone. They deduced a rate constant of about 2×10^6 cm^3 mole^{-1} sec^{-1} on the assumption that the ammonia-acid reaction is first order in each reactant. An approximate value of 59.5 kcal mole^{-1} for the heat of vaporization of ammonium perchlorate was obtained from the observation that solid formation occurred in the mixing chamber at 362°C but not at 367°C.

Sibbett and Lobato (*165*) studied the reaction between undiluted ammonia and anhydrous perchloric acid at 25°, 48.4°, and 60°C. Reaction was initiated by rupturing a break seal between two Pyrex vessels at zero time, and conditions were arranged so that a jet of ammonia always passed rapidly into the acid vapor to start the reaction. The reaction appeared to be instantaneous since the pressure-measuring system showed a single pressure rise to a fixed level. Analysis of the products indicated simultaneous oxidation of the ammonia by the perchloric acid, along with direct combination to yield ammonium perchlorate. Results (*89*) at 230°C indicated that the ammonia triggered the decomposition of the acid. Attempts were also made to stabilize a diffusion flame, using an opposed jet reactor with ammonia and anhydrous perchloric acid. Reactor pressures of 1–60 torr, acid flow rates of 4.3×10^{-6} to 2.6×10^{-4} mole min^{-1}, mole ratios of $HClO_4/NH_3$ of 0.05–7.7, temperatures from ambient to 180°C, and various nozzle orifices of 0.5–2.0 mm were used. In no case could a stable flame be obtained despite the use of a spark or hot wire (*166*) igniter system.

Very recently, burning rates of mixtures of polymeric fuels with 72% perchloric acid have been studied at the University of Louvain (*29*). Burning rate–mixture ratio curves were obtained similar to those found with ammonium perchlorate in place of the perchloric acid. Detonations occurred with very lean mixtures.

C. FLAMES

The earliest reference to perchloric acid flames in the literature is in a brief note by Dietz in 1939, when it was reported that perchloric acid vapor (72%) ignited at 400°–405°C in the absence of fuel (*44*). Hydrogen passed into hot acid vapor ignited spontaneously at the same temperature, but in the presence of steel turnings this ignition temperature was reduced to 215°C. A value of 400°–405°C for the spontaneous ignition temperature of methane–72% perchloric acid vapor has recently been obtained (*134*).

In 1958 Powling (*137*) stabilized flat diffusion flames of perchloric acid (72%) with ammonia and propane. The perchloric acid appeared to decompose in a flame zone, emitting a reddish glow before reacting with the fuel. A thermocouple trace across the flame indicated an exothermal bump on the acid side. Since no spectral difference could be detected between ammonia–perchloric acid flames and ammonia–oxygen–chlorine flames, it was concluded that the perchloric acid probably decomposed before it reacted with the fuel.

Very recently, Hall and co-workers (*35*, *37–39*) have succeeded in stabilizing premixed flames of perchloric acid (72%) both at 760 mm and at about 20 mm pressure. The production of premixed flames with ammonia was made difficult by the formation of solid ammonium perchlorate, but other fuels have been successfully used. The flames which have been studied are presented in Table X. A diffusion flame of methane and 72% perchloric acid was also studied briefly.

TABLE X

PREMIXED PERCHLORIC ACID FLAMES[a]

Fuel	Low pressure	Atmospheric pressure
None	—	*Su*, *T*, spectra
Hydrogen	—	*Su*, *T*, spectra
Methane	*Su*, spectra	*Su*, *T*, spectra
Ethane	Spectra	*Su*, spectra
Carbon monoxide	*Su*	*Su*, spectra
Formaldehyde	Spectra	—
Methyl alcohol	—	*Su*, spectra

[a] *Su* indicates burning velocity measured; *T* indicates temperature measured.

Spectroscopic studies of premixed methane–perchloric acid flames showed not only the C_2, CH, and OH bands usually observed in hydrocarbon–oxygen flames but also "cool flame" bands. These bands were also observed in perchloric acid flames with methyl alcohol but not with formaldehyde. Low pressure flame studies indicated that these "cool flame" bands were confined to the early part of the flame, whereas the C_2 and CH bands appeared later.

Methane–perchloric acid–oxygen flames have a second flame zone on the downstream side of the first zone and separated by a gap having little or no luminosity. The second zone was extinguished by removing the oxygen. Spectra at low pressure showed that the first zone had the usual perchloric acid flame structure, and that the second zone had the bands expected for a methane–oxygen flame.

Burning velocity measurements showed that in general the acid flames were about three times faster than the corresponding oxygen flame at the same temperature. The burning velocity maximum occurred at about $\lambda = 1.5$ (where λ is the ratio of the fuel present to that required for stoichiometric combustion) for acid flames, and at $\lambda = 1.15$ for oxygen flames. The effect of nitrogen dilution on the burning velocity of stoichiometric methane–perchloric acid flames was examined. The results could be correlated with an activation energy of 29 kcal mole^{-1}, using the same assumptions and equation as were used by Van Tiggelen to obtain an activation energy of 38 kcal mole^{-1} for methane–oxygen flames. Flame temperature measured by the OH reversal method gave values in good agreement with theoretical flame temperatures.

The effect of addition of inhibitors was also studied. A stoichiometric methane–perchloric acid flame with 3 moles of nitrogen per mole of acid ($HClO_4$) had a burning velocity of 99 cm sec^{-1} (relative to the unburnt gas at 20°C); replacement of 5 moles of nitrogen by hydrogen chloride reduced the burning velocity to 84 cm sec^{-1}, and the theoretical flame temperature was decreased by 30°C. Addition of 1% by volume of trifluorobromomethane to the original mixture reduced the burning velocity to 89 cm sec^{-1}. This is to be contrasted with the 50% reduction in burning velocity observed by a similar addition of trifluorobromomethane to a methane–oxygen flame.

All these observations suggest that in perchloric acid flames the acid does not decompose into hydrogen chloride or chlorine and oxygen before reacting with the fuel, but that some intermediate chlorine-oxygen compound or radical is involved, which reacts much more rapidly with the fuel than does oxygen.

A decomposition flame of perchloric acid vapor alone has been stabilized at 1 atmosphere (*83*). Analysis of the product gases from a decomposition flame showed a ratio of chlorine to hydrogen chloride of 0.7. This is appreciably greater than the equilibrium ratio of 0.057 expected for a theoretical flame temperature of 1076°K. Correction of the flame temperature for the observed chlorine distribution gives a value of 1160°K, since the heat release is greater for chlorine formation:

$$HClO_4 \rightarrow HCl + 2O_2 \qquad \Delta H = -21 \text{ kcal mole}^{-1} \tag{56}$$

$$HClO_4 \rightarrow \tfrac{1}{2}Cl_2 + \tfrac{1}{2}H_2O + \tfrac{7}{4}O_2 \qquad \Delta H = -28 \text{ kcal mole}^{-1} \tag{57}$$

The observed flame temperature after correction for heat loss from the thermocouple was 1125°K, in good agreement with the calculated temperature. The observed burning velocity was 19 cm sec^{-1} (referred to unburnt gas at 210°C). This was in very good agreement with the value of 20.3 cm sec^{-1} calculated from the Zeldovitch, Frank-Kamenetsky, and Semenov equation using parameters obtained by Levy in his study of the thermal decomposition at 250°–450°C. It may be inferred that the overall activation energy is about 45 kcal $mole^{-1}$. Different rate-determining steps are probably involved in premixed fuel–acid flames, since a hydrogen–perchloric acid flame with 10 moles of added nitrogen and having the same flame temperature as a decomposition flame had a burning velocity about three times as fast as the decomposition flame. Burning velocities could be correlated with an activation energy of 15 kcal $mole^{-1}$, using the Zeldovitch–Frank–Kamenetsky–Semenov equation for a second-order reaction.

Recent work has been devoted to obtaining composition and temperature profiles of methane–perchloric acid flames by batch sampling and mass spectrometric analysis.

XI. Uses

Perchloric acid is used very widely in analytical laboratories and in industry as a solvent for many materials, since it does not readily form complexes (*91*), and for the destruction of organic matter (*5*, *84*). Smith in particular has pioneered the use of perchloric acid in the wet oxidation of organic material either by the acid alone (*171*) or with sulfuric (*42*, *177*) or periodic acid (*178*), and even by use of ammonium perchlorate with nitric and hydrochloric acids (*176*). Monk has modified the method, which he found to be somewhat unreliable [see also references (*174*, *194*)], by addition of nitric acid (*123*, *124*). Perchloric acid has been used in the determination of ammonia and nitrogen (*22*, *125*), silica and aluminum (*75*, *182*), and sulfur (*17*), and in the analysis of coal (*188*), cosmetics (*79*), drugs (*136*), and propellants (*104*).

Other applications have included extraction of iron compounds and ores by perchloric acid solutions (*58*, *159*). In particular, cation exchange behavior in perchloric acid has been studied and used for a wide range of cations (*128*). Perchloric acid extraction has been used as a histochemical technique (*4*). The extraction of perchloric acid by basic organic solvents has been studied [reference (*216*) reviews earlier work in this field]. Deuterium perchlorate has been used as a solvent for spectrophotometry (*211*).

Perchloric acid has been applied to the fractionation of deuterium, since this is concentrated in the water molecules at the expense of the hydrogen ions (*59*, *206*, *214*).

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REFERENCES

1. Accascina, F., and Schiavo, S., *Proc. Intern. Symp. Electrolytes, Trieste, Yugoslavia, 1959*, pp. 301–308. 1962; see *Chem. Abstr.* **61,** 8918d (1964).

2. Adams, G. K., Newman, B. H., and Robins, A. B., *Symp. Combust., 8th, Pasadena Calif., 1960* pp. 693–705. Williams & Wilkins, Baltimore, Maryland, 1962.

3. Akishin, P. A., Vilkov, L. V., and Rosolovskii, V. Y., *Kristallografiya* **4,** 353–359 (1959); *Soviet Phys.-Cryst.* **4,** 328–333 (1960).

4. Aldridge, W. G., and Watson, M. L., *J. Histochem. Cytochem.* **11,** 773–781 (1963); see *Chem. Abstr.* **60,** 9854c (1964).

5. Analytical Methods Committee, *Analyst* **85,** 643–656 (1960).

6. Andrussow, L., *Chim. Ind.* (*Paris*) **86,** 542–545 (1961).

7. Babaeva, V. P., *Zh. Neorgan. Khim.* **8,** 1809–1813 (1963); *Russ. J. Inorg. Chem.* **8,** 941–943 (1963).

8. Babaeva, V. P., and Zinov'ev, A. A., *Dokl. Akad. Nauk SSSR* **149,** 592–594 (1963); Ministry of Aviation R.P.E. Translation No. 3.

9. Babaeva, V. P., and Zinov'ev, A. A., *Zh. Neorgan. Khim.* **8,** 567–572 (1963); *Russ. J. Inorg. Chem.* **8,** 288–291 (1963).

10. Banerjee, K., and Srivastava, R. D., *Z. Physik. Chem.* (*Frankfurt*) [N.S.] **38,** 234–239 (1963).

11. Barth-Wehrenalp, G., and Gardner, D. M., U. S. Patent 3,113,895 (Dec. 10, 1963—Appl. June 13, 1960); see *Chem. Abstr.* **60,** 6694h (1964).

12. Bastress, E. K., Princeton Univ. Aeronaut. Eng. Rept. No. 536 (1961).

13. Bayliss, N. S., and Watts, D. W., *Australian J. Chem.* **16,** 927–932 (1963).

14. Bayliss, N. S., Dingle, R., Watts, D. W., and Wilkie, R., *Australian J. Chem.* **16,** *933–942* (1963).

15. Berthelot, M., *Compt. Rend.* **93,** 291–292 (1881); *Ann. Chim. Phys.* [5] **27,** 222–224 (1882); Ministry of Aviation R.P.E. Translation No. 4.

16. Bethell, D. E., and Shephard, N., *J. Chem. Phys.* **21,** 1421 (1953).

17. Bethge, P. O., *Anal. Chem.* **28,** 119–122 (1956).

18. Bidinosti, D. R., and Biermann, W. J., *Can. J. Chem.* **34,** 1591–1595 (1956).

19. Bircumshaw, L. L., and Newman, B. H., *Proc. Roy. Soc.* **A227,** 115–132 and 228–241 (1954).

20. Bircumshaw, L. L., and Phillips, T. R., *J. Chem. Soc.* pp. 4741–4747 (1957).

21. Birky, M. M., and Hepler, J. G., *J. Phys. Chem.* **64,** 686–687 (1960).

22. Bradstreet, J. B., *Anal. Chem.* **26,** 185–187 (1954).

23. Brickwedde, L. H., *J. Res. Natl. Bur. Std.* **A42,** 309–329 (1949).

24. Bruckenstein, S., and Kolthoff, I. M., *J. Am. Chem. Soc.* **78,** 10–15 (1956).

25. Bugaenko, L. T., *Tr. 2-go [Vtorogo] Vses. Soveshch. po Radiats. Khim., Akad. Nauk SSSR, Otd. Khim. Nauk, Moscow, 1960* pp. 144–148 Izd. AN SSSR, Moscow (1962); see *Chem. Abstr.* **58,** 5184d (1963); U. S. Air Force Systems Command Translation FTD-MT-63-194, STAR N 65-11619, Astia Document AD 602600.

26. Bugaenko, L. T., *Vestn. Mosk. Univ., Ser. II: Khim.* **16,** 21–26 (1961); see *Chem. Abstr.* **56,** 11102e (1962).

27. Bugaenko, L. T., *Vestn. Mosk. Univ., Ser. II: Khim.* **18,** 37–42 (1963); see *Chem. Abstr.* **59,** 2145e (1963).

28. Bugaenko, L. T., and Belevskii, V. N., *Vestn. Mosk. Univ., Ser. II: Khim.* **16,** 77–79 (1961); see *Chem. Abstr.* **56,** 126c (1962).

29. Burger, J., and van Tiggelen, A., *Acad. Roy. Belg. Classe Sci. Mem.* **34,** (1964); Ministry of Aviation R.P.E. Translation No. 13; *Bull. Soc. Chim. France* pp. 3122–3130 (1964).

30. Burton, H., and Praill, P. F. G., *Analyst* **80,** 4–15 (1955).

31. Cassel, H. M., and Liebman, I., *J. Chem. Phys.* **34,** 342 (1961).

32. Cottin, M., *J. Chim. Phys.* **53,** 903–916 and 927–928 (1956).

33. Cottrell, T. L., "The Strengths of Chemical Bonds," p. 280. Butterworth, London and Washington, D. C., 1958.

34. Covington, A. K., and Prue, J. E., *J. Chem. Soc.* pp. 1567–1572 (1957).

35. Cummings, G. A. McD., and Hall, A. R., Ministry of Aviation, R.P.E. Tech. Note 222, May 1963.

36. Cummings, G. A. McD., and Pearson, G. S., Ministry of Aviation, R.P.E. Tech. Note 224, Oct. 1963.

37. Cummings, G. A. McD., and Pearson, G. S., Ministry of Aviation, R.P.E. Tech. Note 226, Oct. 1963.

38. Cummings, G. A. McD., and Pearson, G. S., *Combust. Flame* **8,** 199–202 (1964).

39. Cummings, G. A. McD., and Hall, A. R., *Symp. Combust., 10th, Cambridge, England, 1964* pp. 1365–1372. The Combustion Institute, Pittsburgh, Pennsylvania, 1965.

40. Dahl, A. J., Trowbridge, J. C., and Taylor, R. C., *Inorg. Chem.* **2,** 654–655 (1963).

41. Dibeler, V. H., Reese, R. M., and Mann, D. E., *J. Chem. Phys.* **27,** 176–179 (1957).

42. Diehl, H., and Smith, G. F., *Talanta* **2,** 209–219 (1959).

43. Dieter, W. E., Cohen, L., and Kundick, M. E., *U. S. Bur. Mines Rept. Invest.* **6473** (1964).

44. Dietz, W., *Angew. Chem.* **52,** 616–618 (1939); Ministry of Aviation R.P.E. Translation No. 8.

45. Elliott, M. A., and Brown, F. W., *U. S. Bur. Mines Rept. Invest.* **4169** (1948).

46. Figini, R. V., Coloccia, E., and Schumacher, H. J., *Z. Physik. Chem. (Frankfurt)* [N.S.] **14,** 32–48 (1958).

47. Forman, E. J., and Hume, D. N., *Talanta* **11,** 129–137 (1964).

48. Frazer, J. H., Perry J. W., and Johnson, W. R., U. S. Patent 2,504,119 (April 18, 1950); see *Chem. Abstr.* **44,** 6130f (1950).

49. Friedman, R., and Levy, J. B., Atlantic Research Corporation, Final Tech. Rept. AFOSR 2005, Dec. 31, 1961.

50. Galway, A. K., and Jacobs, P. W. M., *J. Chem. Soc.* pp. 837–844 (1959).

51. Galway, A. K., and Jacobs, P. W. M., *Proc. Roy. Soc.* **A254,** 455–469 (1960).

52. Galway, A. K., and Jacobs, P. W. M., *Trans. Faraday Soc.* **56,** 581–590 (1960).

53. Giguère, P. A., private communication, 1964; value of entropy in ref. [*54*] incorrectly printed as 71.7.

54. Giguère, P. A., and Savoie, R., *Can. J. Chem.* **40,** 495–502 (1962).

55. Gilliland, A. A., and Johnson, W. H., *J. Res. Nat. Bur. Std.* **A65,** 67–70 (1961).
56. Glasner, A., and Makovky, A., *J. Chem. Soc.* pp. 1606–1610 (1953).
57. Goddard, D. R., Hughes, E. D., and Ingold, C. K., *J. Chem. Soc.* 2559–2575 (1950).
58. Goetz, C. A., and Wadsworth, E. P., Jr., *Anal. Chem.* **28,** 375–376 (1956).
59. Gold, V., *Proc. Chem. Soc.* pp. 141–143 (1963).
60. Goodeve, C. F., and Marsh, A. E. L., *J. Chem. Soc.* pp. 1161–1166 (1937).
61. Goodeve, C. F., and Marsh, A. E. L., *J. Chem. Soc.* pp. 1332–1337 (1939).
62. Guibert, C. R., Klodowski, H. F., and McElroy, A. D., studies of complex perchlorates, Callery Chemical Co., Ann. Rept., Oct. 27, 1964.
63. Gyani, P., and Prasad, R. K., *J. Indian Chem. Soc.* **41,** 179–182 (1964).
64. Haase, R., Lehnert, G., and Jansen, H. J., *Z. Physik. Chem.* (*Frankfurt*) [N.S.] **42,** 32–44 (1964).
65. Halász, A., and Jánosi, A., *Veszpremi Vegyip. Egyet. Kozlemen.* **4,** 151–158 (1960); see *Chem. Abstr.* **55,** 14147a (1961).
66. Hale, J. D., Izatt, R. M., and Christensen, J. J., *Proc. Chem. Soc.* p. 240 (1963).
67. Hale, J. D., Izatt, R. M., and Christensen, J. J., *J. Phys. Chem.* **67,** 2605–2608 (1963).
68. Hall, A. R., and Pearson, G. S., Ministry of Aviation, R.P.E. Tech. Note 232, May 1964.
69. Harvey, A. E., Edmuson, M. T., Jones, E. D., Seybert, R. A., and Catto, K. A., *J. Am. Chem. Soc.* **76,** 3270–3273 (1954).
70. Hathaway, B. J., and Underhill, A. E., *J. Chem. Soc.* pp. 648–654 (1960).
71. Hathaway, B. J., and Underhill, A. E., *J. Chem. Soc.* pp. 3091–3096 (1961).
72. Heath, G. A., and Majer, J. R., *Trans. Faraday Soc.* **60,** 1783–1791 (1964).
73. Heidt, L. J., *Proc. World Symp. Appl. Solar Energy, Phoenix, Ariz., 1955* pp. 275–280. Assoc. for Appl. Solar Energy, Phoenix, Arizona, 1956.
74. Heidt, L. J., Koster, G. F., and Johnson, A. M., *J. Am. Chem. Soc.* **80,** 6471–6477 (1959).
75. Henicksman, A. L., Apel, C. T., Ashley, W. H., and Zerwekh, A., Los Alamos Sci. Lab. Rept. LA-3134, Oct. 12, 1964; see STAR N 64-33066.
76. Hogfeldt, E., *Acta Chem. Scand.* **14,** 1597–1611 (1960).
77. Hogfeldt, E., *Acta Chem. Scand.* **17,** 785–796 (1963).
78. Hood, G. C., Redlich, O., and Reilly, C. A., *J. Chem. Phys.* **22,** 2067–2071 (1954).
79. Hopwood, J. S., *Perfumery Essent. Oil Record* **53,** 692–694 (1962).
80. Horne, R. A., *J. Chem. Eng. Data* **7,** 1–2 (1962).
81. Inami, S. H., Rosser, W. A., and Wise, H., *J. Phys. Chem.* **67,** 1077–1079 (1963).
82. Ingold, C. K., Millen, D. J., and Poole, H. G., *J. Chem. Soc.* pp. 2576–2589 (1950).
83. Johnson, W. H., and Gilliland, A. A., *J. Res. Natl. Bur. Std.* **A65,** 63–65 (1961).
84. Kahane, E., *Oesterr. Chemiker-Ztg.* **55,** 209–215 (1954).
85. Kakiuchi, Y., and Komatsu, H., *J. Phys. Soc. Japan* **7,** 380–382 (1951).
86. Kakiuchi, Y., Shono, H., Komatsu, H., and Kigoshi, K., *J. Chem. Phys.* **19,** 1069 (1951).
87. Kakiuchi, Y., Shono, H., Komatsu, H., and Kigoshi, K., *J. Phys. Soc. Japan* **7,** 102–106 (1951).
88. Katakis, D., and Allen, A. O., *J. Phys. Chem.* **68,** 3107–3115 (1964).
89. Kispersky, J. P., Aerojet Gen. Rept. No. 0372-01-13, Mar. 31, 1963; STAR N 63-14488.
90. Klages, F., and Hegenberg, P., *Angew. Chem.* **74,** 902 (1962).
91. Klanberg, F., Hunt, J. P., and Dodgen, H. W., *Inorg. Chem.* **2,** 139–141 (1963).
92. Klochko, M. A., and Kurbanov, M. S., *Izv. Sektora Fiz. Khim. Analiza, Inst. Obshch. Neorgan. Khim., Akad. Nauk SSSR* **24,** 237–251 (1954).

93. Krivtsov, N. V., Rosolovskii, V. Y., and Zinov'ev, A. A., *Russ. J. Inorg. Chem.* **5,** 372–373 (1960).

94. Kroh, J., Green, B. C., and Spinks, J. W. T., *Can. J. Chem.* **40,** 413–425 (1962).

95. Kurbangalina, R. K., *Zh. Fiz. Khim.* **22,** 49–51 (1948).

96. Latimer, W. M., and Ahlberg, J. E., *J. Am. Chem. Soc.* **52,** 549–553 (1930).

97. Lee, F. S., and Carpenter, G. B., *J. Phys. Chem.* **63,** 279–282 (1959).

98. Levy, J. B., Atlantic Res. Corp. AFOSR TN 1555; Astia Document AD 265,051, Oct. 4, 1961.

99. Levy, J. B., *J. Phys. Chem.* **66,** 1092–1097 (1962).

100. Levy, J. B., *Symp. Combust., 10th, Cambridge, England, 1964* p. 1371. The Combustion Institute, Pittsburgh, Pennsylvania. 1965. Discussion on ref. (*39*).

101. Livingston, R., and Weinberger, A. J., *J. Chem. Phys.* **33,** 499–508 (1960).

102. Livingston, R., Zeldes, H., and Taylor, E. H., *Discussions Faraday Soc.* **19,** 166–173 (1955).

103. Mack, J. L., Tompa, A. S., and Wilmot, G. H., *Symp. Mol. Struct. Spectroscopy, Ohio State Univ., Columbus, Ohio, 1962;* abstr. in *Spectrochim. Acta* **18,** 1375 (1962).

104. Macorkindale, J. B., and Lamond, J. J., *Anal. Chem.* **35,** 1058–1060 (1963).

105. Mader, D. L., and Hoyle, M. C., *Soil Sci.* **98,** 295–299 (1964).

106. Mani, N. V., *Proc. Indian Acad. Sci. Sect. A* **56,** 143–151 (1957).

107. Manufacturing Chemists Assoc., Inc., Washington, D. C., Chemical Safety Data Sheet SD-11, Perchloric acid solution, May 1947.

108. Manufacturing Chemists Assoc., Inc., Washington, D. C., Case Histories of Accidents in the Chemical Industry, Vol. I, History No. 581 (1962).

109. Markowitz, M. M., *J. Inorg. Nucl. Chem.* **25,** 407–414 (1963).

110. Markowitz, M. M., and Boryta, D. A., *ARS* (*Am. Rocket Soc.*) *J.* **32,** 1941–1942 (1962).

111. Markowitz, M. M., Harris, R. F., and Stewart, H., Jr., *J. Phys. Chem.* **63,** 1325–1326 (1959).

112. Martin, R. J. L., *Australian J. Chem.* **15,** 409–415 (1962).

113. Martin, R. J. L., *Australian J. Chem.* **16,** 84–92 (1963).

114. Mascherpa, G., *Bull. Soc. Chim. France* pp. 1259–1260 (1961); p. 1132 (1963).

115. Mascherpa, G., *Compt. Rend.* **252,** 1800–1802 (1961).

116. Mascherpa, G., *Compt. Rend.* **257,** 3414–3416 (1963).

117 Mascherpa, G., Pavia, A., and Potier, A., *Compt. Rend.* **254,** 3213–3215 (1962).

118. Mellor, J. W., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. II, p. 370. Longmans, Green, New York, 1946.

119. Mellor, J. W., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Suppl. II, Pt. I, p. 598. Longmans, Green, New York, 1956.

120. Millen, D. J., and Vaal, E. G., *J. Chem. Soc.* pp. 2913–2915 (1956).

121. Milling, B., Stein, G., and Weiss, J., *Nature* **170,** 710 (1952).

122. Missan, A. E., and Sukhotin, A. M., *Zh. Neorgan. Khim.* **4,** 606–622 (1959); *Russ. J. Inorg. Chem.* **4,** 276–283 (1959).

123. Monk, R. G., *Analyst* **87,** 64–66 (1962).

124. Monk, R. G., *Analyst* **88,** 476–478 (1963).

125. Moore, F. B., and Diehl, H., *Anal. Chem.* **34,** 1638–1641 (1962).

126. Mullhaupt, J. T., *Dissertation Abstr.* **19,** 1581 (1959).

127. Mullhaupt, J. T., and Hornig, D. F., *J. Chem. Phys.* **24,** 169 (1956).

128. Nelson, F., Murase, T., and Kraus, K. A., *J. Chromatog.* **13,** 503–535 (1964).

129. Neros, C. A., and Eversole, W. G., *J. Phys. Chem.* **45,** 388–395 (1941).

130. Nordman, C. E., *Acta Cryst.* **15,** 18–23 (1962).

131. Ogur, M., and Rosen, G., *Arch. Biochem.* **25,** 263–276 (1950).

132. Osada, H., and Sakamoto, E., *Kogyo Kayaku Kyokaishi* **24,** 236–244 (1963); see *Chem. Abstr.* **60,** 7669a (1964).

133. Padmini, P. R. M. L., Subba Rao, K., and Ramachandra Rao, B., *J. Chem. Phys.* **33,** 1268–1269 (1960).

134. Pearson, G. S., *Symp. Combust., 10th, Cambridge, England, 1964* pp. 1371–1372. The Combustion Institute, Pittsburgh, Pennsylvania, 1965. Discussion on ref. (*39*).

135. Phillips, T. R., Ph.D. thesis, Univ. of Birmingham, England, 1953; quoted in ref. (*152*).

136. Posgay, E., Gyogyszereszet **6,** 336–338 (1962); see *Chem. Abstr.* **58,** 3269h (1963).

137. Powling, J., private communication, 1964.

138. Powling, J., and Smith, W. A. W., *Symp. Combust., 10th, Cambridge, England, 1964* pp. 1373–1380. The Combustion Institute, Pittsburgh, Pennsylvania, 1965.

139. Powling, J., and Smith, W. A. W., *Combust. Flame* **6,** 173–181 (1962).

140. Powling, J., and Smith, W. A. W., *Combust. Flame* **7,** 269–275 (1963).

141. Prosen, R., Ph. D. thesis Univ. of California, Berkeley, California, 1955; quoted in ref. (*198*).

142. Richards, T. W., and Rowe, A. W., *Proc. Am. Acad. Arts Sci.* **49,** 171–199 (1913).

143. Rigg, T., Stein, G., and Weiss, J., *Proc. Roy. Soc.* **A211,** 375–397 (1952).

144. Robinson, E. A., *Can. J. Chem.* **41,** 173–179 (1963).

145. Robinson, E. A., *Can. J. Chem.* **41,** 3021–3033 (1963).

146. Robinson, R. A., and Stokes, R. H., "Electrolyte Solutions," 2nd ed. Butterworth, London and Washington, D. C., 1959.

147. Rosolovskii, V. Y., Krivtsov, N. V., and Zinov'ev, A. A., *Russ J. Inorg. Chem.* **5,** 374–376 (1960).

148. Rosolovskii, V. Y., and Zinov'ev, A. A., *Zh. Neorgan. Khim.* **3,** 1589–1591 (1958); see *Chem. Abstr.* **56,** 8067a (1962).

149. Rosolovskii, V. Y., Zinov'ev, A. A., and Prokhorov, V. A., *Russ. J. Inorg. Chem.* **5,** 334–335 (1960).

150. Rosolovskii, V. Y., Zinov'ev, A. A., and Prokhorov, V. A., *Russ. J. Inorg. Chem.* **5,** 1042–1044 (1960).

151. Rossini, F. D., Wagman, D. D., Evans, W. H., Levine, S., and Jaffe, I., *Natl. Bur. Std.* (*U. S.*), *Circ.* **500** (1952).

152. Russell-Jones, A., Final Rept., Imperial College, London, September 1964.

153. Sandberg, W. A., Erikson, T. A., and Riesz, C. H., U. S. Patent 2,925,368 (Feb. 16, 1960); see *Chem. Abstr.* **54,** 1140g (1960).

154. Savoie, R., Ph.D. thesis, Laval University, Quebec, 1962.

155. Savoie, R., and Giguère, P. A., *Can. J. Chem.* **40,** 991–996 (1962).

156. Savoie, R., and Giguère, P. A., *J. Chem. Phys.* **41,** 2698–2705 (1964).

157. Schulz, R. D., and Dekker, A. O., *Symp. Combust., 6th, Yale Univ., New Haven, Conn., 1956* pp. 618–626. Reinhold, New York, 1957.

158. Schumacher, J. C. (ed.), "Perchlorates, Their Properties, Manufacture, and Uses." Reinhold, New York, 1960.

159. Seryakova, I. V., and Zolotov, U. A., *Zh. Neorgan. Khim.* **9,** 190–195 (1964).

160. Shchukarev, S. A., Andreev, S. N., and Balicheva, T. G., *Proc. Acad. Sci. USSR, Chem. Sect.* (*English Transl.*) **144,** 417–418 (1962).

161. Shchukarev, S. A., Andreev, S. N., and Balicheva, T. G., *Vestn. Leningr. Univ., Ser. Fiz. i Khim.* **17,** 128–134 (1962).

162. Shchukarev, S. A., Balicheva, T. G., and Borcha, K. Y., *Zh. Neorgan. Khim.* **8,** 1437–1441 (1963).

163. Shchirova, N. A., Zinov'ev, A. A., and Mikheeva, V. I., *Dokl. Akad. Nauk SSSR* **152,** 346–348 (1963).

164. Sibbett, D. J., and Geller, I., private communication, 1964.

165. Sibbett, D. J., and Lobato, J. M., Aerojet Gen. Rept. No. 1782; Astia Document. AD 240,274, April 1960.

166. Sibbett, D. J., Cheselke, F. J., Geller, I., Lobato, J. M., Sutherland, J. E., and Chaiken, R. F., Aerojet Gen. Corp. Abstr. in AFOSR 2348, Astia Document AD 274,132, April 1962.

167. Silverman, L., and First, M. W., *Am. Ind. Hyg. Ass. J.* pp. 463–472 (1962).

168. Simon, A., and Weist, M., *Z. Anorg. Allgem. Chem.* **268,** 301–326 (1952).

169. Singer, K., and Vampew, P. A., *J. Chem. Soc.* p. 3971–3974 (1956).

170. Skuratov, S. M., Vorob'ev, A. F., and Privalova, N. M., *Russ. J. Inorg. Chem.* **7,** 343–345 (1962).

171. Smith, G. F., *Anal. Chim. Acta* **8,** 397–421 (1953).

172. Smith, G. F., *J. Am. Chem. Soc.* **75,** 184–186 (1953).

173. Smith, G. F., *Talanta* **7,** 212–214 (1961).

174. Smith, G. F., *Talanta* **8,** 364 (1963).

175. Smith, G. F., *Talanta* **10,** 413–416 (1963).

176. Smith, G. F., *Talanta* **11,** 633–640 (1964).

177. Smith, G. F., and Diehl, H., *Talanta* **3,** 41–46 (1959–1960).

178. Smith, G. F., and Diehl, H., *Talanta* **4,** 185–193 (1960).

179. Smith, G. F., and Diehl, H., *Anal. Chem., Proc. Intern. Symp., Birmingham Univ., Birmingham, England, 1962* pp. 394–396. Elsevier, Amsterdam, 1963.

180. Smith, G. F., and Goehler, O. E., *Ind. Eng. Chem., Anal. Ed.* **3,** 61–63 (1931).

181. Smith, G. F., and Lamplough, C. E., *Chemist Analyst* **41,** 7–8 (1952).

182. Smith, G. F., and Taylor, W. H., *Talanta* **10,** 1107–1109 (1963).

183. Smith, H. G., and Rundle, R. E., *J. Am. Chem. Soc.* **80,** 5075–5080 (1958).

184. Smith, J. A. S., and Richards, R. E., *Trans. Faraday Soc.* **47,** 1261–1274 (1951).

185. Smith, J. A. S., and Richards, R. E., *Trans. Faraday Soc.* **48,** 307–315 (1952).

186. Smith, T. L., and Elliott, J. H., *J. Am. Chem. Soc.* **75,** 3566–3571 (1953).

187. For example, see Solymosi, F., and Revesz, L., *Z. Anorg. Allgem. Chem.* **322,** 86–100 (1963).

188. Spielholtz, G. I., *Dissertation Abstr.* **24,** 1368–1369 (1963).

189. Sullivan, J. C., Cohen, D., and Hindman, J. C., *J. Am. Chem. Soc.* **79,** 3672–3674 (1957).

190. Taketa, T., *J. Sci. Hiroshima Univ. Ser. A* **19,** 193–202 (1955).

191. Taube, H., *Trans. Faraday Soc.* **53,** 656–665 (1957).

192. Tauber, S. J., and Eastham, A. M., *J. Am. Chem. Soc.* **82,** 4888–4901 (1960).

193. Taylor, R. C., and Vidale, G. L., *J. Am. Chem. Soc.* **78,** 5999–6002 (1956).

194. Thomson, J., *Talanta* **8,** 276 (1963).

195. Tokareva, S. A., *Zh. Neorgan. Khim.* **9,** 2265–2267 (1964); see *Chem. Abstr.* **61,** 12687g (1964).

196. Trowbridge, J. C., and Westrum, E. F., Jr., *J. Phys. Chem.* **68,** 42–49 (1964).

197. Truter, M. R., *Acta Cryst.* **14,** 318–319 (1961).

198. Truter, M. R., Cruickshank, D. W. J., and Jeffrey, G. A., *Acta Cryst.* **13,** 855–862 (1960).

199. Tsentsiper, A. B., *Zh. Neorgan. Khim.* **4,** 1086–1091 (1959); *Russ. J. Inorg. Chem.* **4,** 493–496 (1959).

200. Turney, T. A., and Wright, G. A., *J. Chem. Soc.* pp. 2415–2418 (1958).

201. U. S. Atomic Energy Commission. Perchloric acid ventilating system hazards. Serious Accidents No. 184, June 20, 1962.

202. Usanovich, M. L., Sumarokova, T., and Udovenko, V., *Zh. Obshch. Khim.* **9,** 1967–1975 (1939); see *Chem. Abstr.* **34,** 31569 (1940).

203. Van Wyk, H. J., *Z. Anorg. Chem.* **48,** 1–52 (1906).

204. Vanderzee, C. E., and Swanson, J. A., *J. Phys. Chem.* **67,** 285–291 (1963).

205. Vanderzee, C. E., and Swanson, J. A., *J. Phys. Chem.* **67,** 2608–2612 (1963).

206. VEB Vakutronik, German Patent 1,144,697 (March 7, 1963); see *Chem. Abstr.* **59,** 241a (1963).

207. Venkatesan, K., *Proc. Indian Acad. Sci. Sect. A* **56,** 134–142 (1957).

208. Volmer, M., *Ann. Chem.* **440,** 200–202 (1924).

209. Vorob'ev, A. F., and Privalova, N. M., *Vestn. Mosk. Univ., Ser. II: Khim.* **1963,** 22–26 (1963).

210. Vorob'ev, A. F., Privalova, N. M., Monaenkova, A. S., and Skuratov, S. M., *Proc. Acad. Sci. USSR, Phys. Chem. Sect.* (*English Transl.*) **135,** 1439–1441 (1960).

211. Waggener, W. C., Weinberger, A. J., and Stoughton, R. W., *Abstr. Papers, Am. Chem. Soc. 148th Meeting, Chicago, Illinois, 1964.* Abstr. 38B.

212. Wagman, D. D., private communication, 1965.

213. Wagman, D. D., *Natl. Bur. Std.* (*U.S.*) *Rept.* **7437,** 79–95 (1962).

214. Wetzel, K., USSR Patent 148,793 (July 20, 1962); see *Chem. Abstr.* **58,** 2109d (1963).

215. Wharton, A. E., Jr., U. S. Patent 2,968,539 (Jan. 17, 1961); see *Chem. Abstr.* **55,** 13852h (1961).

216. Whitney, D. C., and Diamond, R. M., *J. Phys. Chem.* **67,** 209–216 (1963).

217. Woolf, A. A., *J. Inorg. Nucl. Chem.* **3,** 250 (1956–1957).

218. Yates, K., and Wai, H., *J. Am. Chem. Soc.* **86,** 5408–5413 (1964).

219. Zeldes, H., and Livingston, R., *Phys. Rev.* **96,** 1702 (1954).

220. Zinov'ev, A. A., *Zh. Neorgan. Khim.* **3,** 1205–1209 (1958); Ministry of Aviation R.P.E. Translation No. 6.

221. Zinov'ev, A. A., *Usp. Khim.* **32,** No. 5, 590–616 (1963); *Russ. Chem. Rev.* **32,** 268–282 (1963).

222. Zinov'ev, A. A., and Babaeva, V. P., *Zh. Neorgan. Khim.* **2,** 2188–2195 (1957); Ministry of Aviation R.P.E. Translation No. 9.

223. Zinov'ev, A. A., and Babaeva, V. P., *Zh. Neorgan. Khim.* **3,** 1428–1432 (1958); see *Chem. Abstr.* **53,** 17650e (1959).
J. Inorg. Chem. **6,** 138–144 (1961).

224. Zinov'ev, A. A., and Babaeva, V. P., *Zh. Neorgan. Khim.* **6,** 271–282 (1961); *Russ. J. Inorg. Chem.* **6,** 138–144 (1961).

225. Zinov'ev, A. A., and Rosolovskii, V. Y., *Zh. Neorgan. Khim.* **3,** 2382–2389 (1958).

226. Zinov'ev, A. A., and Rosolovskii, V. Y., *Russ. J. Inorg. Chem.* **5,** 1239–1241 (1960).

227. Zinov'ev, A. A., and Tsentsiper, A. B., *Zh. Neorgan. Khim.* **4,** 724–729 (1959); *Russ. J. Inorg. Chem.* **4,** No. 4, 329–332 (1959).