UNCLASSIFIED

AD NUMBER

AD242192

NEW LIMITATION CHANGE

TO

Approved for public release, distribution unlimited

FROM

Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; 15 May 1960. Other requests shall be referred to Bureau of Weapons, Dept. of the Navy, Washington, DC.

AUTHORITY

BUWEPS ltr, 5 Nov 1965

THIS PAGE IS UNCLASSIFIED

UNCLASSIFIED

AD 242 192

Reproduced
by the

ARMED SERVICES TECHNICAL INFORMATION AGENCY
ARLINGTON HALL STATION
ARLINGTON 12, VIRGINIA



UNCLASSIFIED

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

CATALOGED BY ASTIA
AS AD No. 212 912

NAVORD REPORT 7147 (Vol. 1)

CHLORATES AND PERCHLORATES
THEIR MANUFACTURE, PROPERTIES AND USES

Prepared by

Department of Chemistry and Chemical Engineering
Southwest Research Institute

Contract NOrd 18471

XEROX

A BUREAU OF NAVAL WEAPONS PUBLICATION

NAVORD REPORT 7147 (Vol. 1)

CHLORATES AND PERCHLORATES
THEIR MANUFACTURE, PROPERTIES AND USES

Prepared by

Department of Chemistry and Chemical Engineering
Southwest Research Institute

FRANCIS A. WARREN
JOHN D. MILLAR
DR. FRANKLIN E. MASSOTH
WILLIAM E. HENSEL
IRWIN A. RABEN



Contract NOrd 18471

15 MAY 1960

FOREWORD

NAVORD REPORT 7147, Volume 1, contains a summary of the available information on chlorate and perchlorate compounds. Only the inorganic compounds have been considered.

An effort has been made to assemble all available technical and economic data from literature, patents, and industrial and governmental sources. A concerted effort has been made in this report to obtain detailed data, since the interest in chlorate and perchlorate compounds has been suddenly stimulated by the success achieved with ammonium perchlorate as the major ingredient in composite-type solid propellants for rockets and missiles. The inherent limitations of this compound as a high-energy source have focused attention on the related perchlorate compounds.

This report is transmitted for information purposes only. Volume 2 of this report is concerned with the characteristics and uses of these compounds and is classified CONFIDENTIAL.

Volume 1 was prepared for the Bureau of Naval Weapons, Navy Department, by the Department of Chemistry and Chemical Engineering of Southwest Research Institute. The project was begun under the broad direction of Dr. Eugene P. Whitlow, Department Director, and completed under the present director, Dr. William E. Thompson.

Allow 10 picas
Margin to trim

ACKNOWLEDGMENT

The following members of the Southwest Institute staff contributed to the preparation of this volume: Russell G. Weichlein, Charles W. Lawler, Gladys Henke, and Clarke Scheutze.

The editorial staff is indebted to other members of the Institute staff for their efforts in compiling the vast amount of property data included as Appendix A. In particular, the assistance of Mrs. Maureen Biering and Edward Vaught of the Institute's Library staff in securing numerous journals and texts is acknowledged. The assistance of the following companies in supplying information on the manufacture of chlorates and perchlorates is also acknowledged: American Potash and Chemical Corp., Swenson Evaporator Co., and Bird Machine Co.

The authors wish to thank Mr. E. E. Katcher, Bureau of Naval Weapons, for his technical suggestions and encouragement in the preparation of this document.

TABLE OF CONTENTS

Chapter		Page
1	CHLORATE AND PERCHLORATE COMPOUNDS	1
	Historical	2
	Methods of Manufacture	4
	Characteristics	4
	Nonmilitary Uses	6
	Compounds Included in This Work	7
	BIBLIOGRAPHY	9
2	MANUFACTURE	11
	Introduction	12
	Historical Background	13
	Process Descriptions	19
	General	19
	The Chlorates	19
	The Perchlorates	32
	Process Equipment	48
	Chlorate Electrolytic Cells	48
	Perchlorate Electrolytic Cells	52
	Crystallizers	55
	Centrifuges	58
	Dryers	59
	Process Developments	60
	Lead Dioxide Anodes	61
	Improved Anodes and Cathodes	65
	Product Specifications	66
	Sodium Chlorate	67
	Potassium Chlorate	68
	Potassium Perchlorate	70
	Ammonium Perchlorate	71
	Operating Problems	74
	Safety Considerations	80

TABLE OF CONTENTS (Cont'd)

Chapter		Page
	Economics	84
	Sodium Chlorate	85
	Potassium Chlorate	86
	Sodium Perchlorate	87
	Potassium Perchlorate	87
	Ammonium Perchlorate	88
	BIBLIOGRAPHY	90
3	REACTIONS AND MECHANISM	94
	The Oxyacids of Chlorine	95
	General Considerations	95
	Hypochlorous and Chlorous Acids and Their Salts	96
	Chloric Acid	100
	Perchloric Acid	101
	Chlorates	104
	Preparation	104
	Reactions in Aqueous Solution	109
	Reactions in Nonaqueous Media	123
	Thermal Decomposition	124
	Solid Reactions	141
	Perchlorates	145
	Preparation	145
	Aluminum Perchlorate	146
	Ammonium Perchlorate	146
	Barium Perchlorate	147
	Calcium Perchlorate	147
	Lithium Perchlorate	148
	Magnesium Perchlorate	148
	Potassium Perchlorate	149
	Silver Perchlorate	149
	Sodium Perchlorate	150
	Reactions in Aqueous Solution	150
	Metathesis	151
	Reactions in Nonaqueous Media	156
	Thermal Decomposition	159
	BIBLIOGRAPHY	181

TABLE OF CONTENTS (Cont'd)

Chapter		Page
4	USES OF CHLORATES AND PERCHLORATES	193
	Sodium Chlorate for Bleaching	194
	Pyrotechnics Application	195
	General	195
	Primers, Matches, and Signals	196
	Smoke Grenades	198
	Smoke Shells	200
	Parachute Flares	201
	Signal Flares	201
	Tracer Bullet	202
	Smoke Screens	202
	Explosives Applications	203
	General Uses	204
	Perchlorate Propellants	208
	Chlorates as Herbicides	209
	Perchlorates as Drying and Absorptive Agents	210
	Miscellaneous Uses	211
	BIBLIOGRAPHY	213
	APPENDIXES	218
	A. Properties of Chlorate and Perchlorate Compounds	219
	Bibliography	587
	B. The Analysis of Chlorates and Perchlorates	605
	Bibliography	664
	C. Calculations of Production Costs	672

LIST OF ILLUSTRATIONS

Figure		Page
2-1	Vat Used in Manufacture of $CaClO_3$ (Ref. 27)	683
2-2	Schematic Flow Diagram for Manufacture of $NaClO_3$ by Electrolysis Method	684
2-3	Flow Sheet for Manufacture of $NaClO_3$ by Electrolysis Method (Ref. 3)	685
2-4	Graphite Attack as a Function of Reciprocal of NaCl Concentration (Ref. 20)	686
2-5	Effect of NaCl Concentration on Cell Voltage (Ref. 20)	687
2-6	Schematic Flow Diagram for Manufacture of $KClO_3$	688
2-7	Flow Sheet for Manufacture of $KClO_3$ (Ref. 19)	689
2-8	Flow Sheet for Manufacture of $KClO_4$ (Ref. 33)	690
2-9	Schematic Flow Diagram for Manufacture of NH_4ClO_4	691
2-10	Flow Sheet for Manufacture of NH_4ClO_4 (Ref. 36)	692
2-11	Sectional Views of a Batch-Type Chlorate Cell (Ref. 18)	693
2-12	Design of a Continuous Chlorate Cell (Ref. 45)	694
2-13	Design of a Continuous Perchlorate Cell (Ref. 43)	695
2-14	Schematic Sketch of a Surface-Cooled Crystallizer System	696
2-15	Schematic Sketch of a Vacuum-Cooled Crystallizer System (Ref: Swenson Evaporator Co.)	697
2-16	Sectional View of a Vacuum-Cooled Crystallizer (Ref: Swenson Evaporator Co.)	698
2-17	Typical Vacuum-Cooled Crystallizer Installation (Ref: Swenson Evaporator Co.)	699

LIST OF ILLUSTRATIONS (Cont'd)

Figure		Page
2-18	Typical Continuous Centrifugal Filter Installation (Ref: Bird Machine Co.)	700
2-19	Production of $NaClO_3$ in United States (1939-1958) (Ref. 4, 13)	701
2-20	Selling Price of $NaClO_3$ in United States (1938-1958) (Ref. 4, 13)	702
2-21	Plant Investment Versus Capacity for $NaClO_3$ Plants (Ref. 15)	703
2-22	Production of $KClO_3$ in United Stated (1935-1955) (Ref. 4, 13)	704
2-23	Selling Price of $KClO_3$ in United States (1936-1956) (Ref. 4, 13)	705

LIST OF TABLES

Table		Page
1-1	Chlorate Compounds	707
1-2	Perchlorate Compounds	708
2-1	Definition of Electrical Terms	709
2-2	Operating Characteristics of a Typical Sodium Chlorate Cell(3)	711
2-3	Operating Characteristics of a Typical Perchlorate Cell(5)	712
2-4	Summary of Data on Thermal Decomposition of Sodium Chlorate(12)	713
2-5	Typical Chemical Analysis for Potassium Chlorate	714
2-6	Typical Chemical Analysis for Ammonium Perchlorate(5)	715
2-7	Typical Chemical Analysis for Lithium Perchlorate	716
2-8	Details of Batch-Type Chlorate Cell(18)	717
2-9	Details of Batch-Type Perchlorate Cell(18)	718
2-10	Comparative Data on Perchlorate Conversion with Platinum and Lead Dioxide Anodes(14)	719
2-11	Granulation Requirements for $KClO_3$	720
2-12	Comparison of Various Chemical and Physical Requirements for NH_4ClO_4(26)	721
2-13	Comparison of Various Particle Size Requirements for NH_4ClO_4(26)	722
2-14	Corrosion of Various Metals by NH_4ClO_4(36)	723
2-15	Effect of Operating Temperature on Performance of a Chloride Crystallizer(36)	724

LIST OF TABLES (Cont'd)

Table		Page
2-16	Estimated Breakdown of a Typical $NaClO_3$ Plant Investment	725
2-17	Estimated Cost of Production of Sodium Chlorate	726
2-18	Estimated Return on Investment for a Sodium Chlorate Plant	727
2-19	Estimated Cost of Production of Sodium Perchlorate	728
2-20	Estimated Cost of Production of Ammonium Perchlorate	729
2-21	Estimated Return on Investment of an Ammonium Perchlorate Plant	730

CHAPTER 1. CHLORATE AND PERCHLORATE COMPOUNDS

CHAPTER 1

CHLORATE AND PERCHLORATE COMPOUNDS

Historical

The early experimental studies leading to the discovery of the chlorates and perchlorates were closely tied to the discovery and identity of the element chlorine. According to Partington[4], Glauber in 1648 heated moist salt in a charcoal furnace and obtained a strongly acid "spirit of salt" by condensing the resulting fumes. Later (in 1658) Glauber wrote in his De Natura Salium of having made spirit of salt by condensing the vapors obtained from the reaction of sulfuric acid on salt. This concentrated solution was called "spiritus salis Glauberi" by Boerhaave in his Elementa Chemiae (1732). Priestley found in 1772 that the gas produced from the reaction of sulfuric acid and salt could be collected over mercury. He deduced that it was a permanent gas. The solution of this gas was then Glauber's spirit of salt or the marine acid as it was then called. This later became muriatic acid (from muria, the Latin for brine). Lavoisier considered muriatic acid as the oxide of an unknown element.

Scheele, who is credited with the discovery of chlorine, noted that the gas evolved from the reaction of muriatic acid and manganese dioxide bleached vegetable colors and had the odor of aqua regia. He concluded that this gas was muriatic acid derived of its phlogiston. Since he considered hydrogen to be phlogiston, his deduction was correct. Berthollet in 1785 found that the exposure to light of a solution of this new gas in water evolved bubbles of oxygen. Following the principle of Lavoisier's theory of acids, he considered the gas to be oxymuriatic acid. Davey who supported the elemental nature of oxymuriatic acid studied the gas in 1810 but never found any oxygen present. He then considered this gas as an element and propsed to call it chlorine (Greek for pale green).

While Berthollet was studying the gas chlorine, he apparently passed some through a solution of caustic potash and obtained the first known quantities of potassium chlorate. Since he was a proponent of Lavoisier's theory of acids, however, he called this compound hyperoxymuriate of potash[4]. The discovery of the salt potassium perchlorate did not occur until Stadion obtained it in 1815. It is presumed that he made it by decomposing potassium chlorate by heat, although he could have fused this salt with barium peroxide and extracted the perchlorate with water.

Chloric acid which generically can be considered the forebearer of the chlorates was first made by Gay-Lussac in 1814[4]. He prepared it by treating barium chlorate with sulfuric acid and recovering the chloric acid from the precipitated $BaSO_4$. Concentrations of chloric acid in excess of 40 percent decompose into chlorine, oxygen and perchloric acid.

Although Stadion is credited with having the first prepared perchloric acid in 1816, he actually prepared the monohydrate $HClO_4 \cdot H_2O$. Pure $HClO_4$ was first prepared in 1863 by Roscoe[4]. The pure acid was obtained from the hydrated form by distillation.

Methods of Manufacture

Sodium chlorate and sodium perchlorate are usually manufactured by the electrochemical oxidation of sodium chloride and sodium chlorate solutions, respectively. From these compounds, other chlorates and perchlorates are made, generally, by processes employing metathetical reaction. Although several wet chemical processes for preparing chlorates and perchlorates are known, and sodium perchlorate has been made by the thermal decomposition of sodium chlorate, none of these processes is presently of commercial importance.

Details of processes, equipment, and economics are covered in Chapter II.

Characteristics

Chloric acid which can be considered as the forebearer of chlorates is never obtained in the pure state. As indicated above, if a solution is concentrated beyond 40 percent $HClO_3$, the acid begins to decompose into chlorine, oxygen and perchloric acid. The concentrated solution is an oily liquid which is a strong oxidizing agent.

According to Sidgwick[5] there are numerous metallic chlorates, all solids, most of which are very soluble in water, the potassium salt being less so than most. The salts of bismuth, tin and mercury require a little

free acid to effect solution.[3] The chlorates decompose on heating to yield chloride and oxygen, or chloride and perchlorate. The decomposition reaction yielding oxygen is exothermic and may occur with explosive violence. This reaction is also greatly hastened at the melting point of the chlorate by the addition of certain catalysts, such as manganese dioxide.[3,5] According to Ephraim[2], the chlorates of the univalent metals are not hydrated while the salts of the bivalent metals have moderate water contents. On heating, the hydrated salts lose their water of crystallization without further decomposition.

Perchloric acid occurs in two forms, a stable ionized state and an unstable covalent one.[5] It can usually be considered an equilibrium mixture of the acid $HClO_4$ with small quantities of the anhydride Cl_2O_7 and water which forms a hydrate with the perchloric acid.[2] Perchloric acid reacts vigorously with water to form six solid hydrates. In aqueous solution the acid is almost completely dissociated, the solution possessing the characteristics of the perchlorate ion.[5]

The perchlorates are noted for their solubility characteristics. They are either extremely soluble or sparingly so in water. In addition, many of these salts are noted for their solubility in oxygen-containing organic solvents. Silver perchlorate is a noteworthy example of high solubility. At 25°C, a saturated solution contains 557 g of the salt in 100 g of water. It is also soluble in toluene (101 g per 100 g solvent).[5] Potassium perchlorate is only slightly soluble in water.

The fact that some of these salts have a high affinity for water makes them valuable as dehydrating agents. $Ba(ClO_4)_2$ is as effective a drying agent as H_2SO_4 and $Mg(ClO_4)_2$ is as efficient as P_2O_5.[2] This latter salt occurs in the anhydrous form and also with 2, 3, 4 and 6 molecules of water.[5]

The perchlorates when heated evolve oxygen and leave the chloride as residue.[3] They are, however, very stable to heat, the alkaline salts (e.g., Li and K) withstanding temperatures of 300° to 400° C without decomposing.

A detailed discussion of the reactions and a description of the mechanisms for chlorate and perchlorate compounds are presented in Chapter III.

Nonmilitary Uses

The chlorates find their greatest nonmilitary use at present in the conversion of sodium chlorate to chlorine dioxide for bleaching purposes in the paper pulp industry. However, it has been estimated that the quantity of sodium chlorate used as an intermediate in the manufacture of perchlorates may soon equal or surpass the tonnage consumed in the above application.[1] In the manufacture of perchlorates, sodium chlorate is converted to sodium perchlorate which in turn is made into other perchlorates, principally the ammonium salt. A substantial portion of the total sodium chlorate produced is used as a weed killer. The other major chlorate, potassium chlorate, is consumed largely by the match industry.

Of the total quantity of perchlorates produced, only a small percentage is consumed in the chief nonmilitary uses of drying agents, laboratory reagents, and manufacture of signal flares and pyrotechnics.

More detailed information on nonmilitary uses may be found in Chapter IV.

Compounds Included in This Work

Many chlorate and perchlorate compounds are known which are not listed herein. After a preliminary survey of the literature had been made, the decision was reached to restrict the accumulation, tabulation, and treatment of information to the compounds of nine elements: Al, N, Ba, Ca, Li, Mg, K, Ag, and Na. These compounds include the ones of current major use and interest and, perhaps, the compounds of major interest in the near future. Other compounds have been omitted for various reasons, including lack of sufficient information on them, lack of uses for them, lack of sufficient stability, or for practical reasons of presentation.

The compounds of primary interest in this work were sodium and potassium chlorates and ammonium and potassium perchlorates because of their high consumption compared to the other compounds included. Sodium perchlorate is not marketed as such (except for reagent use and other minor purposes) but is of great importance as an intermediate in the production of other perchlorates. Lithium and aluminum perchlorates appear to be of particular future interest in the field of solid propellants.

The compounds listed below have been treated in this work. For detailed property data on them see Appendix A. Appendix B contains

analytical procedures for compounds of special significance and a survey of methods which have been applied to chlorates and perchlorates in general.

BIBLIOGRAPHY

. Chemical Week, July 19, 1958.

. Ephraim, Fritz (revised by Thorne, P. C. L., and Roberts, E. R.) Inorganic Chemistry, Intersciences Inc., New York, N.Y., 1947.

. Moeller, Therald, Inorganic Chemistry-An Advanced Textbook, John Wiley and Sons, Inc., New York, N.Y., 1952.

. Partington, J.R., A Textbook of Inorganic Chemistry, MacMillan and Co., London, 1937.

. Sidgwick, N.V., The Chemical Elements and Their Compounds, Oxford, At the Clarendon Press, London, 1950.

CHAPTER 2. MANUFACTURE

CHAPTER 2. MANUFACTURE

Introduction

Although there are numerous chlorate and perchlorate compounds, only the sodium and potassium chlorates and the sodium, potassium and ammonium perchlorates are manufactured in any sizable quantities. Several methods for manufacturing these compounds have been explored, but the electrolytic method is the only procedure being used to any large extent at the present time. In general, it can be said that the manufacture of chlorates and perchlorates begins with the production of sodium chlorate by the electrolysis of an acidified sodium chloride solution, the other chlorates being formed by double decomposition. Likewise, sodium perchlorate is made by the electrolysis of a sodium chlorate solution. Other perchlorates are produced by a double decomposition reaction with this compound.

In the following sections of this chapter the history of chlorate and perchlorate manufacture is reviewed briefly. Then the processes used to manufacture the several important members of this class of compounds are described in some detail. Particular emphasis is placed on sodium and potassium chlorate, and sodium, potassium and ammonium perchlorate. This is followed by an examination of special process equipment such as chlorate and perchlorate cells, crystallizers and dryers. In addition, special problems of manufacture such as safety, handling and storage, and product specifications are discussed. Finally, the economics involved in the manufacturing processes are examined and calculations on estimated plant investment and production costs are presented.

Historical Background

Potassium chlorate was discovered by Berthollet in 1786[27] when he passed chlorine into a solution of caustic potash. This method formed the basis for its (and the sodium salt's) manufacture in Europe for many years.[52] One main disadvantage to this process was that only one part of chlorate was produced to each five parts of low value chloride. This low yield was greatly improved in the Liebig process which followed.[52] In this process calcium chlorate was first produced from chlorine and hydrated lime. Then the calcium salt was reacted with potassium chloride to give potassium chlorate and calcium chloride.[27]

Industrial electrolytic production of chlorate in Europe did not begin until the 1880's.[52] In fact, this production was preceded by only a few years by the first successful commercial production of alkali and chlorine by the electrochemical process.[20] The original cells were constructed with diaphragms in order to prevent cathodic reduction. It was thus necessary to mix the products formed at the anode and cathode afterward by mechanical means. This added to the cost of operation. Production was only economical when electrical energy was cheap.[20] The discovery that the addition of chromate solution would cause a protective film to be formed on steel cathodes led to the elimination of the diaphragms. Next, it was found that current efficiencies could be improved if the pH of the electrolyte was maintained below seven by the addition of acid. Finally, graphite was used successfully as a substitute for platinum as anode material. These

discoveries resulted in practically complete conversion to the electrolytic process. Today some production by the Liebig process still exists in Europe, but it is insignificant.

The manufacture of chlorate in the United States by the electrolytic method did not take place until near the close of the nineteenth century. According to Wallace[51], the National Electrolytic Company of Niagara Falls, New York, operating under the U. S. patents of W. T. Gibbs, commenced manufacture of potassium chlorate in 1897. * During the same period North American Chemical Company of Bay City, Michigan began manufacture of potassium and sodium chlorate by a process used by United Alkali Company in England. In 1899, Oldbury Electro-Chemical Company, Niagara Falls, began production of potassium chlorate based on the parent company's (Albright and Wilson, Ltd.) process in England.

The cells used in these plants were mechanically different but had about equal efficiencies. They used platinum anodes and copper cathodes. Total production in the United States was 750 tons of sodium chlorate and 5000 tons of potassium chlorate. Potassium chlorate was used mainly in matches (in 1903) with a small amount consumed in explosives, oxygen generation and pharmaceuticals. Sodium chlorate was used in textiles, color manufacture, farm explosives and oxygen generation.

* Wallace[51] has prepared a very interesting summary of the history of the chlorate industry. Most of the material in this section has been taken from this article.

Production of chlorates slowly increased under the protection of the Payne Aldrich Tariff with the result that substantially all chlorates and perchlorates consumed in the United States prior to World War I were produced domestically. In 1913 the Underwood Tariff reduced the rates to 0.5 cents/pound on each of the chlorates and to 15% ad valorem tax on potassium perchlorate.

During World War I, sodium chlorate production was increased to some extent, improvement in cell efficiency occurred and platinum as an electrode was eliminated. With the end of the war, chlorates were again imported in large quantities. Although only 600 tons were imported in 1913, compared to a total consumption of 6000 tons, imports from Europe of potassium chlorate alone, increased to 1000 tons in 1921, 4400 tons in 1922 and 4500 tons in 1923, despite an increase in tariff to 1-1/2 cents/pound.

As a result of these high imports into the United States, the National Electrolytic Plant closed in 1921 followed by the North American Chemical Company's plant in 1926, leaving Oldbury Electro-chemical Company as the only manufacturer of chlorate (sodium chlorate). Oldbury operated continuously to produce sodium chlorate (and also potassium perchlorate) from 1926 to 1933, while all of the potassium chlorate came from Europe.

Sodium chlorate had been used as a weed killer in Europe prior to World War I and the adoption of this use in the United States led to an increase in production to 5000 tons/year prior to World War II.

In 1933, as a result of unrest in Europe, Oldbury Electrochemical Company began to produce potassium chlorate. The Diamond Match

Company (largest user of potassium chlorate) built a plant to produce this material in Oswego, New York. Production was increased until in 1940, these two plants satisfied the entire requirements of the United States.

In 1937, both French and German producers considered manufacturing sodium chlorate and potassium chlorate in one of our Western States, but the war changed their plans. In 1941 Western Electrochemical Company started the production of potassium chlorate on a small scale in Los Angeles.

Pennsylvania Salt Manufacturing Company began production of sodium and potassium chlorate in 1942 at Tacoma, Washington, and International Minerals and Chemical Company built a plant to produce potassium chlorate in 1943 but closed down after World War II.

Diamond Match Company also closed their plant after World War II. The Western Electrochemical Company converted a government owned basic magnesium plant at Henderson, Nevada, to the manufacture of chlorates and perchlorates and began production in January 1944. This plant has been purchased by American Potash and Chemical Corporation and is presently being operated by them.

Although the manufacture of perchlorates is generally associated with the production of chlorates, these compounds were not made in this country until just prior to World War I. In 1910, the manufacture of potassium perchlorate was begun by the Oldbury Electrochemical Company. The entire production of 150 tons was used in railway signal fusees and pyrotechnics. Until that time all potassium perchlorate had been imported.

In 1941, unable to obtain sufficient potassium perchlorate, Cardox Corporation built a plant in Claremore, Oklahoma to produce both sodium chlorate and potassium perchlorate. A small plant of 200 tons/month of perchlorate was built for the government but was shut down after World War II. (The Cardox Corporation has announced recently that manufacture of chlorates and perchlorates has now been discontinued.)

According to Schumacher[36], ammonium perchlorate has been used as a solid oxidizer since 1895, when Oscar Carlson combined ammonium perchlorate with organics to make explosives. Carlson also reported the manufacture of ammonium perchlorate at Manshoe in 1895 and production in Germany was officially reported in 1901. Several patents on the manufacture of this compound have been issued dealing with reactions of ammonium chloride, sulfate and nitrate with sodium perchlorate.

Western Electrochemical Company started production of ammonium perchlorate in 1943 on a very limited scale.[36] Vick Chemical Company built a plant in 1943 at Greensboro, North Carolina, and Electric Production Company of Canada was in production during World War II. Western Electrochemical Company built a pilot plant in Henderson, Nevada in 1948, and in 1953 completed construction of a large scale plant which had a capacity of 40 tons/day. Schumacher[36] was granted a patent for the continuous production of ammonium perchlorate by reacting sodium perchlorate with anhydrous ammonia and hydrochloric acid.

At present there are four manufacturers operating chlorate plants:

American Potash and Chemical Corporation (purchaser of Western Electrochemical Company)

Hooker Chemical Corporation (purchaser of Oldbury Electrochemical Company)

HEF, Inc. (owned jointly by Hooker Chemical Corporation and Foote Mineral Company)

Pennsalt Chemical Corporation

At the close of World War II yearly production in the U. S. was as follows: Sodium chlorate - 15,000 tons; potassium chlorate - 10,500 tons; and potassium perchlorate - 2000 tons.

New uses developed since the war for sodium chlorate are bleaching, cotton defoliation and chlorite manufacture. Potassium perchlorate was used in propellants, metallurgy and other government products, resulting in increased production of these products. Thus, in 1950 the production of sodium chlorate was 22,000 tons, and potassium perchlorate 4500 tons. The production of potassium chlorate remains about the same at 7500 tons/year. The demand for ammonium perchlorate in solid propellants has been increasing so that production of this material has also risen during the past few years. U. S. sodium chlorate capacity by early 1959 will be approximately 100,000 tons/year.[10] The consumption in 1957 was 59,142 tons. (Additional production information will be found in section on Economics.)

Process Descriptions

General

As has already been pointed out the manufacture of the chlorates takes place first, followed by its conversion to the perchlorate. It is thus appropriate to discuss chlorates first, then perchlorates. Because of their importance sodium and potassium chlorate are considered in detail while barium, lithium and magnesium chlorates are discussed much less extensively. Likewise the manufacturing processes for sodium, potassium and ammonium perchlorate are described in detail while the procedures used for the perchlorates of barium, lithium and magnesium are covered only briefly.

Any description of the electrolytic methods for manufacturing either chlorates or perchlorates requires the frequent use of numerous electrical terms. To ensure that such terms are understood by the reader, a summary of the definition of these terms is given in Table 2-1.

The Chlorates

Chlorates were originally produced by the double decomposition reaction between a chloride salt and calcium chlorate.[27] The latter compound was made by the chlorination of calcium hydroxide (hydrated lime). Economic factors brought about the replacement of this method of manufacture by the less expensive electrolytic process. Today all the chlorates produced for sale in the United States are prepared by the electrolysis of sodium chloride. Sodium chlorate is the major chlorate produced. Other chlorates are made from sodium chlorate by a double decomposition reaction.

Sodium Chlorate

Double-Decomposition Method. The manufacture of sodium chlorate by the double-decomposition reaction between sodium chloride and calcium chlorate has never been followed in this country, but it was used in Europe during the early production of both the sodium and potassium compounds. The lower cost of the electrolytic process has accounted for the adoption of the latter method in this country.

In the double-decomposition process calcium chlorate is formed by chlorinating a hot calcium hydroxide (milk of lime) solution. According to Partington[27] this operation was carried out in cast-iron vats equipped with agitating paddles. A sketch of a typical vat is shown in Figure 2-1.

Faith, et al[13], describes another technique for producing the calcium chlorate in which the aqueous quicklime suspension is charged into the first of a series of chlorinating towers. Chlorine is introduced into the last tower and passes countercurrent to the lime flow. The chlorine is absorbed to form calcium hypochlorite. The temperature in the towers is maintained between 104°F and 131°F to prevent the formation of insoluble basic compounds and undue decomposition. The partially chlorinated product flows into the last tower where at 158°F the solution is over chlorinated resulting in the conversion of hypochlorite to calcium chlorate. The chlorinated product is discharged from the last tower and is passed through a filter to remove the unreacted lime which is reused.

Whichever method is used the following reaction takes place:

$$6Ca(OH)_2 + 6Cl_2 \longrightarrow 5CaCl_2 + Ca(ClO_3)_2 + 6H_2O \qquad (2\text{-}1)$$

In this reaction it is believed[27] that free hypochlorous acid is formed in an intermediate reaction and acts as an oxygen carrier to the hypochlorite to form the chlorate. This reaction might be represented as follows:

As long as the solution remains alkaline, chloride and hypochlorite are produced according to the reaction:

$$Cl_2 + 2OH^- \longrightarrow Cl^- + OCl^- + H_2O \qquad (2\text{-}2)$$

When the solution is no longer alkaline, the hypochlorite ion will react with the free hypochlorous acid to form chlorate and chloride ions as in the reaction:

$$OCl^- + 2HOCl \longrightarrow ClO_3^- + 2Cl^- + 2H^+ \qquad (2\text{-}3)$$

The hypochlorite and hydrogen ions then react to form hypochlorous acid which in turn reacts according to Equation (2-3):

$$H^+ + OCl^- \longrightarrow HOCl \qquad (2\text{-}4)$$

If the Equation (2-2) is multiplied by 6 and Equation (2-4) by 4 and the resulting equations added, there follows the original Equation (2-1).

To produce sodium chlorate, sodium chloride is added to the hot calcium. Concentrating and cooling this solution causes crystals of hydrated calcium chloride to form. They are removed by filtration while the highly soluble sodium chlorate remains in solution. The remainder of calcium salts are precipitated as the sulfate after the addition of an excess of sodium sulfate. Evaporation of the filtered solution causes the sodium chloride to separate out so that it also can be removed. Upon cooling, the sodium chlorate is crystallized out. Over-all yield, based on lime, is 85-90%.

Electrolytic Method. The production of sodium chlorate by the electrolytic method takes place in a series of process steps beginning with electrolysis in the electrolytic cells and continuing with evaporation, crystallization, drying, screening and packaging operations.[3, 23, 24, 35] Figure 2-2 outlines schematically the various steps in the process.

The basic raw material is sodium chloride which is dissolved in soft water to produce a saturated solution. If the salt contains appreciable amounts of calcium and magnesium, they can be precipitated by the addition of sodium carbonate and removed by filtration.[3, 24] The saturated salt solution is then run into a feed tank where hydrochloric acid is added to maintain a pH of 6.5 in the cells. Sodium dichromate (about 0.2%) is added to inhibit cell corrosion caused by liberated hyprochlorous acid.

In the electrolysis step the saturated, acidulated brine (including recycled mother liquor, high in chloride and low in chlorate) is

fed into banks of electrolytic cells, operating continuously[35] or batch-wise[19] and maintained in the temperature range of 104°-113°F by circulating cooling water. Generally, the cell bodies are constructed of steel (some are cement-lined) and make use of steel cathodes and graphite anodes. There is no diaphragm and the cathode and anode surfaces are quite close (e.g., one inch apart) to allow adequate mixing of the products. During electrolysis, the pH is controlled by HCl addition.

The electrolysis actually yields sodium hydroxide and chlorine, but good mixing converts them to sodium chlorate and sodium hypochlorite (NaClO). The latter is oxidized to chlorate by the hypochlorous acid present. Hydrogen is liberated during the electrolysis and may be recovered.

The following reactions describe the mechanism of chlorate formation:[15]

$$6NaCl + 6H_2O + 6\ \text{Faradays} \longrightarrow 3Cl_2 + 6NaOH + 3H_2 \qquad (2\text{-}5)$$

$$2NaOH + Cl_2 \longrightarrow NaOCl + NaCl + H_2O \qquad (2\text{-}6)$$

$$2Cl_2 + 2H_2O \rightleftharpoons 2HOCl + 2HCl \qquad (2\text{-}7)$$

$$NaOCl + 2HOCl \rightleftharpoons NaClO_3 + 2HCl \qquad (2\text{-}8)$$

$$4HCl + 4NaOH \longrightarrow 4NaCl + 4H_2O \qquad (2\text{-}9)$$

The summation of Equations (2-5) through (2-9) leads to the following:

$$NaCl + 3H_2O + 6\ \text{Faradays} \longrightarrow NaClO_3 + 3H_2 \qquad (2\text{-}10)$$

The cells require d-c power which is obtained by converting a-c power to d-c power in mercury arc rectifiers or by means of a motor-generator converter. For example, in a typical plant, power enters at 34,500 volts a-c and is stepped down by transformers to 4800 volts. A motor generator converts this a-c power to d-c power and supplies it to a long line of series-connected cells at 250 volts. The cells are usually operated with currents from 2000 to 3000 amp per cell. The voltage drop across each cell is between 3.0 to 3.5 volts. Typical current densities at the anode and cathode are 30 and 50 amp/ft^2, respectively. An average current efficiency for $NaClO_3$ is 80%. Operating characteristics for a typical sodium chlorate cell are summarized in Table 2-2. The next section, Process Equipment, will describe the cells in greater detail.

The cell liquors after electrolysis are discharged to a settler. Graphite mud from the anodes settles to the bottom, while clarified liquor containing 50% sodium chlorate is decanted from the settler. The liquor is then charged to double-effect evaporators where it is concentrated to 70-75% sodium chlorate. Sodium chloride being less soluble than the chlorate at the boiling temperature is thrown out of solution and is removed by filtration.

The filtrate is passed into a crystallizer, where it is cooled below 75°F to precipitate sodium chlorate crystals. The product is centrifuged, washed, and dried in rotary dryers. The dried product is ground to proper mesh and screened, yielding a product of 99.5% purity.

Over-all yield based on salt charged is about 95%. A typical flow diagram is shown in Figure 2-3 for Pennsalt Chemical Corp. 's production plant.[3]

Material requirements per ton of sodium chlorate are as follows:[15]

Sodium Chloride	1150 lb
Hydrochloric Acid	27 lb
Sodium Dichromate	10 lb

Electrical requirements are 5100 kw-hr per ton of sodium chlorate.

The efficient operation of the cells is dependent upon proper control of several variables. The following are considered to be important operating variables:[52]

(1) Cell pH (conversion to chlorate is greater in an acid solution)

(2) Chromate concentration (prevents reduction at the cathode)

(3) Current concentration

(4) Anode and cathode current densities

(5) Cell temperatures

(6) Chloride concentration

Decreasing current concentration (amperes per unit volume) increases current efficiency. As an offset to this factor, this increase requires an increase in fixed charges due to higher cell cost and cell building cost.[52] There are wide differences in cell designs among

the several producing plants; some have large cell bodies with the cathodes and anodes occupying a small fraction of the volume, while others have the entire cell body taken up by cathode or anode, current concentrations vary from 50 to 400 amp/cu ft. Cathode current densities may vary from 10 to 50 amp/sq ft. Anode current densities may vary more widely from 10 to 150 amp/sq ft. Increasing the current density tends to increase the voltage drop across the cell and reduce power efficiency. It also increases rate of attack on graphite anodes, but, within limits, decreases the graphite consumption per pound of chlorate produced.

Current efficiency improves with lower operating temperatures from 158° to 86°F, but the voltage requirements increase. The chemical production of chlorate by conversion of the hypochlorite produced in the cells is slowed by the reduction in temperature. Graphite consumption decreases quite rapidly at first with a decrease in temperature and a balance between these factors has to be established. The majority of plants in this country are believed to operate in the range 95° to 113°F, since graphite losses at the higher temperatures of 140° to 158°F are more than sufficient to offset any advantages.

The over-all consumption of graphite is of importance from the economic point of view. Janes[20] presents some interesting conclusions based upon a series of laboratory studies. The usual belief is that the graphite consumption is related to the discharge of hydroxyl ions which occurs in addition to Cl^- and OCl^- ion discharge.

$$4OH^- \longrightarrow O_2 + 2H_2O + 4e^- \qquad (2\text{-}11)$$

The following reaction probably occurs at the anode:

$$4OH^- + C \longrightarrow CO_2 + 2H_2O + 4e^- \qquad (2\text{-}12)$$

In addition to the above, there is a second reaction which can lead to a loss of graphite.

$$C + 2HClO^- \longrightarrow CO_2 + HCl$$

In the study conducted by Janes, it was shown that graphite anode attack was strongly affected by chloride ion concentration and cell temperature. A 22 fold variation occurred within a temperature range of 25° to 66°C and a concentration range from 75 to 250 g/l. Figure 2-4 shows that the graphite loss follows essentially a linear variation with the reciprocal of NaCl concentration for concentrations above 100g/l. The slope of this curve increases sharply with increasing temperature with indications of a maximum slope between 125° and 150°F. Graphite attack was also found to increase with a decrease in anode current density - the rate of increase being greater at the higher temperatures.

Although not a part of the study of graphite loss, some information was obtained on cell voltage variations. Figure 2-5 shows the effect of sodium chloride concentration on cell voltage. The rise in cell voltages as chloride decreases is largely due to the increase in anode potential, as oxygen is liberated at a higher potential than the chloride and the hypochlorite ions.

Potassium Chlorate. The second major chlorate compound is potassium chlorate. It is produced principally from sodium chlorate and potassium chloride by a double-decomposition reaction.

Like the sodium salt this compound was produced in the early history of the industry by chemical reaction between the chloride (i. e., potassium chloride) and calcium chlorate. (See Double-Decomposition Method for sodium chlorate.) This method is still used to a small extent in Europe. (13)

Potassium chlorate has also been produced directly from potassium chloride by an electrolytic process. International Mineral and Chemical Corporation built such a plant during World War II and operated it until recently.

Double-Decomposition Method. The principal method for producing potassium chlorate is by means of the double-decomposition reaction between potassium chloride and sodium chlorate. The series of process steps is outlined schematically in Figure 2-6.

In this process a saturated solution of sodium chlorate is prepared and is pumped to a crystallizer. At the same time a solution of potassium chloride is also charged to the crystallizer. The crystallizer is a cylindrical tank approximately 6 ft in diameter by 20 ft in height and is equipped with a conical bottom. It is maintained at a temperature of approximately 40°–50°F. The potassium chlorate crystallizes out and the mixture of liquor and crystals flow to a centrifuge where the crystals are separated

from the liquor. The liquor goes to storage. The crystals are washed, dried and packaged for shipment.

Electrolytic Method. Although no plant at present is utilizing the electrolytic method for the production of potassium chlorate, it is of interest to summarize the procedure which had been followed.

White[52] describes a process for the production of $KClO_3$ from KCl electrolytically. In this process a mixed solution of potassium chloride and potassium chlorate containing approximately 250 g/l KCl, 50 g/l $KClO_3$ with 2 g/l potassium bichromate added at a pH of approximately 5.5 is fed from a constant head tank into the cells.

The cells are rectangular steel tanks, approximately 20 in. by 30 in. by 48 in. high. They are divided into six sections by five perforated plates of 1/4 in. steel, 30 in. by 40 in., which are welded to the 20 in. tank sides and which, together with the tank side, form the cathode. The anodes are of treated graphite, 2 in. by 8 in. by 48 in. in 6 groups of 3 each. Each group is cast into a lead anode bar and is lowered into one of the cell sections. The anode bars rest on porcelain supports on the flanged top of the cell and butt together to form a solid top. Feed to the cell is through a calibrated nozzle into a pyrex tube which extends to the bottom of the cathode plates. The discharge of cell liquor is through an opening on one side just below the top of the cell body.

A cell installed with new anodes is normally operated without replacement until all usable graphite has been consumed. It is then

removed with an overhead crane and a rebuilt unit put in place. The cells are usually operated at approximately 3000 amp in 200 volt series in which the voltage drop across an individual cell is approximately 3 volts.

In a single pass through the cell, 3 to 10 g/l of chloride is converted to chlorate and some hypochlorite at a pH of approximately 6.9. From the cells this solution is pumped to a series of brick lined concrete reaction tanks providing a retention time of 7 hours, during which the bulk of the hypochlorite produced in the cell is converted to chlorates and chlorides.

From the reaction tanks the solution is pumped to an evaporative cooler consisting of an unlined concrete tower into which liquor is sprayed. The solution is cooled with consequent crystallization of chlorate.

The slurry goes to a settler, from which the mother liquor, after being refortified with potassium chloride equivalent to that electrolyzed in the cell, is returned to constant-head cell-feeding tanks.

The crystalline chlorate is roughly dried in a centrifuge. In order to meet the applicable military specification, the chlorate is redissolved, chemically treated to remove impurities, filtered and recrystallized. The crystals are separated in a settler and centrifuged, dried in a rotary dryer and then processed through screening and milling for final packaging. Figure 2-7 is a flow diagram of this process.

Other Chlorates. There are a large number of chlorates, but the majority of them are made only in laboratory quantities for special experimental studies. An examination of available information on the manufacture of some of these compounds reveals some data on the chlorates of barium, lithium and magnesium.

Barium Chlorate. This compound is still prepared as it was in the days of Gay-Lussac.[23, 27] The method consists of reacting barium chloride with sodium chlorate according to the reaction

$$BaCl_2 + 2NaClO_3 \longrightarrow 2NaCl + Ba(ClO_3)_2 \qquad (2\text{-}14)$$

A solution of barium chloride is mixed with a solution of sodium chlorate. Upon evaporation the sodium chloride separates out and the hot filtered solution is evaporated further. Monoclinic crystals of $Ba(ClO_3)_2 \cdot H_2O$ are obtained in the subsequent crystallization process. The salt is purified by recrystallizing.

Lithium Chlorate. The lithium salt is one of the most soluble of the chlorates and is very hygroscopic.[23] It is prepared by adding lithium chloride to sodium chlorate solution in a manner similar to that for the barium salt. Because of its lower solubility the sodium chloride crystallizes out first. After further concentration by evaporation the lithium chlorate is crystallized. The salt is removed by filtration and is then dried.

Calcium Chlorate. The method for manufacturing this compound has already been described under sodium chlorate (see Sodium Chlorate - Double-Decomposition method).

Magnesium Chlorate. Cunningham[42] is credited with developing a method for producing magnesium chlorate. This process follows the same basic reaction used for calcium chlorate. When magnesium hydroxide is chlorinated, a mixture consisting essentially of magnesium chlorate is formed.

$$6Mg(OH)_2 + 6Cl_2 \longrightarrow 5MgCl_2 + Mg(ClO_3)_2 + 6H_2O \qquad (2\text{-}15)$$

The reaction proceeds efficiently provided the magnesium hydrate supplied to the chlorination is associated with water in the molecular ratio of $MgO:H_2O$ of between 1:1 to 1:1.5. In this range the magnesium hydroxide appears to be peculiarly active.

Chlorination can be carried out in conventional apparatus such as is used in the production of bleaching powder from calcium hydroxide, mechanical agitation promotes the chlorination. The reaction proceeds best at 100°-120°F.

The separation of magnesium chlorate from the mixture of chlorate and chloride is accomplished with acetone. It is considered important to keep the water content so that the ratio of $H_2O:MgCl_2 + Mg(ClO_3)_2$ does not exceed about 6:1. When this condition is met, no evaporation is needed.

The Perchlorates

There are several methods available for preparing perchlorates from chlorates.[27] For example, potassium chlorate decomposes upon heating to give the perchlorate according to the reaction

$$4KClO_3 \longrightarrow 3KClO_4 + KCl \qquad (2\text{-}16)$$

The perchlorate can also be obtained by fusing potassium chlorate with barium peroxide as follows:

$$KClO_3 + BaO_2 \longrightarrow KClO_4 + BaO \qquad (2\text{-}17)$$

The fused material is extracted with hot water and the perchlorate obtained by crystallizing.

Commercially, though, the only method used to produce perchlorates in quantity is the electrolytic method. According to Schumacher[35] predominant commercial practice is to manufacture sodium perchlorate first and to make the other perchlorates by a double-decomposition reaction. Therefore, although the major perchlorates marketed commercially are the potassium and ammonium compounds and sodium perchlorate is not marketed commercially, this practice places sodium perchlorate in its intermediate role in a position of being the most important of the perchlorates.

Sodium Perchlorate

Electrolytic Methods. The principal method used for the production of sodium perchlorate by the electrolysis of a solution of sodium chlorate is a two-step process.[32] This procedure is followed because it results in a higher over-all efficiency than is possible with a single-step process. The first step is a continuous operation; the second step is a batch operation. About 70 percent of the sodium chlorate is converted to the perchlorate in the first step. The chlorate content is reduced to its

final concentration in the second electrolysis step. An important factor in this operation is that the volume of solution can be kept small in the last step. (This process is shown diagramatically as part of the over-all production process for potassium perchlorate in Fig. 2-8.)

Although not used at present, a single-step batch method of production of sodium (and potassium) perchlorate has been used.[19] This method gives a product with a higher $NaClO_3$ content than the two-step process.

A complete understanding of the mechanism by which the electrochemical formation of perchlorates takes place has not been developed. However, according to a theory proposed by Oechsli and later by Knibbs and Palbruman[23], the first step in perchlorate formation begins with the discharge of chlorate ions at the anode.

$$2ClO_3^- \longrightarrow 2ClO_3 + 2 \text{ Electrons} \qquad (2\text{-}18)$$

The chlorate is then converted to perchlorate by the following reactions:

$$O_2ClO + OClO_2 \longrightarrow O_2Cl\text{-}O\text{-}O\text{-}ClO_2 \qquad (2\text{-}19)$$

$$O_2ClOOClO_2 + HOH \longrightarrow O_2ClOOH + O_2ClOH \qquad (2\text{-}20)$$

$$O_2ClOOH \longrightarrow O_3ClOH \qquad (2\text{-}21)$$

The sum total of these reactions may then be written as:

$$NaClO_3 + H_2O + 2 \text{ Faradays} \longrightarrow NaClO_4 + H_2 \qquad (2\text{-}22)$$

Production of sodium perchlorate in a typical plant[32] is begun by dissolving sodium chlorate in water and allowing it to flow by gravity through a regulating valve to the perchlorate cells. The pumping,

cooling and pump-out designs are identical with those of the chlorate system, except that a smaller volume of liquor is handled and the cell characteristics are different.

As indicated above, the electrolysis takes place in two stages, the first stage is a continuous operation and the second stage a batch operation, thereby providing flexibility in operating conditions for each of two ranges of concentration, that is, the range above 90 g/l and the range below 90 g/l chlorate. Of greater importance, however, is the fact that the operating volume of solution can be kept small.

A concentrated sodium chlorate solution containing 600 g/l $NaClO_3$ and adjusted to a pH of 6.1-6.4 is fed continuously to the first step electrolytic cell circuit, while a stream of near-equal volume is withdrawn from the circulating electrolyte. The composition of the removed solution is approximately 500 g/l $NaClO_4$ and 90-110 g/l $NaClO_3$. A volume of solution equivalent in perchlorate content to a 24-hour operation is produced and serves as the working volume of electrolyte for the batch operation which follows.

In this second step, the chlorate concentration is lowered by electrolysis to the desired level (5 g/l maximum). Electrolysis capacity of this step is about one-fifth that of the first.

Two kilowatt hours are required for each pound of sodium perchlorate produced. This figure includes auxiliary power for pumps, fans, centrifugal filters, dryers, etc.

The operating characteristics for a perchlorate cell used

in a plant are summarized in Table 2-3. According to Schumacher[32] much larger cells using 5000 amp/cell have been developed for use in a more recent plant with a capacity of 1200 ton/month (American Potash and Chemical Corp.'s Henderson, Nevada plant). These cells are arranged in long rows and connected in series to make circuits of 360 v and 5000 amps. Electrolyte flows through the cells in parallel and is maintained at a temperature of 113°F. The potential drop across each cell is 6.8 volts. Current efficiency in the first-step circuit averages 90% and in the second, 70%. Current efficiencies are based on cell gas analyses. These cells are reported to perform very well, and there is no reason to believe any operating advantage could be gained by going to a larger capacity.

In the single-step batch process referred to earlier, the cells are 33 in. high, 30 in. long and 16 in. wide and have a volume of 50 gal. The production per cell is 2 lb/hr; operating temperature is 113°F; voltage is 6.8 volts; and current is 500 amp. Current efficiency is reported to be 93-97%.

In the operation of these cells the concentrated sodium chlorate feed solution containing 650-700 grams/liter $NaClO_3$ is run into the electrolysis cells, where it is oxidized to perchlorate. From the cells the perchlorate solution, with its composition now changed to 800 gram/liter $NaClO_4$ and 20 gram/liter $NaClO_3$, is pumped to storage.

According to Schumacher[35, 37], an efficient and economical perchlorate process must be able to satisfy the following requirements:

(1) Efficient electrolytic cell

(2) Product of high purity and special particle size to meet market requirements

(3) High electrical load factor

(4) Continuous or partially continuous process

(5) Effluent electrolyte with a maximum chlorate concentration of 5 grams/liter.

There are a number of side reactions which account for a loss of current. The presence of chloride results in a discharge of chloride ions. Chlorine formed in this process reacts with water to form hypochlorite ions and chloride ions. Some hypochlorite ions are discharged and form chlorine and oxygen, according to the following reactions:

$$2Cl^- \longrightarrow Cl_2 + 2 \text{ Electrons} \qquad (2\text{-}23)$$

$$Cl_2 + HOH \longrightarrow H^+ + ClO^- + Cl^- \qquad (2\text{-}24)$$

$$2ClO^- \longrightarrow Cl_2 + O_2 \qquad (2\text{-}25)$$

A loss of current, due to the presence of chlorides is not considered serious when the chlorate concentration is above 90 g/l, but when the concentration falls below 90 g/l the effect of chloride-ion discharge is much more noticeable. Chloride-ion concentration is established at an equilibrium level depending on the electrolyte temperature. The presence of chloride ions is a result of the use of impure chlorate containing a small amount of chloride, or if pure chlorate is used, it may result from the disproportionation of chlorate, for example,

$$4ClO_3^- \longrightarrow 3ClO_4^- + Cl^- \qquad (2\text{-}26)$$

The chlorate-chloride ratio is important since it is necessary, in order to avoid chlorate impurity in the finished product, to lower the chlorate concentration to a maximum of 5 grams/liter. Since there is always an equilibrium concentration of chloride, it is evident that near the end of the run the discharge of chloride ions becomes a large proportion of total anodic discharge. Current efficiency will drop to as low as 50% or less as the chlorate concentration approaches the chloride concentration. As a result, it has become a practice to stop the electrolysis when the ratio of chlorate to chloride becomes unfavorable. The remaining

chlorate is decomposed by concentrated HCl. A more desirable method is to change conditions of operation for the two different sets of concentration.

Discharge of hydroxyl ions at the anode also accounts for a loss of current but can be largely avoided by pH control. Chlorate ions discharged at the anode can react with water to form oxygen and chloric acid. Current losses arising from this side reaction depend on the anode current density and the cell temperature. Reduction of chlorate or hypochlorite at the cathode to form chlorides can largely be prevented by use of compounds which will form a protective film on the cathode. Soluble chromates are most commonly used for this purpose.

Recent studies by Sugino and Soyagi[39] on the mechanism of perchlorate formation showed that the first step in the electrolysis process is the discharge of chlorate ions which takes place at a higher potential than that of oxygen evolution. A high anodic current density is thus necessay to maintain the anodic potential at a high enough value to promote the discharge of ClO_3^- ions. The complete conversion of chlorate to perchlorate is due to the coexistence of large amounts of perchlorate in the same solution.

Thermal Method. Although never used for quantity production of sodium perchlorate, a thermal method has been developed for converting sodium chlorate to sodium perchlorate.[46] In this process sodium chlorate is thermally decomposed into sodium perchlorate in a continuous process in which the unreacted sodium chlorate is returned for

recycling. The time and temperature to which the melted sodium chlorate is subjected is controlled. The $NaClO_4$ is then extracted by a water crystallization process which avoids any possibility of uncontrolled explosive reactions.

In the thermal decomposition of sodium chlorate, the salt is melted at a temperature in the range of 750°-1100°F, under which conditions the melt gradually thickens because of the formation of sodium chloride and sodium perchlorate, both having higher melting points than the chlorate.

The reactions are believed to be as follows:

$$4NaClO_3 \longrightarrow NaCl + 3NaClO_4 \qquad (2\text{-}27)$$

$$2NaClO_3 \longrightarrow 2NaCl + 3O_2 \qquad (2\text{-}28)$$

$$2NaClO_4 \longrightarrow 2NaCl + 4O_2 \qquad (2\text{-}29)$$

The rate of decomposition of the sodium perchlorate at 750°-1100°F is less rapid than the rate of formation of the perchlorate from the chlorate and, therefore, is dependent upon the time and temperature and the mixtures of $NaClO_3$, NaCl, and $NaClO_4$ that are obtained. When the amounts of chloride, perchlorate, reach the point where they thicken and behave like a solid, decomposition is rapid. This occurs when NaCl composition becomes 2.25 parts by weight of sodium chloride. Table 2-4 summarizes the data on the thermal decomposition of sodium chlorate based upon Equation (2-27).

The production version of the thermal process envisions the introduction of sodium chlorate crystals obtained from any suitable source

into a continuous melter and transfer of the resulting liquid to a reactor chamber in which the melted material is held at a selected temperature 750°-1100°F until the mixture begins to thicken as a result of the production of sodium perchlorate and sodium chloride. Oxygen gas is given off in the reactor and is collected.

The liquids melt after retarded passage through the reactor is transferred to a cooler where the temperature is reduced to 200°-300°F. From this cooler the solidified material, crushed to a suitable form is transferred to a leaching vessel, where the most soluble portion is extracted with an aqueous solution which is then recycled after the sodium chlorate has been removed. An amount of recirculated aqueous solution is used which will substantially dissolve all of the $NaClO_3$ and $NaClO_4$ from the cooled melt leaving the NaCl undissolved. The mixture then flows to a centrifuge where the less soluble NaCl crystals are separated from the liquid. The liquid is concentrated in an evaporator until the $NaClO_4$ crystallizes out. These crystals are then separated in a centrifuge.

The liquid finally goes to a crystallizer where it is cooled and crystals of $NaClO_3$ are formed and are removed in a centrifuge.

The aqueous liquor from this centrifuge is the liquid used as the leaching solution. The sodium chlorate crystals which contain some sodium perchlorate are recycled to the melter to supplement the make-up sodium chlorate introduced into the process.

Potassium Perchlorate. Commercial quantities of potassium perchlorate are prepared almost exclusively by the addition of a hot concentrated solution of commercial, chemical grade potassium chloride in slight excess over the stoichiometric amount to a saturated sodium perchlorate solution[32] (see Sodium Perchlorate - Electrolytic Method). The chemical reaction involved for the production of potassium perchlorates is as follows:

$$NaClO_4 + KCl \longrightarrow KClO_4 + NaCl \qquad (2\text{-}30)$$

The rate of cooling of the resultant slurry is controlled in order to produce consistently a product of uniform quality and of desired particle size distribution. After cooling the crystallizer contents are pumped to a continuous centrifugal filter where the moisture content is reduced and the product is washed to remove chlorides. The solid product is discharged from the centrifuge directly into a direct fired rotary dryer where its moisture content is lowered further to the final desired level. The dried product either as is or in pulverized form is packed for shipment in 100 lb bags or steel drums.

The mother liquor containing chlorides is concentrated in an evaporator. This causes the salt to settle out whereby it can be separated from the liquor by filtration.[32]

The process details for a typical production plant

are presented in Figure 2-8.[32] The entire operation beginning with the conversion of NaCl to $NaClO_3$ and ending with the packaging of the finished

$KClO_4$ is carried out in this plant and is shown diagramatically in the figure. The portion of the operation of interest here, however, is the conversion of sodium perchlorate to potassium perchlorate.

Sodium perchlorate, the manufacture of which has already been described, is filtered to remove any graphite particles and is charged to a potassium perchlorate crystallizer, along with a saturated KCl solution. Potassium perchlorate precipitates, and is separated from the liquor in a centrifuge. Solid, wet potassium perchlorate is dried, ground and packaged for market in 100 lb paper bags or steel drums. Final product assays are usually 99.8% $KClO_4$. A typical chemical analysis for $KClO_4$ is shown in Table 2-5. The mother liquor goes to an evaporator, where it is concentrated. The salt which is precipitated is returned to the NaCl solution tank as raw material for $NaClO_3$ production.

Ammonium Perchlorate. The manufacture of ammonium perchlorate is carried out by means of a double-decomposition reaction, similar to the other perchlorates. A number of different ammonium salts may be used in this reaction. In the early production plants ammonium chloride was reacted with sodium perchlorate. This particular ammonium salt was selected because it made separation of the products easier. When the need arose for large-scale production of ammonium perchlorate, it was found that the production capacity for ammonium chloride was inadequate. Attention was then turned to other means for accomplishing the same reaction. The replacement of ammonium chloride with ammonia and

hydrochloric acid proved so attractive that this procedure is now believed to be followed in practically all production plants in this country. Figure 2-9 is a schematic sketch showing the various steps in this process.

The chemical reactions involved in the production of ammonium perchlorate by either procedure are relatively simple and are quite similar. Using ammonium chloride, the following reaction takes place:[36]

$$NH_4Cl + NaClO_4 \longrightarrow NH_4ClO_4 + NaCl \qquad (2\text{-}31)$$

The reaction using ammonia and hydrochloric acid is

$$NH_3 + HCl + NaClO_4 \longrightarrow NH_4ClO_4 + NaCl \qquad (2\text{-}32)$$

The manufacture of ammonium perchlorate by the ammonia-acid process is characterized by five steps:[1, 36]

(1) Reaction of anhydrous ammonia, hydrochloric acid, and sodium perchlorate.

(2) Fractional crystallization of ammonium perchlorate.

(3) Centrifugal separation of the ammonium perchlorate.

(4) Fractional crystallization of by-product sodium chloride.

(5) Drying, blending and packaging of ammonium perchlorates.

These steps are shown diagramatically in Figure 2-10. Operation of the largest production plant in this country (the 40 ton/day Henderson, Nevada plant of the American Potash and Chemical Corporation) is described in the following sections.[36]

Reactor System. The reactor system consists of two stages operating continuously and sequentially under automatic control. The

first-stage operation takes place in a 1000-gal glass-lined reactor (66 in. diameter by 93 in. height) while the second-stage operation occurs in a 750-gal glass-lined reaction vessel. (Stainless steel is currently being used at the Henderson plant.) The reaction is initiated in the first vessel and completed in the second.

The heart of the process is the steam-jacketed reactor in which the ammonia, hydrochloric acid and sodium perchlorate are mixed continuously with only mild agitation required to maintain a uniform mixture. The arrangement of the "dip pipes" used to introduce the ammonia and HCl was found to be important. A Teflon dip pipe introduces ammonia about 10 in. from the wall and about 2 ft from the bottom of the reactor. Simultaneously HCl is introduced through a molded rubber pipe surrounding, but 10 in. shorter than, the ammonia dip pipe.

Under typical operating conditions an average of 8290 pounds/hr of 56% sodium perchlorate, 3918 pounds/hr of 35% hydrochloric acid and 640 pounds/hr of anhydrous ammonia are introduced into the first reactor. In addition, 12,600 lb/hr of mother liquor and wash waters are recycled to this reactor. The mother liquor contains 29% ammonium perchlorate, 16% sodium chloride and 35% water.

The pH in the reactor is held at 5.5 through the addition of HCl. Because of the highly exothermic nature of the reaction it proceeds at atmospheric pressure and at a temperature of 175°F with the addition of little outside heat. Retention time is about 30 min. From the primary

reactor the mixture passes to the secondary reactor for reaction completion and pH adjustments.

In order to obtain adequate automatic control of the reaction process all feed streams to the main reaction vessel are ratio controlled. The NH_3: $NaClO_4$ input ratio is controlled by one ratio controller. A second controller maintains the proper ratio of HCl to $NaClO_4$. A third controller maintains optimum pH. These three controllers are incorporated into a cascade-type system which allows the pH controller to adjust the HCl-$NaClO_4$ ratio automatically by small increments until the proper pH level is attained. The pH of the discharge from the second reactor is automatically adjusted by means of another controller to a higher level (this is believed to be desirable from a reduced corrosion point of view) by the addition of ammonia from a secondary stream. All controllers have high- and low-level alarms for safety.

NH_4ClO_4 Crystallization. From the reactor the mixture flows to a stainless steel vacuum-cooled crystallizer. This unit operates continuously, crystallizing out the NH_4ClO_4 by cooling the reactor effluent from 175° to 95°F by means of vacuum evaporative cooling. In this operational step the feed from the reactor is mixed continuously with a large amount of mother liquor which is being circulated from the bottom of the crystallizer to the upper, vaporizing section. (See Fig. 2-10.) In this upper section supersaturation of the input liquor occurs as water is vaporized. This supersaturated solution is then relieved of its

supersaturation as it flows upward through the dense bed of NH_4ClO_4 crystals which were formed earlier in the process. The size of the crystals is controlled by temperature and retention time.

A slurry containing the desired crystal size distribution is removed continuously. This slurry contains 40% ammonium perchlorate in crystal form, about 10% in solution, about 13% sodium chloride, with the remainder water.

NH_4ClO_4 Separation. The slurry from the crystallizer is fed to a centrifugal filter where the mother liquor is removed continuously and the crystals are washed.[36] The crystals are discharged directly into a tank of saturated ammonium perchlorate solution. This saturated solution serves to reduce the chloride concentration of the solid and also serves as a safe means for transferring the ammonium chlorate to the drying system. Wash water and mother liquor are collected and pumped to the sodium chloride crystallizer.

The slurry of NH_4ClO_4 crystals goes to a flash dryer where the moisture content of the crystals is decreased to 0.5%. The mother liquor (filtrate) is recycled to the primary reactor. The partially dried crystals are further dried in a three-stage vibrating pan dryer to a moisture content of less than 0.2%. (It is planned to do away with the pan driers, using only the flash driers.) After screening, the product passes through automatic weighing scales into polyethylene lined shipping drums.

The final product is made to meet several different specification requirements. (See section on Product Specifications.) A typical product analysis is presented in Table 2-6.

NaCl Cycle. The mother liquor which is depleted of ammonium perchlorate is concentrated in a vacuum crystallizer containing an external heat exchanger which raises the temperature of the liquor to 175°F. This unit operates similarly to the ammonium perchlorate crystallizer except that NaCl is crystallized out. The sodium chloride slurry is fed to a centrifuge where solids are discharged for disposal.

The wash water and mother liquor from the centrifuge are rich in perchlorate and are returned to the reactor system. The discarded sodium chloride solids average better than 99% pure so that very little NH_4ClO_4 is lost here.

Other Perchlorates. There are a few perchlorates in addition to those whose manufacture has already been described in quite some detail which are made in more than laboratory quantities. These are lithium perchlorate and barium perchlorate.

Lithium Perchlorate. This compound is made by the double-decomposition reaction between ammonium perchlorate and lithium hydroxide.[23]

$$LiOH + NH_4ClO_4 \longrightarrow LiClO_4 + NH_4OH \qquad (2\text{-}33)$$

Upon evaporation to dryness the NH_4OH is volatilized and the anhydrous $LiClO_4$ obtained. A typical chemical analysis for the final product is shown in Table 2-7.

Barium Perchlorate. The barium salt is made by reacting barium chloride with sodium perchlorate and selectively crystallizing out the product.[23]

$$BaCl_2 + 2NaClO_4 \longrightarrow Ba(ClO_4)_2 + 2NaCl \qquad (2\text{-}34)$$

Barium perchlorate can also be made by direct electrolysis of a barium chlorate solution.[23]

Process Equipment

The manufacture of chlorates and perchlorates has led to the development of special processing equipment. In order to gain a clear understanding of some of the features of product manufacture, it is believed helpful to examine these special pieces of equipment in greater detail. Of particular interest are the chlorate and perchlorate electrolytic cells, the crystallizers and the dryers.

Chlorate Electrolytic Cells

There are two basic types of cells used in the electrolysis method for sodium chlorate manufacture. One is the batch type which was used for some sixteen years by the Cordox Corporation in their Oklahoma plant. The other is the continuously operated cell such as is used in the American Potash and Chemical Corporation's plants.

Batch-Type Cell. The batch-type cell was studied extensively by Groggins, et al[18], and has been discussed by Hampel and Leppla[19]. According to these sources, this batch cell was constructed with vertical graphite anodes

and steel cathodes. Figure 2-11 shows a sectional view of such a cell. The cell body was an uninsulated sheet-steel rectangular tank strengthened by 1-1/2 in. angle irons. Two vertical sheet-steel cathodes divide the cell into three sections lengthwise. They were so installed as to allow the cell liquor to circulate in an up and down path around them.

Graphite electrodes, in two rows of five each, hung between cathode sheets. Between anode rows was positioned a steel cooling chamber about the same height as the cathodes and 3 in. wide. The graphite electrodes were 7 in. wide, 1 in. thick and 40 in. long and rested on concrete blocks placed at the cell bottom. The electrodes were positioned at the top by five rectangular porcelain insulators, each slotted to receive two opposing anodes. The insulators rested in the cell cover. (Each of the cells had a capacity of about 200 gal of sodium chloride feed solution.) The anodes extended about 4 inches above the cover, and copper bus bars running along each side of the two rows were bolted to them.

Cooling water flowed through the cells in parallel, entering and leaving the cooling chamber by rubber hoses. Hydrogen discharged at cathodes caused circulation of the cell liquor up the central section and down the outer sections. This gas was vented through the roof from each cell by means of a plastic tube leading from the cell cover.

Table 2-8 summarizes the pertinent data on construction and operating characteristics of the batch cell.

Continuous-Type Cells. The continuous cell has proved to have a greater production capacity than the batch cell. A patent granted to Schumacher[45] describes one of these cells. Figure 2-12 shows the detailed construction of such a cell.

The cell consists of a twin arrangement of two pairs of electrodes housed in a single tank divided by a lengthwise vertical partition. It has been found that this arrangement gives good operating conditions, saves space, and allows economy in the use of structural materials.

Referring to Figure 2-12, the steel tank 11 is of welded steel and is an elongated trough-like structure which provides space for the parallel rows of electrodes. For the twin cell structure, a partition (member 12) dividing the cell into two elongated compartments is provided, this partition conveniently being a perforated steel plate with openings 13 in the electrolyte portion to permit the flow of electrolyte from one half cell to the other.

A heavier structural steel member 14 having a flat horizontal surface is welded to the top edge of the partition plate 12 to provide a firm support surface for the cover plates for the cell. The upper edges of the cell walls are provided with flanges 15 which together with top edge of the structural member 14 provide means of attaching and supporting the cover plate 16.

The cover plate 16 is conveniently made of compressed sheets of asbestos-Portland Cement composition, in which slots 19 are provided.

for four rows of graphite anodes 18, two in each half-cell on both sides of the partition member 12.

The anodes are constructed of dense graphite or graphitized carbon plates mounted in a cast lead block 20 with copper dowel pins 21 for maintaining good electrical and mechanical connection between the graphite and the lead. These lead block members are conveniently made by casting the lead around the ends of the graphite plates and dowel pins and headed bolts 22 for making electrical connections to the bus bars.

Banks of steel cooling water tubes are provided longitudinally between pairs of rows of graphite anodes, these tubes being supported in the perforated steel end plates 24 of the tank 11 forming one wall of the manifolds 24A. At the ends of the cells are suitable horizontal baffles 25 to regulate the flow of cooling water to various portions of the bank of tubes as desired. Circulation can occur from one end to the other providing uniform temperature throughout the space in which the electrolysis takes place.

These steel, water cooling tubes serve as cathode surfaces along with the walls and partition member 12 of the steel tank. Electrical connection for the cathodes is conveniently made by upstanding bar 26 welded to the edge of the flange of the tank along one side of the cell with suitably spaced connector bolts provided therein. The cooling water enters at one end by the inlet pipe 29 and leaves at outlet pipe 29A.

A settling space is provided below the anodes and the water cooling tubes for the accumulation of sediment, mostly derived from the disintegration of graphite anodes, a clean-out connection 28 being provided at the ends of the cells.

The space between the electrolyte and the cover plate 16 is provided for the collection of gases which are formed during electrochemical reactions. In order to prevent the formation of explosive mixtures, an inlet pipe 31 is provided which admits inert gas, and a similarly placed outlet pipe 30 at the other end of the cell provides for exit gases, which are a mixture of inert gas and generated gases.

The electrolyte is brought into the cell by means of inlet pipes 33 at one end of the cell and is discharged from the overflow pipes 34 at the other end.

Perchlorate Electrolytic Cells

Electrolytic cells used in converting sodium chlorate to sodium perchlorate have been developed for either batch or continuous operation. The two types of cells have certain structural differences which are described in the following sections.

Batch-Type Perchlorate Cells. According to Hampel and Leppla[19] the cell body is constructed similarly to that used for making the chlorates. It is fabricated of sheet steel reinforced with angle iron. A cooling chamber, 30 in. long, 27 in. high, and 2 in. wide is placed vertically in the center of the cell. Suitable cooling water connections are provided. When filled to within 2 in. of the cover, each cell has a capacity of about 50 gal.

The cathodes are four vertical 3 in. diameter steel tubes 33 in. long and are spaced two on each side of the cooling chamber. Each cathode pipe has 8 to 10 hole (0.5 in. diameter) drilled through the pipe wall near each end to permit the entrance of solution at the bottom and exit of hydrogen and liquor at the top.

Anodes are 0.5 in. copper rods clad with a 0.02 in. thick platinum sheet. The 30 in. long anodes are centered in the cathode tube by two porcelain spacers. Table 2-9 summarizes the characteristics of a typical batch-type perchlorate cell.

Continuous - Type Perchlorate Cells. The continuous cell has been generally accepted on the basis of constantly good performance. Schumacher[43] describes in detail the construction of such a cell. Figure 2-13 shows the details.

Referring to Figure 2-13, it is seen that the electrolyte cell consists of an elongated steel tank 11 with an open top and outwardly extending flanges 12 around the upper edge. Channels for cooling liquid are provided by longitudinally placed steel jackets 13 welded to the side walls 11A, these being subdivided by horizontal partitions 14 to distribute the circulating cooling liquid.

Further control of temperature in the cell is attained by the use of tiers of steel tubes 15 extending centrally through the electrolyte compartment of the cell between the anodes 17. The ends of these tubes are connected to manifolds 16 on the two ends of the tank so that the cooling

liquid may be circulated not only through the side wall jackets 13 but also through these tubes disposed between the platinum anode within the cell.

The cell cover plates 18 consist of sheets of chemically resistant artificial stone material made of compressed mixtures of Portland Cement and asbestos. The sheets are attached by bolting to the flange around the upper edge of tank.

Slit openings 19 fitting the platinum electrode sheets 20 are provided in the cover for insertion of the anodes. The steel surfaces of the tank and water-cooling tubes 15 in contact with the electrolyte serve as cathodes for the cell. The electrolyte is introduced through pipe 21A and is withdrawn through the overflow or effluent pipe 22A.

In most electrochemical processes of the type in which this cell has been adopted, there is evolved a mixture of gases, often in explosive proportions. In the case of the electrochemical process of converting sodium chlorate to sodium perchlorate varying amounts and proportions of hydrogen, oxygen and chlorine gases are evolved. It is necessary to remove these gases or to dilute them to avoid explosion. Provision is therefore made for introducing a sweeping-out gas through pipe 23 and removing the mixture of gases through pipe 24.

The platinum electrodes consist of a thin sheet of platinum about 0.006 in. thick which is punched with numerous holes in order to provide ready circulation of the electrolyte through and around all portions of the platinum surface. The thin sheet of platinum is inserted through an opening in the cover plate. Above the cover plate the upper end of the thin

platinum is pressed between relatively heavy sheets of copper 25 and the sandwich thus formed is bolted together with bolts 29 between vertical portions of L-shaped bars 26.

In order to prevent twisting and buckling of the extremely thin electrode sheet within the cell, it is held in a fixed position between glass bars 28 which are suspended from and rigidly held closely adjacent to platinum sheets.

The glass bars are disposed at intervals along the length of the electrode and extend as far as the depth of the platinum sheet.

The cathode of the cell consists of the surfaces of the steel tank and the steel tubes used for water cooling which are in contact with the electrolytes. An upright bar member welded to the flange on one side of the cell at the top edge of the tank provides a convenient electrical connection for the cathode to the bus bars of the electrical system.

Crystallizers

Two types of crystallizers can be used in chlorate and perchlorate manufacture, depending upon the process scheme. One type is the surface-cooled unit, which requires no preconcentration before crystallization occurs. The second type is the vacuum-cooled unit which requires preconcentration of the liquor before crystallization can take place. In the next sections some design details of these two types of units are presented.

Surface-Cooled Crystallizers. This type of crystallizer, which is used in the manufacture of sodium chlorate, requires two open

vessels made with 60 degree conical bottoms. Each tank is equipped with a circulating pump and a heat exchanger. In a typical sodium chlorate plant the vessels might be 5 ft diameter by 10 ft high and be made from stainless steel. A production rate of about 30 ton/day could be realized from such a unit. Figure 2-14 is a schematic sketch of such a process scheme.

In the operation of a typical crystallizer, fed from the chlorate cells at 104°F, containing, for example, 41.0% $NaClO_3$, 9.3% NaCl and the remainder water, enters the first tank at a rate of 14,450 lb/hr. The mother liquor which is now cooled to 20°F is discharged at a rate of 11,950 lb/hr from the centrifuge for recycling through the first heat exchanger back to the brine preparation tank. It now contains 28.8% $NaClO_3$, 11.3% NaCl and the remainder water. The yield is thus 2500 lb/hr of $NaClO_3$ or 30 ton/day.

Vacuum-Cooled Crystallizers. The vacuum crystallizer is a continuously-operated device.[5] Its operation depends upon the principle that a warm, saturated solution, introduced into a vessel maintained under a vacuum which corresponds to a boiling point of the solution lower than the feed temperature, must flash and be cooled by the resulting adiabatic evaporation. Crystallization must also occur as the solution is super-saturated as a result of the evaporation and the cooling.

This type of crystallizer requires the preconcentration of the feed liquor before crystallization can take place efficiently. When used in the sodium chlorate plant two units are operated in series. The first unit

cools the solution sufficiently to effect removal of most of the sodium chloride. The second unit crystallizes the sodium chlorate. Figure 2-15 is a schematic sketch of a typical processing system.

The vacuum crystallizer is a simple apparatus which has few moving parts (only a small propeller stirrer).[29] A sketch of a typical crystallizer is shown in Figure 2-16. The crystallizer proper is the cone-shaped bottom section. The feed enters at the bottom of the cone and flows upward through the center of the crystallizer. A centrally-located tubular section called a "draft tube" with a stirrer inside prevents short circuiting of the feed. Different schemes are used to introduce the feed. It should be noted that in Figure 2-16 the feed enters the crystallizer directly while in Figure 2-10 and Figure 2-15 the feed is mixed with the circulating mother liquor. This latter system permits a longer hold-up which is desirable for obtaining a particular crystal size distribution. The crystallizer in Figure 2-16 also contains an elutriating leg to aid in the classification of the product. Figure 2-17 is a photograph of this crystallizer in a typical plant installation.

Cooling of the liquors is accomplished by the evaporation of water in the vapor space in the upper section of the crystallizer. A vacuum is maintained in this section by means of a steam-jet ejector located on the vapor discharge line. Further information concerning the operation of this unit for crystallizing ammonium perchlorate can be found in the section on NH_4ClO_4 Crystallization.

Centrifuges

There are a number of continuous centrifuges which can be used to separate crystalline material from its mother liquor. The most common type used in the perchlorate manufacture is the Bird centrifugal filter. This machine will handle feeds of 1800 lb/hr containing 25% solids and produce a crystalline product with only 3-6% moisture. Figure 2-18 is a photograph of a typical installation. This particular type of continuous centrifugal filter effects the separation of solids from liquids by a sedimentation process. [7] The machine consists essentially of two rotating elements. The outer element is a solid bowl; the inner element is a helical screw. The screw rotates at a slower speed (10-40 rpm) than the bowl (1000-2000 rpm). This machine thus consists of a conveyor mounted inside a revolving bowl. Effluent ports are so located that the solid-discharge area is not submerged. In this way a drainage deck is provided on which the solids may be washed if desired and then drained by centrifugal force.

Feed is introduced through a stationary pipe and spills into the conveyor hub which delivers it to the bowl. The feed ports are located so that the slurry does not spill upon the drainage deck. As the filtrate travels toward the effluent discharge ports centrifugal force is so applied and the feed rate so controlled that the discharged filtrate is essentially clear.

The solids are thrown out of suspension during this operation and against the bowl wall where they are consolidated and conveyed towards the solids discharge ports. Centrifugal force causes the liquor to separate

from the solids as they move up on the drainage deck. The drained solids are then discharged through the discharge ports. Both effluent and solids discharge into a stationary case which is equipped with baffles that prevent mixing of solids and liquids.

Dryers

A variety of drying equipment is used in the manufacture of chlorates and perchlorates. In general, vibrating pan or screen dryers and flash dryers are used for drying ammonium perchlorate. Continuous rotary dryers (either direct or indirect heated) are used for sodium and potassium chlorate and potassium perchlorate.

Vibrating-Pan Dryers. A vibrating-pan dryer is an example of a through-circulation dryer.[29] It employs a vibrating screen or grate to carry the material while hot air or flue gases are passed upward or downward through the bed of material. Continuous through-circulation dryers operate on the principle of blowing hot air through a permeable bed of wet material while it is passing continuously through the dryer.

Flash Dryers. A flash dryer is an example of a pneumatic conveying dryer.[9] In this type of dryer, moisture removal is accomplished by dispersing the material to be dried in a hot gas zone, followed by conveying at high velocities. The dryer consists essentially of a device for dispersing the wet solids in the hot gases, a duct through which these gases convey the dispersed particles and a cyclone-type collection system for removing the dry product from the air stream. Temperature-sensitive

materials can be dried satisfactorily at relatively high temperatures because of the short drying times possible with this type of dryer.

Rotary Dryers. Rotary dryers are designed for the continuous drying of materials. Three common types are recognized on the basis of how heat is supplied to the unit: (1) direct-heat rotary in which the flue gases or hot air are passed through the dryer in direct contact with the material, (2) indirect-direct rotary in which heat is transferred both indirectly through the walls of the dryer and by direct contact with the materials, and (3) the totally indirect where heat is transferred only through the walls of the dryer.[29] Both direct-heat and steam-tube indirect type dryers have been used in drying the chlorates and perchlorates.

The totally indirect rotary dryer having steam tubes running the length of the dryer along its inner surface has a high thermal efficiency and operates with low dust losses.[6] A typical dryer used for sodium chlorate is fabricated from aluminum and has the following characteristics:

Size:	54 in. diameter by 30 ft length
Capacity:	Feed input of 9000 lb/hr wet chlorate at 3% moisture. Output product not to exceed 0.2% moisture
Exhaust:	300 CFM at 180° F and 75% saturated
Steam:	1100 lb/hr at 60 psig
Drive:	5 hp

Process Developments

In the period between the time of Gay-Lussac (1814) and the middle 1940's, very few changes were made in the processes for manufacturing the

various chlorate and perchlorate compounds. It became evident in the late 1940's that the composite-type solid propellants which utilized potassium and ammonium perchlorate as a solid oxidizer possessed many desirable characteristics. It was also deduced at that time that the production capacity for these compounds was not sufficient to supply all contemplated needs, especially if a major conflict developed.

Any increase in the productive capacity of this country is influenced by two major factors. First, an increase in production requires a large increase in electrical power to operate the chlorate-perchlorate plant. Secondly, an increase in production capacity causes an increase in the requirements for platinum needed in the electrolytic conversion of chlorate to perchlorate. The normal requirement was already extremely high. As a result, a number of programs were initiated under government sponsorship (1) to find ways to replace the platinum anodes with some less critical material and (2) to produce chlorate and perchlorate by purely chemical rather than electrochemical reactions. In addition some studies were conducted aimed at improving the graphite anodes and iron cathodes used in sodium chlorate manufacture. A brief summary of some of these developments follows. (Additional information will be found in Volume 2.)

Lead Dioxide Anodes

One of the more interesting developments reported in recent years for the chlorate and perchlorate industry is the use of lead dioxide anodes as a possible replacement for the platinum anodes in perchlorate

production. Two recent articles[14, 37] and one patent[50] present relatively complete summaries of these developments. Schumacher and co-workers[37] report their results obtained with lead dioxide anodes in both small laboratory cells and in larger bench-scale units. The conclusions drawn from the small laboratory cells were:

(1) Sodium perchlorate can be made by electrolysis using lead dioxide anode with copper, carbon steel, nickel or stainless steel cathodes.

(2) Current efficiencies appear to be higher with nickel, stainless steel,and copper than with carbon steel.

(3) Sodium fluoride appears to be a better additive than sodium dichromate. Minimum effective sodium fluoride concentration is 0. 5 grams/liter.

(4) Lower voltages appear to be possible.

(5) Data obtained with lead dioxide anode, Ni cathode and NaF additive is practically independent of current density and temperature. The current efficiency reported was 93. 7% at an anodic current density of 15. 5 amps/dm^2.

The results reported[37] for the large-bench scale unit (4-liter capacity) using lead dioxide anodes and cathodes of Ni, Cu, and stainless steel were:

(1) Lead dioxide anodes produce sodium perchlorate at high cumulative current efficiencies.

(2) The cumulative current efficiency for a given anodic current density is a function of chlorate concentration, the cathode material, the cathodic current density and the additive used.

(3) The wire on which the PbO_2 is plated in forming an anode appears to have no effect on the production of sodium perchlorate.

(4) Sodium perchlorate can be produced using cathodes of Ni, Cu, stainless steel and carbon steel; efficiency is low with carbon steel.

(5) Sodium dichromate has a detrimental effect on current efficiency by forming a thin deposit on the surface of the PbO_2 anode.

(6) Decreasing the cathodic current density increased the current efficiency when Ni and stainless steel cathodes were used.

(7) One PbO_2 anode was used in cell operation for 3000 hours.

(8) Ammonium perchlorate was prepared satisfactorily from sodium perchlorate produced in these experiments.

(9) A comparison of energy requirements calculated for identical experimental conditions indicates Ni and stainless steel are the best cathode materials and that PbO_2 offers energy advantages over Pt as an anode.

(10) Energy results of 1.04 kw-hr/lb of sodium perchlorate with a cumulative current efficiency of 91.5% were reported. These results were obtained with stainless steel cathodes and a cathodic current density of 7.25 amp/dm^2 and a final chlorate concentration of 50 g/l.

Recent information indicates that one plant-size cell has been converted to lead dioxide anodes.

Although operation of this cell is reported to be satisfactory, there are believed to be some problems associated with anode behavior which made additional study necessary. At least at present there seems to be no plans for making any additional conversions.

Grigger et al[14] also present a summary of the results of their work in developing a lead dioxide anode for use in a perchlorate cell.

Several different lead plating baths were studied, among which were lead tartrate, lead perchlorate and lead nitrate.

According to their results electro-deposition of massive lead dioxide is preferably carried out from a lead nitrate bath. Uniquely, anodic deposition on tantalum is possible without polarization or erosion of the base. Careful pH control in the 2-4 range is necessary. To provide a suitable means for making an operable, low resistance current contact to the lead dioxide, silver is sprayed over the top end of the electrode. Silver forms a jacket with a low contact resistance. In order to protect the silver and to form a rugged contact, the silver-coated area is sprayed with a heavy layer of copper.

The large PbO_2 electrode (. 16 cm thick) formed on a titanium screen was used with a sprayed copper over silver contact in a 100-amp perchlorate cell at a current density of 0. 028 amp/cm^2 and a temperature of 85°-120°F. The cathodes were type 430 stainless steel and the electrolyte was 3 liters of $NaClO_3$ solution having an initial concentration of 600 g/l. This cell was operated for 860 hours without noticeable erosion of the anode and less than 0. 25 ppm of lead in the recovered $NaClO_4$. The results of comparative runs with Pt and PbO_2 electrodes are presented in Table 2-10.

From Table 2-10 it is seen that the current efficiency of PbO_2 anodes in the conversion of chlorate to perchlorate, although less than Pt, is relatively high when the concentration of sodium chlorate in the electrolyte is above 100 g/l. Below this concentration the efficiency drops sharply.

In order to obtain higher current efficiency additives were used. $K_2S_2O_8$ was found quite effective, raising current efficiency from 23% to 50%, in chlorate concentration range of 30 g/l.

A comparison of these two independent development programs shows that the conversion of sodium chlorate to sodium perchlorate can be effected with the use of a lead dioxide anode. Differences in observed current efficiencies seem to be the major differences. In one case (i. e., American Potash study) current efficiencies as high as 93. 7% were obtained. The maximum efficiency reported by the other group (i. e., Pennsalt) was 75%. Because of probable differences in experimental design, it is not fair to make a direct comparison between the two sets of data. Of importance, however, are the conclusions that little or no erosion of anodes is observed by either group and that there is evidence that high efficiencies may be possible.

Improved Anodes and Cathodes

From time to time attempts have been made to improve the electrolysis of the chloride to the chlorate. In the case of graphite anodes, the efforts have been centered on reducing the graphite losses. For the iron cathodes new methods for preventing reduction at the cathode have been devised.

According to a recent patent[48] a method has been devised for treating graphite anodes with an inert impregnating agent which renders them waterproof. The use of plastics and resins such as formaldehyde and

polyvinyl chloride resins is recommended. It is claimed that the consumption of graphite per 100 lbs $NaClO_3$ produced is reduced to 0.1-0.2 kg as compared to 0.4-1 kg for normal operation. It was also reported that current density can be varied between 0.02-.15 amps/sq cm without a change in current efficiency.

The improvement in the iron cathode consisted of using dull chromium plated iron cathodes in place of iron cathodes.[48] Present practice is to add chromate to the electrolyte to prevent high reduction of cathode. This chromate imparts a yellow color to the product which must be removed. The effect displayed by the dull chromium plated electrode is due to the fact that deposited chromium is oxidized to chromium acid by means of hypochlorite and subsequently to chromic chromate which displays its protective action.

Chromium plated cathodes were not used up to now because it was not possible to produce chromium layers which were free of pores and flaws and accordingly their use over a period of time caused a reduction in the cathode. These disadvantages are overcome when cells containing cathodes of chromium nickel plated wire are used. Cells provided with these cathodes display reduction values which correspond to iron values to which chromate was added if the acidity of the electrolyte is kept between 02-.04 mol HCl/liter.

Product Specifications

Those chlorate and perchlorate compounds which are produced in large quantities are manufactured to certain product specifications. In

many cases the specifications are specific for the particular company purchasing the material. In other cases only in-plant specifications exist. This is true in the case of sodium perchlorate, since this product is not marketed commercially. However, because it is an intermediate compound used in the production of other compounds, its quality must meet certain requirements.

Where a product is used commercially it is difficult to find an over-all specification since each purchaser has his own requirements. This seems to be true for sodium chlorate. Potassium chlorate and perchlorate both have military specifications. There is a military specification for ammonium perchlorate, but it is currently being rewritten. As far as is known no definitive specifications exist for the other chlorate and perchlorate compounds examined during the preparation of this book. Some details concerning the above specifications are given in the following sections.

Sodium Chlorate

This compound finds its greatest use in bleaching (see Chapter 4). Attempts to find an over-all specification covering this use were unsuccessful. It is evident that each paper company either purchases this product on the basis of the vendor's normal product assay or on the establishment of some specific requirement.

From one source[28] the following specification for sodium chlorate was obtained:

$NaClO_3$ Minimum Purity	99.0%
Conditioning Agent to Prevent Caking	0.7% max.
Color	White to Pale Yellow
Moisture	0.05% max.
Water Insoluble Material	0.1% max.
Screen Analysis	98% thru 20 mesh 85% thru 28 mesh (Tyler Standard Screen)

Potassium Chlorate

Potassium chlorate is used by both industry (e.g., matches) and military (see Chapter 4). No information was found concerning the requirements of industrial concerns. The military have established a military specification, MIL-P-150A, to cover this material when used in the manufacture of ammunition. Details of this specification follow:

MIL-P-150A 19 July 1956

Potassium Chlorate Specification

Scope

$KClO_3$ used in manufacture of ammunition

Classification

Potassium Chlorate

Grade A	Low Bromate
Grade B	High Bromate
Grade C	With Magnesium Carbonate
Class 1	80 Mesh, nominal
Class 2	100 Mesh, nominal

Class 3	60 Mesh, nominal
Class 4	100 Mesh, nominal, fine
Class 5	50 Mesh, nominal
Class 6	325 Mesh, nominal
Class 7	80 Mesh, nominal, find

Requirement

1. Form - The material shall be a crystalline powder

2. Chemical Requirement

Property	Grade A	Grade B	Grade C
Moisture, % max.	0.05	0.05	0.5
Patassium Chlorate, % min.	99.5	99.5	99.5
Water Insoluble Material, % max.	0.02	0.10	0.10
pH Value	5 to 8	5 to 8	--
Hypochlorites	none	none	none
Chlorites	none	--	--
Chlorites (as KCl), % max	0.10	0.10	0.10
Bromates (as $KBrO_3$), max. %	0.02	0.10	0.10
Heavy Metals	none	none	none
Alkaline Earths	none	none	none
Sodium Salts (as $NaClO_3$), max.	0.09	0.09	0.09
$Mg(CO_3)_2$, % max.	--	--	3.0 ± 0.2

3. Granulation (see Table 2-11)

Potassium Perchlorate

The major use for potassium perchlorate has been for military applications. Industrial uses have been small. (See Chapter 4.) Consequently, the main specification against which this compound has been produced is that established by the military. At the present time potassium perchlorate is purchased by the military according to JAN-P-217. The contents of this specification follow:

Joint Army Navy Spec.
Potassium Perchlorate
JAN-P-217
29 May 1945
Amended 4/22/53

Army No. 50-11-101A Navy No. 51 P35

Potassium perchlorate shall conform to the chemical and physical requirements shown below:

	Grade A	Grade B	Grade C	Grade D
Odor	none	none	none	none
Color(1)	pass	pass	pass	pass
Moisture % max.	0.20	0.20	0.15	0.20
Grit	none	none	none	none
Acidity or Alkalinity	none	none	none	none
Chloride as KCl % max.	0.1	0.26	0.1	0.1
Chlorates as $KClO_3$ % max.	0.1	1.0	0.1	0.1

(1) By means of a colorimeter, intensity of color is less than that of solution of 0.005 gm of pure potassium chromate in 1 liter of distilled water.

	Grade A	Grade B	Grade C	Grade D
Hypochlorites	none	none	none	none
Bromates as $KBrO_3$ % max.	0.04	0.04	0.02	0.04
Sodium Salts as $NaClO_4$ % max.	0.2	0.2	0.2	0.2
Calcium & Magnesium Salts as Oxides % max.	0.20	0.20	0.20	0.20
Purity, % min.	99	98.5	99	99
Granulation:				
Thru 420 micron (40) sieve % min.	--	--	99.9	--
Thru 177 micron (80) sieve % min.	99.9	99.9	--	--
Thru 149 micron (100) sieve % min.	--	--	--	99.9
Thru 74 micron (200) sieve % min.	60	60	--	--

Grade A Ingredient of photographic flashlight powder
Grade B Ingredient of pyrotechnic composition
Grade C Ingredient of smoke mixtures
Grade D Ingredient of special pyrotechnic composition

Ammonium Perchlorate

This compound has found its greatest use with the military (see Chapter 4) To cover its purchase a specification was established in 1945, JAN-A-192. This specification calls for two grades based upon chemical analysis and three classes based on granulation. These materials

were used mainly in tracers and smoke mixtures. A summary of this specification follows:

Ammonium Perchlorate
JAN-A-192
1 March 1945

Requirements

Color	White
Odor	None
Acidity	pH > 4

Chemical Requirements

	Grade I	Grade II
Moisture, max. %	0.15	0.15
Chloride as NH_4Cl, max. %	0.20	0.10
Sodium, max. %	0.30	0.60
Bromate as NH_4BrO_3, max.	0.003	--
Chlorate as NH_4ClO_3, max.	0.0035	0.10
Ca & Mg as Oxides, max.	0.20	--
Purity, NH_4ClO_4, min.	99.0	98.0
Grit	none	none

Grade I Use in tracers

Grade II Use in HC smoke mixtures

Granulation	Class A	Class B
Thru U.S. Std. Sieve # 40 (420 micron) (min) %	99.9	--
Thru U.S. Std. Sieve # 50 (297 micron) (min)	98.0	99.9
Thru U.S. Std. Sieve # 140 (105 micron) (max.)	--	1.0

Class C

NH_4ClO_4 shall be furnished in unground pieces having a maximum diameter of 1-1/2 inches.

Packaging

Ammonium perchlorate shall be packaged in air tight metal cans of 5 lb capacity.

NH_4ClO_4 shall be shipped in moisture proof, air tight removable head, steel drums of approximately 100 lb net weight capacity so constructed as to insure acceptance by common carrier.

The utilization of ammonium perchlorate as the solid oxidizer in solid propellants has introduced a number of new requirements not contained in JAN-A-192. As time has progressed each of the major producers of composite propellants has developed individual specifications to meet their own requirements. At the present time the following companies are known to have a specification for ammonium perchlorate:

Aerojet General Corporation	AMS-C66f
Astrodyne, Incorporated	RFDMS-5-T
Atlantic Research Corporation	ARC
Grand Central Rocket Company	GCR-MS-2
Thiokol Chemical Corporation	MPD 282/282A

In order to show the wide differences in requirements which have resulted for ammonium perchlorates, physical and chemical data on typical material supplied by one manufacturer are compared in Table 2-12 and the particle sizes data as shown in Table 2-13.

JAN-A-192 is being revised and will be issued as MIL-A-192A. A preliminary draft has been circulated recently.

Analytical procedures for ammonium perchlorate have been summarized in Chapter 1 (Appendix B). These methods may also be modified when MIL-A-192A is finally issued.

Operating Problems and Safety Conditions

In the manufacture of chlorate and perchlorates as in the production of most items there exist two kinds of problems. On one hand there are the problems concerned with operating the plant so that the product can be made at some reasonable profit. On the other hand, there are the problems associated with operating the plant safely. The tendency today is to place the worker above the product and to design and operate the plant so that lost-time accidents are held to a minimum. Both kinds of problems are examined in the following sections.

Operating Problems

The main operating problems involved in the production of chlorates and perchlorates are the following:

(1) Corrosion

(2) Efficient crystallization

(3) Drying of the product.

Corrosion. In producing and handling the chlorate and perchlorate compounds consideration has to be given to corrosion problems from two points of view. There is always the economics involved in selecting equipment on the basis of a balance between long use life and low replacement cost. In addition there is the very serious problem of keeping the product free of contaminants. Because of the high purity requirements for these compounds an effort is made to keep corrosion to a minimum. Some recent corrosion data on various materials of construction are summarized in Table 2-14.

General practice in the ammonium perchlorate plant[30] is to use type 347 stainless steel for all welded piping and for medium size reaction vessels. When type 347 is not available, type 316 is used. In those sections of the plant where there is contact with excess HCl, glass-lined steel or Hastelloy C is used.

In the sodium chlorate plant mild steel is generally used for tanks, piping and most other equipment.[28] This is very satisfactory for equipment which handles dry sodium chlorate. Because of its oxidizing effect a chlorate solution will tend to rust steel. In such cases type 316 stainless steel has given very satisfactory service and is recommended, especially where heat is involved. Copper and brass may also be used, as can some of the aluminum alloys. The latter are especially satisfactory if they can be kept free of electrolysis.

Lubricants must be avoided wherever possible. Pumps used in processing sodium chlorate must be either packless or have water-sealed

packing glands. Teflon or Kel-F packing is considered satisfactory for packing pumps and valves. Ordinary rubber may be used as gaskets. Hoses of the wire-reinforced type are used for tank car connections. Fabrics which might become impregnated with $NaClO_3$ solutions must be avoided.

Crystallization. Crystallization is a field in itself and beyond the scope of this book. However, there is sufficient evidence at present to indicate that in addition to yield and purity, crystal size and shape may become important factors in future requirements for particularly the perchlorates, so as to warrant a brief examination of the problems of crystallization. It is obvious that yield and purity are important factors in perchlorate manufacture and as mentioned above size and shape may become important. It is also evident that uniformity of size is desirable. To control crystal variables there are numerous problems associated with crystal formation and growth.

The yield of product is logically dependent upon the rate of crystal formation and growth. Both of these have a common driving force; supersaturation. Unless a solution is supersaturated, crystals can neither form nor grow.[29] Since the laws and data on crystal formation and growth are still quite incomplete, guides for the design and operation of suitable crystallizers must be developed empirically.

When ammonium perchlorate was first produced, a serious problem of control of crystal size was encountered.[36] Techniques developed in the pilot plant did not work out well in large-scale production.

This problem was finally solved after further pilot runs were made. After the necessary operating conditions of retention time and solution purity were determined, the desired crystal sizes were obtained. The proper design of the crystallization cycle to give the required solution purity is thus of considerable importance.

The purity of the product depends upon how it is processed. A crystal itself is pure. However, it retains mother liquor when it is removed in the separation process. The adhering mother liquor will contain its share of the impurities present in the mother liquor and these impurities will remain on the crystal when it is dried. Centrifuging usually removes all but 2 to 5 percent of the mother liquor.[29] It is common practice to wash the crystals to increase purity. In chlorate and perchlorate production attempts are made to keep the impurities in the mother liquor as low as possible.

The shape of the crystal has been of some concern but is not a requirement for perchlorates at present. With perchlorates now being made in different production plants different shapes are appearing and this could lead to additional plant problems to control shape as well as size. According to McCabe[29] there is considerable disagreement among researchers regarding crystal growth and crystal geometry. Nevertheless certain conclusions can be drawn:

(1) Although a crystal growing under constant external conditions remains nearly geometrically similar to its original shape, relatively slight changes in the condition may alter the shape.

(2) The addition of small amounts of a foreign substance may greatly affect the shape of a growing crystal as well as its rate of growth.

(3) The translation velocities of the different faces of a crystal are usually different.

(4) The rate of growth of any particular face of a crystal is a function of the supersaturation of the bulk of the solution in contact with that face.

From the above it can be concluded that the shape of a crystal can be appreciably affected by the type of equipment used in producing it. In a batch crystallizer supersaturation varies with time. In a continuous crystallizer, conditions are constant only at a given point in the apparatus. In such an apparatus the higher the supersaturation at a given point, the greater will crystal formation dominate crystal growth. Similarly, at low supersaturation, growth will predominate over formation. The problem of crystal formation, growth and geometry are thus all interrelated with the design and operation of the processing equipment.

As an example of the effect of variations in operating conditions, reference can be made to some data obtained in a sodium chloride crystallizer used in connection with ammonium perchlorate production [36] (see Fig 2-10) Table 2-15 summarizes the data.

The above data illustrates the effect of operating temperature on the evaporation load and recycle load of a sodium chloride crystallizer. A lowering of the NaCl crystallizer temperature does not affect the operation of the crystallizer appreciably as long as the perchlorate crystallizer is maintained at a sufficiently low temperature. If the temperature of the

perchlorate crystallizer is raised while the salt crystallizer temperature is lowered, there is a noticeable increase in evaporation load and the recycle load increases appreciably.

Drying. The drying of chlorates and perchlorates presents numerous problems but most of them pertain more to safety than to engineering. These compounds are all heat and shock sensitive.

Ammonium perchlorate, although more stable than the chlorate, is still relatively unstable and highly flammable. It begins to decompose at about 400°F and though this decomposition generally takes place quietly, it still results in loss of product. To overcome the problems of loss and fire, the perchlorate product is dried rapidly through the critical moisture range (0.5-.02%). It has been found that NH_4ClO_4 is more sensitive when slightly moist and contaminated with metallic corrosion products, particularly copper. As a safety precaution, all units of the plant are usually hosed down daily. The drying and packaging are carried in separate and identical three-story buildings housing the flash drying, pan drying, and packaging operations. The buildings have explosion release walls and all electrical equipment is of explosion-proof design.

Drying of chlorate compounds presents similar problems as those associated with perchlorate salts. Although the older existing plants have used direct-fired rotary dryers, the present trend in new plants is to use steam tube indirect-fired dryers made of aluminum because they produce minimum dust and undergo less corrosion. This is an important safety factor.

Safety Considerations

General. Chlorate and perchlorate compounds are extremely sensitive to impact and become even more hazardous when contaminated with organic materials. In general chlorates are considered more hazardous than perchlorates. The unstable characteristics of the chlorates is due to the fact that its acid component, chloric acid, is an unstable acid and is easily decomposed. Perchlorates are much more stable than the chlorates when pure. (Perchloric acid is the most stable of the oxy-acids of chlorine.) However, any contamination with organic matter increases their sensitivity.

The Chlorates. Chlorates may also be dangerous when improperly or carelessly handled.[11, 28] Sodium chlorate is a compound of high oxygen content which will release this oxygen readily when acted upon by heat, acids, reducing agents and organic material. The following is a list of materials with which sodium chlorate should not be permitted to come into contact:[28]

Heat	Acids
Oils	Sulfur
Greases	Sulfide
Powdered metals	Alcohol
Wood	Sugar
Rope	Solvents
Canvas fire hose	Ammonium compounds
Wooden ladders	Paint
Sawdust	Painted metals
Clothes	Organic material (anything
Leather goods	living or that was living)

The following are some of the dangers together with the precautions which should be used in handling, storing or shipping chlorates.

General Hazards and Precautions. Care must be taken to see that fine dust particles are not dispersed when handling dry chlorate. The accumulation of such particles with general dust and lint in a building could lead to a violent fire. Dusting of chlorate must be prevented by preventative means or by continued cleaning.

Water wetted or solutions of chlorate in themselves present no particular hazards. Contact of such material with acids, reducing agents, oils or organic material can result in dangerous conditions, especially after the water is evaporated.

Particular Hazards and Precautions

Storage. This should be in metal, ceramic, glass or chemically inert plastic materials free from any contaminating substances. Utmost precaution must be established that neither dry chlorates nor their solutions become accidentally admixed with or in contact with acids, oils, reducing compounds, organic and combustible materials. Storage should be strictly segregated from the above substances.

Handling Equipment. No oil lubricated bearings nor oxidizable packing material should be used in conveying or mixing equipment or pumps. Teflon or Kel-F water seals have been found suitable in pumps.

Miscellaneous Equipment. Ropes, wooden ladders, canvas hoses or similar maintenance equipment made of organic materials should be disposed of if they have come in contact with chlorates. The

impregnation of the organic materials, particularly so if a chlorate solution soaks into the material and dries leaving a dispersion of minute chlorate crystals, presents a potential incendiary or explosive condition. Any contaminated equipment should be promptly disposed of by trained personnel and must not be set aside nor sent to a public dump.

Welding, cutting or other flame must be avoided in the area where chlorate is stored or on equipment which has handled chlorate; thoroughly wash the equipment to remove any traces of chlorate.

Clothing and Personal Equipment. Persons handling chlorates must be instructed thoroughly in proper and approved methods of handling chlorates. They must be advised of the potential fire hazards which become inherent in mixtures of chlorates and other materials. The clothing of persons exposed to chlorate dusts or solutions presents a serious personal hazard. Personnel so exposed should have washable clothes solely for working purposes and must not wear those clothes away from the immediate work area. These working clothes should be thoroughly washed and rinsed each day, or more often should they become contaminated. Suggested washable clothing should consist of skull or tam type head cover, socks, underwear, coveralls or other suitable outer clothing, rubber shoes, etc. No leather materials should be permitted.

Personal protective equipment where dusting, spillage or splashing may occur should consist of goggles or face shields and, if required, a dust respirator approved for this purpose by the Bureau of Mines.

Smoking should not be permitted on the premises where chlorates are stored or used, nor by anyone who is wearing clothes which might be subject to chlorate contamination.

Fire Hazard. Water is the most effective means of controlling fires. Fire extinguishers which have smothering effects are of little value as the chlorate furnishes the oxygen supply. Heavy flooding showers should be strategically placed for worker protection.

Health Hazards. According to Manufacturing Chemists Association, Inc.[11] "Sodium Chlorate presents no particular health hazard during ordinary handling and storage, beyond the extreme danger of flammability upon contact with organic materials or other oxidizable substances. Irritation to the skin, mucous membranes and eyes may occur from prolonged exposure to dust atmospheres of Sodium Chlorate. Ingestion of relatively large quantities (15-30 gm.) of this material may prove fatal. Abdominal pain, nausea and vomiting, diarrhea, pallor, blueness, shortness of breath, unconsciousness and collapse are the immediate symptoms following ingestion of toxic amounts of Sodium Chlorate.

"Sodium Chlorate may cause skin irritation, as well as irritation to the mucous membranes of the eyes, nose and throat in certain cases."

The Perchlorates. American Potash and Chemical Corporation conducted detonation experiments, thermal decomposition, and impact sensitivity tests with ammonium perchlorate.[36] Based on these studies,

the following recommendations have been followed as guiding principles for safety in plant operation. They are believed to be applicable to the other perchlorates:

(1) Impact sensitivity of high purity ammonium perchlorate is comparable to that of most high explosives.

(2) Metallic contamination increases the sensitivity of ammonium perchlorate; certain metallic perchlorates are extremely sensitive.

(3) Ammonium perchlorate is thermally stable below 300°F.

(4) Contact of organic material with ammonium perchlorate constitutes a fire and explosive hazard.

(5) The handling of solution and wet solid NH_4ClO_4 is not hazardous but the drying process presents a fire and possibly an explosive hazard.

Drying and handling were placed in two isolated units with duplicate equipment. They are also equipped with an automatic deluge system.

Economics

This section is concerned with the cost of production and plant investment for sodium chlorate, sodium perchlorate and ammonium perchlorate. Very little data are available concerning this subject. One article by P. H. Groggins and co-workers[15] gave data on sodium chlorate and was used as a guide for a good part of this section. Production and selling price data for sodium and potassium chlorate are also presented. General comments concerning the uses of chlorate and perchlorate compounds as they bear on their economics are also included.

Sodium Chlorate

U. S. Sodium chlorate capacity in 1959 is estimated to be more than 100,000 tons/yr as a result of new plants and plant expansions.[2, 4] In 1957 the production of sodium chlorate was 59,142 tons.[4] In 1959 production will reach 80,000 tons.[2] American Potash and Chemical Corp. has a 28,000 ton/year plant at Henderson, Nevada, and has started operation of a 15,000-18,000 ton/year plant ($NaClO_3$) at Aberdeen, Miss. It is expected to increase production capacity at Aberdeen to 27,500 ton/year.[2] Pennsalt Chemical Company is planning a 25% expansion of their sodium perchlorate facilities at Portland, Oregon.[9] Hooker Chemical Corporation has doubled its plant capacity at Columbus, Miss. ("over 24,000 ton/yr").[2] The production and price data for sodium chlorate is presented in Figures 2-19 and 2-20, respectively.

The cost of a plant to produce sodium chlorate, according to Faith, Keyes and Clark[13], varies between 15 and 25¢/lb of annual capacity. Thus a 6,000,000 lb/year plant would cost at most $1,500,000, while a 44,000,000 lb/yr plant would cost $6,500,000. In 1937, Groggins and his co-workers[15] presented a detailed breakdown of a plant producing 6,000,000 lb/yr. When this plant investment is corrected for present day costs, it is interesting to note that good agreement is obtained with the data of Faith,et al. Figure 2-21 shows the relationship of investment costs versus production for sodium chlorate, while Table 2-16 shows the percentage breakdown of a typical plant investment.

Production cost data were also developed by Groggins. These data were used as a guide to estimate production costs for sodium chlorate. Table 2-17 summarizes the estimated costs of production for a plant producing 18,000 ton/yr.

It should be noted that the cost of production can vary between 5.93¢/lb (100% capacity) and 9.33¢/lb (50% capacity). The return on the investment was also calculated for different selling prices (e.g., 9, 9.75 and 10.5¢/lb) and at different plant capacities. These results are presented in Table 2-18.

Potassium Chlorate

Potassium chlorate is the second most important commercial chlorate compound. Over the past few years, the demand for this product has been steady at about 7500 ton/yr.[13] Its principal use is in matches (80%). Other uses are explosives and pyrotechnics (see Chapter 4). Figure 2-22 presents the production data for the years 1935-1956.* Sales of potassium chlorate are expected to increase at about 3% per year.[2] Selling price data are presented in Figure 2-23.

Very little data are available on plant investment. Generally, potassium chlorate will be produced at the same plant that produces sodium chlorate, since it is made from the latter product. Plants range in size from 1-4 million pounds per year and it is estimated would cost about

* The U.S. Department of Commerce has discontinued tabulating production data for potassium chlorate since 1955.

20-25¢ per annual pound of capacity. The estimated cost of production of this product would thus be approximately 9-10¢/lb.

Sodium Perchlorate

Sodium perchlorate plays an important role as an intermediate in the production of potassium and ammonium perchlorate. There is no published data on production quantities and costs since it is not marketed commercially. It is estimated that approximately 10,000 ton/yr are currently being produced in its role as an intermediate.

Costs of production have been estimated on the basis of an annual production of 10,000 ton/yr. A plant investment of $3,600,000 was assumed, based on 18¢/annual lb of capacity. Sodium chlorate was priced at 9¢/lb. A summary of the estimated cost of production for this material is presented in Table 2-19. From this table it is seen that the cost of production can vary between 13.7¢/lb (100% capacity) to 17.57¢/lb at 50% capacity.

Potassium Perchlorate

In the past, potassium perchlorate was the principal commercial perchlorate marketed. It was used in explosives, pyrotechnics and JATO rockets. However, due to its less desirable properties as a solid propellant oxidizer, it has been supplanted by ammonium perchlorate. In 1950, 1800 tons were produced, in 1951, 4370 tons, but in 1957 only 784 tons were produced. It has been estimated that the cost of production is approximately 13-14¢/lb in 1000-2000 ton/yr range. The selling price reported in Dec. 1958[8] was 18.5-20¢/lb.

Ammonium Perchlorate

Ammonium perchlorate has replaced potassium perchlorate as a solid oxidizer for propellants and as a result is in much greater demand. Production is estimated to have increased from 18,000 ton/yr at the beginning of 1959 to 24,700 ton/yr at present.

In attempting to estimate the cost of producing ammonium perchlorate it was found that little help could be obtained from the manufacturers because of the highly competitive nature of the business. Plant investment data are almost nonexistent as it is considered proprietary. With the small amount of data which could be found and the report[1] that the Henderson, Nevada plant of American Potash and Chemical Corporation cost $5,000,000 in 1953 and had a capacity of 40 ton/day, a production cost estimate was completed. Correcting the plant costs to 1958, it was estimated that this plant would cost $6,000,000. This represents 20¢/lb of annual capacity. The cost of production was estimated on the assumption that the plant produces both sodium chlorate and perchlorate. An annual production rate of 9,000 ton/yr was used as a basis for the calculation.

Estimated production costs are presented in Table 2-20. From this table it is seen that the estimated cost of production can vary from

22.9¢/lb (100% capacity) to 28.33¢/lb at 50% capacity. The estimated return on investment was computed on the ammonium perchlorate plant. An estimated return of 19.8% at 100% of capacity would be reduced to 5.1% at 50% of capacity (see Table 2-21).

BIBLIOGRAPHY

1. Anon., Ammonium Perchlorate, Chemical Eng., p. 334, Dec. 1955.

2. Anon., Chlorates - Paper Puts Shine in Chlorate Sales, C & E News, Aug. 31, 1959

3. Anon., Electrolytic Sodium Chlorate, Chem. & Met. Eng. Nov. 1944.

4. Anon., U. S. Sodium Chlorate, Chemical Week, p. 91, July 19, 1958.

5. Badger, W. L., and McCabe, W. L., Elements of Chemical Engineering, 2nd Ed. McGraw-Hill Book Co., New York, N. Y. (1936).

6. Bill, C. E., Rotary Steam-Tube Dryer, Ind. Eng. Chem. 30 (1938).

7. Bird Filter Manual, Bird Machine Co., South Walpole, Mass.

8 C & E News, Dec. 1958.

9. C & E News, Feb. 23, 1959.

10. C & E News, March 2, 1959.

11. Chemical Safety Data Sheet, SD-42. Properties and Essential Information for Safe Handling and Use of Sodium Chlorate. Manufacturing Chemists Assoc., Washington, D. C. 1951.

12. de Valera, V., Journal of Elect. Chem. Soc., p. 162, March 1957.

13. Faith, W. L., Keyes, D. B., and Clark, R. L., Industrial Chemicals 2nd Ed., John Wiley and Sons, Inc., New York, N. Y. (1957).

14. Grigger, J. C., Miller, H. C., and Loomis, F. D., Lead Dioxide Anode for Commercial Use, Jour. Electrochemical Society, p. 100, Feb. 1958.

15. Groggins, P. H., et al, Economics of Sodium Chlorate Production, Chem. & Met. Eng., p. 302, Vol. 44.

16. Groggins, P. H., et al, Chem. & Met. Eng., p. 692, Vol. 45, 1938.

17. Groggins, P. H., et al., The Efficieney of Sodium Chlorate Cell with Rod Cathodes., Jour. Elect. Society, Vol. 79, p. 93, 1941

18. Groggins, P. H., Pittman, A. C., and Davis, F. H., Sodium Chlorate Cell Design, Chem. & Met. Eng., p. 468, July 1940.

19. Hampel, C. A., and Leppla, P. W., Production of Potassium Perchlorate, Journal of Electrochemical Society, p. 55, Oct. 1947.

20. Janes, M., Graphite Anodes in Brine Electrolysis, Journal of Electrochemical Soc., p. 23, Oct. 1947.

21. JAN-A-192, Joint Army-Navy Specification for Ammonium Perchlorate.

22. JAN-P-217, Joint Army-Navy Specification for Potassium Perchlorate.

23. Kirk, R. E. and Othmer, D. F. (ed), Chlorine Compounds, Inorganic, Encyclopedia of Chemical Technology, Vol. 3, p. 716-729, The Interscience Encyclopedia, Inc., New York, N. Y., 1949.

24. Mantell, C. L., Industrial Electrochemistry, p. 126-135, 3rd Ed., McGraw-Hill Book Co., New York, N. Y., 1950.

25. Michael, Arthur, and Conn, Wallace T., J. Am. Chem. 23, 444-6 (1900).

26. Notes from files of E. E. Katcher, ReW. 3a, Bureau of Ordnance, Navy Department.

27. Partington, J. R., A Text Book of Inorganic Chemistry, 5th Ed., MacMillan and Co., London, 1937.

28. Pennsalt Chemical Corp., Technical Bulletin No. C-5001 - Sodium Chlorate - Properties and Safe Handling Practices.

29. Perry, John H., (ed), Chemical Engineers' Handbook, 3rd Ed., McGraw-Hill Book Co., New York, N. Y. (1950).

30. Personal Communication with American Potash and Chemical Corp., Los Angeles, Calif., 1958.

31. Rolletson, G. K., JACS 56, 2245-50 (1934).

32. Schumacher, J. S., Continuous Electrolytic Process for Perchlorate, Chem. and Met. Eng., Dec. 1944.

33. Schumacher, J. S., Potassium Perchlorate, Chem. and Met. Eng., Dec. 1944.

34. Schumacher, J. S., The Commercial Production of Perchlorates, Journal Electrochemical Soc., Oct. 1947.

35. Schumacher, J. S., Chlorates and Perchlorates, Chem. Eng. Progress, Vol. 43, No. 4, April 1947.

36. Schumacher, J. S. and Stern, D. R., Large Scale Continuous Production of Ammonium Perchlorate, Chem. Eng. Progress, Sept. 1957.

37. Schumacher, J. S., Stern, D. R., and Graham, P, R., Electrolytic Production of Sodium Perchlorate Using Lead Dioxide Anodes, Journal Electrochemical Soc., March 1958.

38. Schumacher, J. S., U. S. Patent No. 2,512,973, Process for Making Perchlorates.

39. Sugino, K. and Aoyagi, S., Studies on the Mechanism of the Electrolytic Formation of Perchlorate, Jour. Elect. Chem. Soc., Vol. 103, No. 3, p. 166, 1956.

40. U. S. Patent No. 985,724, Method of Producing Ammonium Perchlorate.

41. U. S. Patent No. 1,453,984, Manufacture of Ammonium Perchlorate.

42. U. S. Patent No. 2,047,549, Manufacture of Magnesium Chlorate.

43. U. S. Patent No. 2,475,157, Electrolytic Apparatus.

44. U. S. Patent No. 2,511,516, Process for Making Sodium Chlorate.

45. U. S. Patent No. 2,515,614, Electrolytic Cell.

46. U. S. Patent No. 2,733,982, Process for Making Sodium Chlorate from Molten Sodium Chlorate.

47. U. S. Patent No. 2,739,873, Process for Making Ammonium Perchlorate.

48. U. S. Patent No. 2,756,201, Improvement of Graphite Anode and Iron Cathode.

49. U. S. Patent No. 2,840,519, Peroxidation Process.

50. U. S. Patent No. 2,846,378, Electrode and Its Manufacture.

51. Wallace, W., Progress in the Electrolytic Manufacture of Chlorates and Perchlorates in U. S. and Canada since 1902, Jour. Elect. Society, Vol. 99, No. 11, p. 309C, 1952.

52. White, N. C., Electrolytic Production of Chlorates, Jour. Elect. Soc., p. 15. Oct. 1947.

CHAPTER 3. REACTIONS AND MECHANISMS

CHAPTER 3. REACTIONS AND MECHANISMS

The Oxyacids of Chlorine

General Considerations

Owing to the close relationship between the various oxychlorine compounds, a brief description of the oxyacid compounds of chlorine is given in this section for a firmer understanding of the chlorates and perchlorates, whose reactions are given in the succeeding sections.

The names and formulas of the known oxyacid compounds of chlorine are:

Hypochlorous acid	Chlorous acid	Chloric acid	Perchloric acid
$HClO$	$HClO_2$	$HClO_3$	$HClO_4$

In this series, the oxidation states of chlorine are +1, +3, +5 and +7, respectively. The stability of the series increases from left to right. The two lower members of the series, hypochlorous and chlorous acids, are unstable and have never been isolated in pure form. The maximum concentration attainable for chloric acid is about 50 mole percent while perchloric acid can be obtained in anhydrous form. The greater stability of the higher oxyacids has been attributed to the large amount of double bond character in the Cl-O bonds. (166) Symmetry of the perchlorate ion in perchloric acid makes this the most stable of the chlorine oxyacids.

As a corollary of stability, the relative oxidizing power of the oxyacids is opposite to that of their stability. It is a general phenomenon, that when a compound intermediate in state of oxidation decomposes

spontaneously into a higher and a lower state, it is a more powerful oxidizing agent than the higher compound and a more powerful reducing agent than the lower compound.(55) Thus, hypochlorites, which decompose spontaneously into chlorides and chlorates, are stronger oxidizing agents than the chlorates.

The ions of the chlorine oxyacids follow the same stability trend as the acids, e. g., increasing stability from hypochlorite to perchlorate. However, they are considerably more stable than their respective acid; salts of all four acids are known.

Hypochlorous and Chlorous Acids and Their Salts

These acids have never been isolated and exist only in solution; they are formed by acidifying solutions of their salts. Treatment of a hypochlorite (for instance, bleaching powder) with a weak acid, such as carbonic or boric, produces hypochlorous acid. Some hypochlorous acid results when chlorine is bubbled into water in the presence of a weak base, such as calcium carbonate. Chlorous acid may be formed by reducing chlorine dioxide with hydrogen peroxide. It is also believed to be an intermediate product in the action of water on chlorine dioxide, but it is rapidly decomposed.

Hypochlorous acid is a strongly endothermic compound and consequently decomposes very easily. Decomposition into hydrogen chloride, chloric acid, chlorine, and oxygen takes place on warming according to the following sequence of reactions:

$$2HClO \longrightarrow 2H^+ + 2Cl^- + O_2$$

$$H^+ + Cl^- + HClO \longrightarrow H_2O + Cl_2$$

$$HClO + 2[O] \longrightarrow H^+ + ClO_3^-$$

The decomposition proceeds slowly without stimulus, particularly in concentrated solution. The rate is accelerated by ultraviolet light, catalysts such as platinum black and by the presence of other electrolytes. (197)

The disproportionation of hypochlorite ion into chlorate and chloride is due to interaction between the ion and the undissociated acid,

$$ClO^- + 2HOCl = ClO_3^- + 2H^+ + 2Cl^-$$

The chlorite ion may be an intermediate in the reaction. Since the reaction rate is dependent upon the square of concentration of undissociated acid, addition of a small excess of alkali will suppress the reaction; thus, with a 0.01 normal excess of sodium hydroxide, the rate of formation of chlorate is 1/400 that in a normal solution of NaOCl. (183) Hypochlorite ion also decomposes with release of oxygen, viz.,

$$2ClO^- = 2Cl^- + O_2$$

The mechanism of decomposition has been reported in detail. (197) Both above reactions occur with hypochlorous acid and with its ions, though the latter appear to be more stable. However, with the ions, both reactions are greatly accelerated by light.

Because hypochlorous acid and the hypochlorites are such strong oxidizing agents, their chemical reactions are almost exclusively confined to oxidation-reduction reactions. Iodine and bromine are

oxidized by hypochlorous acid in aqueous solution to iodates and bromates, respectively. Reaction of hypochlorous acid with hydrogen peroxide evolves oxygen with the formation of chloride ion,

$$H_2O_2 + HOCl \longrightarrow H_2O + O_2 + HCl$$

When a hypochlorite is added to solutions of bivalent manganese, lead, nickel, cobalt or iron, the higher hydroxide is precipitated. Similarly, acids in a lower stage of oxidation are oxidized; e. g., phosphorous acid to phosphoric acid.

The hypochlorites are so highly hydrolyzed that salts of the heavy metals cannot be prepared by evaporation - the hydroxide is obtained instead. Only in the case of soluble hydroxides, where hydrolysis is incomplete, can the salt be isolated in solid form. Sodium, potassium and calcium hypochlorite are formed by the direct addition of chlorine to the respective hydroxide, viz.,

$$2OH^- + Cl_2 = ClO^- + H_2O + Cl^-$$

Calcium hypochlorite is the main ingredient in bleaching powder. Lithium hypochlorite can be prepared from NaClO and LiCl or from $Ca(OH)_2$ and Li_2SO_4 or Li_2CO_3.

Chlorates are prepared by the action of chlorine dioxide on the appropriate alkali in solution according to the equation:

$$2ClO_2 + 2OH^- \longrightarrow ClO_2^- + ClO_3^- + H_2O$$

Equal molar quantities of chlorate are also obtained in this reaction. The most important commercial chlorite is that of sodium, which is used as a bleach and a starting material for production of chlorine dioxide.

In addition to the group I salts, several heavy metal chlorites are known, in contradistinction to the hypochlorite salts. Lead, mercury(II), silver and barium are among the insoluble, stable chlorites.

The oxidizing power of the chlorite ion is not as great as that of the hypochlorite. Thus, it is oxidized by permanganate to the chlorate.(132) It must be activated by a small amount of hypochlorite for use as a bleach in some applications. Alkaline solutions of chlorites disproportionate into chlorate and chloride on heating or with sunlight, according to

$$3ClO_2^- \longrightarrow 2ClO_3^- + Cl^-$$

Although the competitive reaction

$$ClO_2^- \longrightarrow Cl^- + O_2$$

occurs simultaneously.(181) The first reaction also describes the behavior of the salt when it is heated above 175°C. Acid solutions decompose due to the formation of the unstable chlorous acid.

$$11HClO_2 \longrightarrow 4ClO_2 + 4ClO_3^- + 3Cl^- + 7H^+ + 2H_2O$$

The chlorite ion reacts much like the hypochlorite ion in solution with most reagents. Both are such powerful oxidizing agents that they react with most organic materials, sometimes quite explosively. For example, potassium chlorite reacts violently with sulfur, rubber, and fabrics.

A rapid exchange of chlorine atoms occurs when chlorine dioxide and a chlorite ion are in contact in solution. It is interesting that

there is no such exchange in the case of chlorine dioxide and a chlorate, perchlorate, chloride ion, or free chlorine.(46)

Chloric Acid

Aqueous solutions of chloric acid may be prepared by either of two metathetical reactions: (1) dilute sulfuric acid and barium chlorate

$$Ba(ClO_3)_2 + H_2SO_4 = 2HClO_3 + BaSO_4$$

or (2) fluorosilicic acid and potassium chlorate

$$2KClO_3 + H_2SiF_6 = HClO_3 + K_2SiF_6$$

Chloric acid solutions may be concentrated under vacuum up to 30 percent without decomposition; further concentration may exceed 40 percent but not without some decomposition. Concentrated solutions of chloric acid decompose spontaneously in the cold and more rapidly on heating, with formation of perchloric acid.

Chloric acid is a powerful oxidizing agent; its reaction with acids are somewhat dependent upon concentration, temperature and the particular acid acted upon. Thus, with hydrochloric acid, weak solutions of chloric acid liberate chlorine while strong solutions liberate chlorine dioxide in addition to chlorine. Chloric acid converts HBr and HI to bromate and iodate, respectively, with resultant reduction of the chlorate ion to chloride ion in both cases. In contact with sulfuric acids, chloric acid disproportionates into perchloric acid and chlorine dioxide,(106) viz.,

$$3HClO_3 \longrightarrow 2ClO_2 + HClO_4 + H_2O$$

This reaction occurs in two steps, chlorous acid being an intermediate product which undergoes subsequent reaction with the chloric acid. Sulfur

dioxide (sulfurous acid) is oxidized to sulfuric acid by dilute solutions of chloric acid according to the equations(120)

$$2HClO_3 + 5H_2SO_3 \longrightarrow 5H_2SO_4 + H_2O + Cl_2$$

$$Cl_2 + H_2O + H_2SO_3 \longrightarrow H_2SO_4 + 2HCl$$

while with concentrated solutions it liberates chlorine dioxide,(98)

$$HClO_3 + H_2SO_3 \longrightarrow H_2SO_4 + HClO_2$$

$$HClO_3 + HClO_2 \longrightarrow 2ClO_2 + H_2O$$

Reaction of chloric acid with oxalic acid produces chlorine dioxide and carbon dioxide. The latter reaction serves for the laboratory preparation of chlorine dioxide as it proceeds at a convenient rate and is free from the danger of spontaneous explosion, which is inherent in some of the above reactions; the chlorine dioxide is easily freed from carbon dioxide by liquefying the former.(55)

Because of its strong oxidizing action, chloric acid reacts violently with organic matter, particularly when concentrated. Its action on metals varies with the reactivity of the metal, acidity and temperature. Magnesium reacts in cold chloric acid with evolution of hydrogen whereas iron dissolves without hydrogen formation. With zinc, varying amounts of hydrogen may be evolved and reduction of chloric acid may be obtained, depending upon conditions. These reactions and others pertinent to the chlorate ion are discussed in detail under the section entitled Chlorates.

Perchloric Acid

Perchloric acid, containing chlorine in its highest known oxidation state, is the most stable of the oxyacids of chlorine, and the

only one that is of commercial interest. The standard methods of production of perchloric acid involve the reaction of a chlorate with an acid. For example, anhydrous $Ba(ClO_4)_2$ is dissolved in concentrated HCl and the filtrate is evaporated at 150° to yield 98.75 percent $HClO_4$ with 1.15 percent $Ba(ClO_4)_2$ impurity.[195] It has also been made by anodic oxidation of hydrochloric acid and chlorates.[120]

One manufacturing method depends upon the oxidation of ammonium perchlorate by nitric and hydrochloric acids.

$$34NH_4ClO_4 + 36HNO_3 + 8HCl \longrightarrow 34HClO_4 + 4Cl_2 + 35N_2O + 73H_2O$$

The reaction also produces nitrous oxide and some chlorine. It is noteworthy that ammonium perchlorate is unreactive to nitric acid in the absence of hydrochloric acid.[120] A closely allied process involves acidification of a concentrated sodium perchlorate solution with hydrogen chloride. Sodium chloride is separated by filtration and the filtrate fractionally distilled to give HCl and $HClO_4$.[197] Another preparation requires the distillation of a mixture of sulfuric acid and a perchlorate. The anhydrous acid is obtained in about 75 percent yield. A similar method is suitable for the preparation of perchloric acid monohydrate.[193] Earlier manufacture depended upon the slight solubility of potassium fluosilicate in the metathetical reaction between $KClO_4$ and H_2SiF_6. In most of these processes, the perchloric acid is purified by fractional distillation under vacuum yielding a product of better than 70 percent purity. Anhydrous perchloric acid may be obtained from this product by

further distillation with a 20 percent fuming sulfuric acid mixture.

Perchloric acid is a strong monobasic acid which forms normal salts - perchlorates - of the type $MClO_4$. The acid and its derivatives occur in two forms, a stable ionized state, and an unstable and often explosive covalent one. The anhydrous acid belongs to the latter type while the hydrated acid to the former.(183) The infrared spectrum(9) and X-ray diffraction pattern(128) of perchloric acid monohydrate are consistent with the hypothesis that the monohydrate exists as

$$[H_3O^+][ClO_4^-]$$

This accounts for the stability of hydrated and aqueous solutions of perchlorate salts in contrast to their extreme sensitivity in pure form. Perchloric acid can be distilled in vacuo, but if heated under ordinary pressure, it breaks up into water, oxygen and chlorine dioxide, often explosively. The anhydrous acid reacts vigorously with water forming six hydrates, the monohydrate being the most stable.(183) The monohydrate is a hygroscopic solid, which melts more than 160° higher than the anhydrous acid (+.50° compared to -112°) and has a crystal lattice closely identical to that of ammonium perchlorate. Perchloric acid forms a constant-boiling mixture at a concentration approximating the dihydrate composition; this mixture has the maxiumum oxidizing power.

In aqueous solution, perchloric acid is practically completely dissociated and thus exhibits the characteristic reactions of the perchlorate ion. The ClO_4^- ion in solution possesses 17 waters of hydration.(65) The reactions of the perchlorate ion are discussed fully under the section

entitled Perchlorates. Suffice it to say that nearly all the reagents that reduce chloric acid are ineffective towards cold perchloric acid, even when concentrated. Thus, cold perchloric acid is not an oxidizing agent and exhibits the typical reactions of a strong acid, e. g., zinc reacts in 72 percent acid with evolution of hydrogen,and iron dissolves to form ferrous perchlorate. Even organic matter may dissolve in the cold acid without oxidation and catalysts are necessary to effect oxidation of coal, coke, leather, and similar substances in a convenient time. (120)

The properties of hot perchloric acid are remarkably different than those of the cold acid, particularly when concentrated. It is a violent oxidizing agent; with organic matter such as wood and paper, and with most organic compounds, the anhydrous acid reacts explosively. Organic material dissolved in the cold acid gives violent explosions on warming. The remarkable dual property of this acid is illustrated by its use in analytical chemistry - the hot concentrated acid serves as an oxidizing agent, whence on cooling to room temperature, the oxidized substance can be titrated with a suitable reducing solution without interference from the excess perchloric acid still left in solution. (120)

Chlorates

Preparation

Laboratory preparations of the chlorates covered by this survey are given in this section. Electrolytic methods are now commonly employed in the commercial preparation of chlorates. Industrial production methods for chlorates are discussed in Chapter II.

The two most common types of reactions involved in the preparation of chlorates are metathesis and oxidation-reduction reactions. The former is the most often utilized in chemical preparations while the latter is mainly confined to electrolytic and thermal decomposition processes. In the syntheses involving a metathesis reaction, a common and readily available chlorate, such as potassium or sodium chlorate, is reacted with a salt of the desired cation; the new chlorate is isolated by utilizing differences in physical properties of the products, such as solubility, crystallization, thermal stability, etc. Preparation by means of thermal decomposition is generally not employed because of the diversity of the products and low yields inherent in these reactions. A special case of a redox reaction is in the preparation of calcium chlorate by reacting chlorine with milk of lime. Also chlorates of different metals may be obtained by the action of the acid on the oxide or carbonate.

Many of the chlorates are deliquescent and highly hydrated. Since the chlorates in general are thermally unstable, obtaining these in anhydrous state may present special complications. On heating, most chlorates lose their water of crystallization without decomposition. In fact, the alkali metal chlorates can be melted without decomposition. Others, however, for instance aluminum chlorate, cannot be obtained in an anhydrous condition without decomposition.

The impurities most frequently found in potassium chlorate are discussed by Taradoire.(206) He gives methods of separation and purification for several chlorates.

In the following sections, preparations for the individual chlorates are found. Specific, detailed directions for preparation are not given as many of these compounds are now commercially available in high purity. Reference to the original articles should be made for specific directions for their preparations.

Aluminum Chlorate. Aluminum chlorate was obtained by treating aluminum fluosilicate with a hot concentrated solution of potassium chlorate; and a solution of the chlorate mixed with alum was obtained by reacting potassium chlorate with aluminum sulfate. When a solution prepared by the interaction of barium chlorate and aluminum sulfate is evaporated over sulfuric acid, it deposits hygroscopic crystals of $Al(ClO_3)_3 \cdot 9H_2O$ from cold solution, and $Al(ClO_3)_3 \cdot 6H_2O$ from hot solution.[143] The former can also be converted to the hexahydrate by vacuum desiccation.[36] A mixed solution of $AlCl_3$ and $Al(ClO_3)_3$ was produced by the chlorination of $Al(OH)_3$ dispersed in water.[154] The anhydrous salt has not been obtained due to the instability of the chlorate on heating.

Ammonium Chlorate. Ammonium chlorate is prepared by neutralizing perchloric acid with ammonium hydroxide and diluting the solution to a specific gravity of 1.25, whereupon the salt settles out in fine needles.[64] It has also been made by the reaction of: (1) barium or calcium chlorate and ammonium carbonate; (2) potassium chlorate and ammonium fluosilicate, $(NH_4)_2SiF_6$ or ammonium hydrogen tartrate; (3) sodium chlorate and ammonium chloride.[143] The latter reactions

depend upon the fact that ammonium chlorate is more soluble than the other constituents in these mixtures.

Barium Chlorate. This salt is prepared by the reaction of barium chloride and sodium chlorate in solution and is precipitated on cooling; it is purified by recrystallization.(179, 182) It has also been made by treating sodium chlorate with hydrofluosilicic acid followed by neutralization with barium carbonate.(143) The monohydrate is obtained from aqueous solutions. The anhydrous salt may be obtained by heating to 140°C in a vacuum.(36) A yield of 75 percent barium perchlorate was reported by heating a solid mixture of ammonium perchlorate with barium oxide or carbonate.(196)

Calcium Chlorate. Calcium chlorate has been made by the action of chlorine on $Ca_2B_4O_7$,(102) $CaCO_3$,(103) or hot lime.(120) The latter reaction was used commercially prior to the electrolytic process. In this method, the hydrated lime is heated to 50°-70°C and acidified by absorption of chlorine, whereupon the reaction proceeds fairly rapidly. Calcium chlorate separates in deliquescent crystals of the dihydrate when its solutions are evaporated over concentrated sulfuric acid. The anhydrous salt is obtained by dehydrating the dihydrate at 50°.(143)

Lithium Chlorate. Lithium chlorate is prepared by adding lithium chloride to sodium chlorate solution; sodium chloride precipitates, the liquor is concentrated, and the lithium chlorate is filtered and dried.(120) Another preparation involves the reaction of a solution of barium chlorate with one of lithium sulfate.(177) It has also been formed by the action

of chlorine on lithium hydroxide, which, however, produces two moles of lithium chloride for every mole of chlorate.

Magnesium Chlorate. Magnesium chlorate is formed by double decomposition between magnesium sulfate and barium chlorate in aqueous solution. After filtration, the solution is concentrated in vacuo. (3) Crystals of hexahydrated magnesium chlorate were obtained by evaporating an aqueous solution of potassium chlorate and magnesium fluosilicate over sulfuric acid. (143)

Potassium Chlorate. This chlorate is available commercially in high purity. It is prepared in a separate step by reaction of potassium chloride with sodium chlorate produced in an electrolytic cell. For details of this process see Chapter II. It can also be prepared by adding a hot saturated solution of potassium chloride to a slight excess of calcium chlorate, the potassium chlorate crystallizing out upon cooling. (120) The system sodium chlorate-potassium carbonate has been shown to quantitatively precipitate potassium chlorate when 67 parts of the former and 71 parts of the latter are added to 100 parts of water. (99) The velocity of nucleus formation in supersaturated potassium chlorate solutions has been measured (200) and the supersaturation temperature determined. (119)

Silver Chlorate. This salt is generally prepared by double decomposition. Silver chlorate of 95 percent purity is obtained by mixing solutions of silver nitrate and sodium chlorate, cooling, decanting and washing with water at 0°, and filtering. Two recrystallizations yield a

product of 99.7 percent purity.[151, 171] Silver chlorate was also prepared by the reaction of chloric acid on silver oxide as well as finely divided silver. Chlorination of silver oxide or carbonate suspended in water produced silver chlorate and silver chloride. The silver chlorate, being soluble, is decanted from the chloride and evaporated until the chlorate crystallizes out.[143]

Sodium Chlorate. This chlorate is one of the basic building blocks for the synthesis of other metal chlorates. It is prepared commercially by electrolysis of sodium chloride. See Chapter II for details It may also be prepared by chemical reaction from hypochlorite solution. The principal reaction is believed to be between hypochlorous acid and hypochlorite ions according to the equation:

$$2HClO + NaClO \longrightarrow NaClO_3 + 2HCl$$

This reaction is favored by heat and mild acidity.[120] Sodium chlorate is formed when chlorine dioxide is hydrolyzed in basic solution. An equivalent quantity of chlorite is always produced by this reaction.[55] Large single crystals of sodium chlorate have been successfully grown in a special apparatus.[19] The velocities of crystal growth of sodium chlorate from aqueous solutions in various degrees of supersaturation and at various temperatures have been determined.[119]

Reactions in Aqueous Solution

The reactions of chlorates naturally fall into two groups, viz., metathesis and oxidation-reduction(redox). Thermal decomposition is considered as a special case of the redox type and is covered fully in the

section entitled Thermal Decomposition.

Of the two types of reaction, redox is by far the most common encountered in solution studies, probably because it is the most interesting chemically. Metathesis reactions are mainly confined to preparations of chlorates from other more readily obtainable chlorates. The latter reactions have been described under the appropriate compound preparation headings on pages 104 through 108 The reactions to be discussed in this section then will be almost exclusively of the redox type.

Gases. Potassium chlorate in neutral solution is reduced by hydrogen in the presence of active platinum forming the chloride.(63) Partial conversion of sodium chlorate to perchlorate may be effected by leading oxygen containing a large percentage of ozone into a solution of one percent chlorate and one percent sulfuric acid. The reaction is accelerated by ultraviolet light.(111) Hydrogen sulfide is oxidized by chloric acid to sulfuric and hydrochloric acids.(143) Reactions of sulfur dioxide with chlorates are discussed in the section entitled Acids and Oxides.

Halogens. The action of halogens on chlorates varies with the electronegativity of the particular halogen - thus, the chlorate ion oxidizes bromine and iodine but itself becomes oxidized by elemental fluorine. Oxidation of iodine by chlorate forms iodates. The over-all reaction may be written:

$$5ClO_3^- + 3I_2 + 3H_2O \longrightarrow 6HIO_3 + 5Cl^-$$

There is no simple mechanism to explain this reaction. Potassium chlorate and iodine alone react but very slowly. In the presence of water,

the reaction proceeds rapidly. Acid and chloride ions catalyze the reaction. One explanation of the action of water is that the chlorine liberated gives HCl and HClO, the latter oxidizing I_2 to IO_3^-. The accelerating action of acid then is due to the more rapid liberation of chlorine. Thus, HCl which liberates chlorine the most rapidly from the chlorate exerts a greater accelerating effect than H_2SO_4 and this greater than that of HNO_3. The acid can be replaced by a stream of Cl_2. The Cl_2 reacts with I_2 to form ICl, which immediately reacts with the $KClO_3$, giving iodate and chlorine, according to the sequence of reactions:(169)

$$Cl_2 + I_2 \longrightarrow 2ICl$$

$$ICl + ClO_3^- \longrightarrow IO_3^- + Cl_2$$

Iodine chloride is even more readily oxidized by chlorate than free iodine.(55) An earlier investigator ascribed the reduction of the chlorate to ICl_3, the latter being formed by reaction between the I_2 and Cl_2 evolved from the original attack of I_2 on the chlorate.(121) Since ICl_3 is completely dissociated into Cl_2 and ICl in solution,(183) this explanation is not essentially different from that of the ICl mechanism given above, although ICl_3 has more recently been reported stable in HCl solution.(197) The presence of sodium chloride accelerates the reaction in neutral solution in direct proportion to its concentration. The accelerating effect decreases with increase in temperature. An accelerating effect of $FeCl_3$ was also observed in NaCl medium as well as acid.(135)

Reaction of iodine with barium chlorate forms barium iodate and chlorine. In a slightly acid solution two reactions appear to be

involved depending upon the relative proportions of the starting materials.[127] The reactions are:

$$3I_2 + 3Ba(ClO_3)_2 + 3H_2O \longrightarrow 3Ba(IO_3)_2 + HClO_3 + 5HCl$$

$$6I_2 + 5Ba(ClO_3)_2 + 6H_2O \longrightarrow 5Ba(IO_3)_2 + 2HIO_3 + 10HCl$$

Chlorate is reduced by iodide ion in the presence of catalysts with the liberation of free iodine. The reaction velocity is dependent upon concentration, temperature and the catalyst employed. The rate of the reaction follows the form,

$$d[I^-]/dt = k[I^-][ClO_3^-]$$

where the rate constant, k, varies with the nature and concentration of the catalyst.[216] Catalysts studied include $VOSO_4$, $FeCl_3$, OsO_4, $RuCl_3$, $MnCl_2$, Na_2SO_4, Ni_2SO_4, $CoSO_4$, $MnSO_4$ and NaCl.[215, 217] The last six mentioned substances retard the reaction. In the presence of arsenious acid, iodine is not obtained and the reaction is autocatalytic.[76] (See the discussion of bromide below).

Apparently chlorates do not react with bromine to any appreciable extent.[143] Bromide ion is converted to free bromine by chlorate ion in acid solution. The reaction rate is given by,

$$-d[ClO_3^-]/dt = k_1[ClO_3^-][Br^-][H^+]^2$$

in the presence of arsenious acid the reaction is autocatalytic and bromine is not formed, due to the latter's reduction back to the bromide by the arsenious acid, the net result being a simple reduction of the ClO_3^- by the H_3AsO_3. The autocatalysis in this reaction was shown to be due to the

H_3AsO_4 formed.[190] A later study of the chlorate-bromide reaction catalyzed by arsenic acid showed that the catalytic action of the arsenic acid can be represented by an additional term to the uncatalyzed, rate equation of the form, $k_2[ClO_3^-][Br^-][H_3ASO_4]$.[76]

Chlorine does not react with chlorate ion in acid solution even at elevated temperatures as evidenced by the very slow exchange obtained in radiotracer studies with Cl^{36} [209] For reaction of chloride ion with chlorate ion, see under reaction with hydrogen chloride given in the section on Acids and Oxides.

Metals and Non-Metals. In acidic solutions, the reaction of a metal with a chlorate may be thought of in terms of reaction in chloric acid. The course of the reaction may take either or both of two paths. The chlorate may be reduced to chloride without liberation of hydrogen,

$$6M + 6nHClO_3 \longrightarrow MCl_n + 5M(ClO_3)_n + 3nH_2O$$

(where M stands for the metal and n its oxidation state) or hydrogen may be formed without reduction of the chlorate,

$$M + nHClO_3 \longrightarrow M(ClO_3)_n + \frac{n}{2}H_2.$$

At least some reduction almost always accompanies the latter reaction. Mellor states "the reduction of chloric acid by the metals cannot in all cases be regarded as the effect of nascent hydrogen, but is rather an effect of the tendency of the metal, under the conditions of the experiment, to oxidize at the expense of the oxygen of the acid, or to go into solution at the expense of the hydrogen which is set free."[143] Chlorates are reduced to the corresponding chloride by zinc, in the presence of dilute H_2SO_4,

H_3PO_3, H_3PO_2 and oxalic acids. Aluminum and iron in dilute sulfuric acid also reduce chlorates(214) as do cadmium, copper, tin and silver in chloric acid. In the case of copper, a layer of cuprous oxide is formed on the metal. It is suggested that reaction proceeds by oxidation to the oxide which dissolves first as cuprous chloride and chlorate, and is then oxidized to the cupric chloride and chlorate. A similar situation obtains for cadmium and nickel. With bismuth, the oxide remains undissolved and thus reaction is considerably slowed by the oxide film. Mercury and antimony are only slowly dissolved in concentrated chloric acid. On the other hand, magnesium dissolved with the evolution of hydrogen with only a small percent reduction of the chlorate to chloride. (143)

Potassium chlorate in aqueous solution is reduced to the chloride in the presence of iron filings. (143) Chlorates are also reduced by zinc in potassium hydroxide solution. (214) Solutions of chlorates and hydrazine salts may be boiled without reaction; but if a piece of tarnished copper or copper oxide is introduced into the cold mixture, reaction takes place readily with evolution of nitrogen. The catalytic action is restricted to metals exhibiting two bivalences, such as copper and iron. (89)

The action of red phosphorous on excess $KClO_3$ in 1N H_2SO_4 produces KCl and H_3PO_4 in 90 percent yield. Small amounts of $MnSO_4$ catalyze the reaction to some extent. (43) A similar reaction with arsenic is reported. (143) The reaction of moist chlorates are more vigorous: explosion with white phosphorous; inflammation with red

phosphorous; incandescence with powdered arsenic. However, no reaction is reported between chlorates and antimony, bismuth carbon(wood or graphite), tin and the other common metals.(4) Moist mixtures of barium chlorate and sulfur inflame spontaneously as they dry due to the formation of H_2SO_4 by reduction of the chlorate, which then liberates $HClO_3$. With potassium chlorate, the action is much slower and no inflammation occurs.(205) The chlorates of barium, calcium and magnesium, among others, in the presence of sulfur and a little water evolve chlorine dioxide below and chlorine plus oxygen above 50°-60°; S_2Cl_2 is an intermediate which is decomposed by the water to sulfate.(37) Moist CuS explodes in a solution of $HClO_3$ or of a chlorate of Mg, Zn, or Cd, while Sb_2S_3, As_2S_3, SnS and SnS_2 become incandescent.(4) Selenium reacts similarly but more vigorously, a slightly moist mixture with any chlorate except potassium becoming incandescent. Telurium is attacked by concentrated aqueous chloric acid or aqueous magnesium chlorate. The addition of an alkali acetate prevents the action of any chlorate on sulfur or selenium.(3) Similar reactions of chlorates at elevated temperatures are discussed below in the Thermal Decomposition section.

Acids and Oxides. An aqueous solution of potassium chlorate reacts slowly with dilute hydrochloric acid with the evolution of chlorine. Raising the temperature increases the rate as does use of a platinum catalyst. A concentrated solution of potassium chlorate gives very little chlorine with dilute hydrochloric acid unless warmed. However, concentrated HCl and a chlorate liberates chlorine dioxide in addition to

chlorine,[143] viz.,

$$2KClO_3 + 4HCl \longrightarrow 2KCl + Cl_2 + 2ClO_2 + 2H_2O$$

Use of radioactive Cl^{38} as a tracer in this reaction showed that the Cl atoms in the ClO_2 are for the most part derived from the chlorate.[209] Dilute nitric acid does not decompose chlorates but concentrated or fuming nitric acid quantitatively reduced potassium chlorate in a sealed tube. Nitrous acid, on the other hand, is rapidly oxidized by chlorates to nitric acid and chlorine. Addition of a little sodium nitrite to a solution of potassium chlorate acidified with nitric acid reduced the chlorate to chloride in ten minutes. Chlorates are decomposed when heated with phosphoric or arsenic acids.[143]

In acid solution, hydrogen peroxide has been reported to reduce chlorates to lower valence chlorine compounds. Due to the similarity of this reaction to that of a chlorate with hydrogen chloride, the primary reaction is postulated to be:

$$2HClO_3 + 2HCl \longrightarrow 2H_2O + 2ClO_2 + Cl_2$$

The hydrogen chloride is assumed to come from the action of a little free chlorine, which is formed by spontaneous decomposition of the chloric acid, with the hydrogen peroxide. Since more chlorine is formed in the primary reaction, only a trace is necessary to initiate the reaction and the reaction is autocatalytic.[143]

Potassium chlorate is quantitatively reduced by sulfur dioxide in aqueous solution to the chloride according to the equation:

$$KClO_3 + 3SO_2 + 3H_2O \longrightarrow 3H_2SO_4 + KCl$$

This reaction was the basis of a proposed use of $KClO_3$ as a standarizing substance for alkali solution - reduction of the chlorate with sulfur dioxide followed by titration of the alkali with the definite amount of sulfuric acid thus formed.(212) Silver chloride is quantitatively precipitated when $AgClO_3$ is reacted with H_2SO_3.(143) The reaction kinetics of the chlorate - sulfite reaction has been extensively studied in acid solution.

$$ClO_3^- + 3H_2SO_3 \longrightarrow Cl^- + 6H^+ + 3SO_4^{--}$$

The reaction is first order both in ClO_3^- and H_2SO_3, the rate being given by(152)

$$-d[ClO_3^-]/dt = k[H_2SO_3][ClO_3^-]$$

The mechanism proposed involves the reaction between H_2SO_3 molecules and chlorate ions as the rate-determining step. Hydrogen ion concentration determines the H_2SO_3 level and thus the reaction rate. Hydroxyl and sulfoxy radicals were suggested as reactive intermediates.(72) In the reduction of potassium chlorate by sodium sulfite in hydrogen chlorate solutions, the acid concentration has a marked effect upon the reaction rate and induction period. Increasing acid concentration accelerates the rate and diminishes the induction period up to a concentration of 0.075 N, above which there is no induction period and only a slight increase in rate. The pH dependence of the rate is interpreted on the basis of a catalytic action of the hydrogen ions consisting in a deformation of the chlorate ion.(56)

In contrast to the above reactions, a metal chlorate can react with SO_2 to produce chlorine dioxide according to the equation:

$$2MClO_3 + SO_2 \longrightarrow 2ClO_2 + M_2SO_4$$

High yields of ClO_2 are claimed by employing a solution saturated with respect to the sulfate and a high chlorate concentration. With sodium chlorate, the reacting gas should contain 8-10% SO_2 in an inert gas. (1) Although sulfuric acid has no action on chloric acid, (143) in the presence of sulfuric acid the above reaction proceeds rapidly in two stages, viz.,

$$HClO_3 + H_2SO_3 \longrightarrow HClO_2 + H_2SO_4$$

$$HClO_3 + HClO_2 \longrightarrow 2ClO_2 + H_2O$$

The $HClO_2$ intermediate is not reduced by the H_2SO_3 as evidenced by the absence of HClO, HCl and Cl_2. A proper acidity must be maintained as excess water prevents the formation of ClO_2 while a very high acid concentration will cause spontaneous decomposition of the $HClO_3$. (98) In a pilot plant study of this process, 6 M sodium chlorate was mixed with 50 percent sulfuric acid at a 1:1 ratio and was introduced into the top of a packed column countercurrently to a 15 percent sulfur dioxide in air mixture. (117) The main reaction produced chlorine dioxide and sodium hydrogen sulfate while a side reaction occurred according to the equation:

$$2NaClO_3 + 5SO_2 + 4H_2O \longrightarrow Cl_2 + 2NaHSO_4 + 3H_2SO_4$$

Chlorine dioxide is sometimes prepared by the action of concentrated sulfuric acid on potassium chlorate. When so made it contains both free chlorine and free oxygen. (183)

The mechanism of reduction of chlorate with sulfite was studied by use of O^{18} tracers separately in the chlorate and sulfite. The results were attributed to a stepwise reduction, e. g., $ClO_3^- \longrightarrow ClO_2^-$ $ClO^- \longrightarrow Cl^-$ The interpretation is consistent with the rate laws.(81) Partial conversion of chlorate to perchlorate is obtained by boiling with sodium persulfate according to the equation:(110)

$$NaClO_3 + Na_2S_2O_8 + H_2O \longrightarrow NaClO_4 + 2NaHSO_4$$

A mixture of Cr_2O_3 and $KClO_3$ upon heating and refluxing reacted according to the equation:

$$Cr_2O_3 + KClO_3 \longrightarrow KCl + 2CrO_3$$

KH_2PO_4 and K_2HPO_4 completely suppressed the reaction, while carbonates slowed the rate of reaction.(134) The use of ferrous hydroxide to eliminate sodium chlorate impurity in electrolytic alkali hydroxide has been mentioned in a patent.(42) The pertinent reaction is:

$$9Fe(OH)_2 + NaClO_3 \longrightarrow 3Fe_3O_4 + NaCl + 9H_2O.$$

Ferric oxide and potassium chloride were obtained when potassium chlorate in solution was heated with ferrous oxide.(105)

The kinetics of the reaction of $KClO_3$ with $NaAsO_2$ in the presence of H_2SO_4 (or HCl) showed a greater dependency on the concentration of $KClO_3$ than on $NaAsO_2$, the kinetic expression being given by:

$$-d[ClO_3^-]/dt = k_1[ClO_3^-][AsO_2^-] + k_2[ClO_3^-][Cl^-]$$

Without a catalyst the reaction takes place only with a large excess of acid and at high temperature (75°) while with OsO_4 present the temperature can be lowered to 20° and the acidity to 0.05 N.(203) The reduction of

arsenious acid by chlorate is independent of the concentration of H_3AsO_3. The reduction does not take place in presence of H_2SO_4 but proceeds smoothly in HCl solution. Kinetic measurements established that the primary reaction is of the first order. The following reactions are believed to take place:(125)

$$ClO_3^- + Cl^- + 2H^+ \longrightarrow H_2ClO_3 + [Cl]$$

$$H_2ClO_3 + 4Cl^- + 4H^+ \longrightarrow 5[Cl] + 3H_2O$$

$$3Cl_2 + 3AsO_3^{---} + 3H_2O \longrightarrow 3AsO_4^{---} + 6Cl^- + 6H^+$$

AsO_3 is rapidly oxidized to H_3AsO_4 by aqueous $KClO_3$ and a little OsO_4.(92)

The oxidation of K_3AsO_3 by $KClO_3$ requires a hydrogen chloride concentration at least as high as 2N; the rate increases with the acidity and there is no autocatalysis.(56) On the other hand, a kinetic study of the oxidation of Na_3AsO_3 with $KClO_3$ in the presence of H_2SO_4 showed the reaction to be autocatalytic and that OsO_4 retards the reaction.(227) It is interesting to note that H_3AsO_4 itself catalyzes the oxidation of bromide by chlorate while H_3AsO_3 and AsO_4^{---} do not.(76) The addition of OsO_4 to chlorate solutions appears to "activate" the latter towards oxidation-reduction reactions through formation of an addition compound. It is believed that the oxidizable substance reduces the OsO_4 to Os_2O_5, the latter compound then being oxided by chlorate according to the equation:

$$Os_2O_5 + KClO_3 \longrightarrow 2OsO_4 + KCl.$$

This explains why neither chlorite nor hypochlorite is formed in the reduction.(93)

Cations. Chlorates are reduced by ferrous ions in solution slowly without catalysts and more rapidly with catalysts present, generally to form the respective chlorides. However, a mixture of $KClO_3$ and $FeSO_4$ in the presence of small amounts of water liberates ClO_2 and Cl_2. In the presence of large amounts of water only the chloride is obtained.[87] In neutral solution, the reduction is incomplete, better results being obtained in acid. Upon addition of stoichiometric amounts of $KClO_3$ to $FeSO_4$ solution preheated to 70°, about 75 percent of the iron precipitated as a compound of the approximate formula $3Fe_2O_3 \cdot 4SO_3 \cdot O \cdot 7K_2O \cdot 6H_2O$, and the remaining portion of the iron remained in solution as $Fe_2(SO_4)_3$.[174] For quantitative conversion of chlorate to chloride, a catalyst is required, viz., a little KI gave 99 percent conversion.[84] The rate of reaction between $KClO_3$ and $FeSO_4$ in the presence of excess acid was found to be second order according to the equation:

$$-d[ClO_3]/dt = k[ClO_3^-][Fe^{++}]$$

The rate was also proportional to the concentration of acid. In the presence of OsO_4, the rate was determined by the expression:

$$-d[ClO_3^-]/dt = k[Fe^{++}]^2[H_2SO_4][OsO_4]^b/[Fe^{+++}]^a;$$

while with Fe^{+++} originally present it was

$$-d[ClO_3^-]/dt = k[Fe^{++}]^2[H_2SO_4]$$

At 20°, the energies of activation for the uncatylzed and catalyzed reactions were 17,675 cals. and 11,605 cals., respectively.[202] An interesting use of the above reaction to prevent scale formation in a pickling bath is given

in a patent;[199] the damaging $FeSO_4$ formed in the process is converted to the original $Fe_2(SO_4)_3$ in the presence of sulfuric acid according to the equation:

$$6FeSO_4 + KClO_3 + 3H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + KCl + 3H_2O$$

The kinetics of the oxidation of stannous ion by potassium chlorate in hydrogen chloride solution has been studied. Stannic ions and chloride ions are obtained. The reaction rate is given by:

$$-d[ClO_3^-]/dt = k_1[ClO_3^-][Sn^{++}] + k_2[ClO_3^-][Cl^-]$$

but at lower temperature and acidity, the rate becomes:

$$-d[ClO_3^-]/dt = k[ClO_3^-][Sn^{++}]$$

The mechanism is similar to that using ferrous or arsenite ions, the relative reactivities increasing in the order: $AsO_2^- < Sn^{++} < Fe^{++} < Ti^{+++}$. (201)

Ammonium thiocyanate can be oxidized in acid solution by sodium chlorate according to the equation:

$$2NaClO_3 + NH_4CNS \longrightarrow 2NaCl + NH_3 + HCNS + 3O_2$$

The reaction takes place in different steps and at various rates depending upon temperature, pH of the medium, and light conditions. (153)

Irradiation and Exchange. The action of light on chlorate ions in solution leads to the formation of hypochlorite and molecular oxygen; the primary process of light absorption is assumed to consist of the transfer of an electron to the hydration layer of the chlorate. (59) Ultraviolet irradiation causes decomposition of a neutral $KClO_3$ solution with liberation of oxygen. (204) On the other hand, $KClO_3$ in solution is only very

slightly decomposed by radium rays. (115)

No exchange of chlorine atoms has been observed between chlorate ions and chloride ions, (41) chlorine dioxide (46) or perchlorate ions (129) in aqueous solution. However, oxygen exchange between chlorate and water is complete in acid solution but not in neutral or alkaline solution. (227) The reaction appears to be catalyzed by both hydrogen and hydroxyl ion. (211) A recent study shows the exchange in acid solution follows the rate law,

$$\text{rate} = k(H^+)^2(ClO_3^-)$$

The activation energy at 100° and an ionic strength of 1.34 is 27,100 cal. per mole. The reaction proceeds faster in heavy water by a factor of 2.83. (90)

Reactions in Non-Aqueous Media

Inorganic Reactions. Potassium chlorate reacts in liquid sulfur trioxide to form $K_2S_3O_{10}$ and $(ClO_2)_2S_3O_{10}$. (130) It is reduced by ammonia to chloride according to the equations

$$KClO_3 + 2NH_3 \longrightarrow KCl + 2[N] + 3H_2O$$

$$KClO_3 + [N] \longrightarrow KNO_3 + Cl$$

The temperature at which the former reaction begins decreases with increase of NH_3 concentration below 300°; about 60 percent of the nascent nitrogen formed is changed to nitrate. (94)

Treatment of $KClO_3$ with BrF_3 yields $KBrF_4$ and probably ClO_2F. Only one-third of the oxygen expected was evolved. (52)

Addition to a mixture of $KClO_3$ in BrF_3 of B_2O_3 yields $KBrF_4$, and addition of Sb_2O_5 yields $KSbF_6$ and $BrF_6 \cdot SbF_6$.[223]

The action of F_2 and $KClO_3$ below -40° gives much Cl_2 and some ClF, chloryl fluoride and $ClO_2 \cdot OF$.[53] Above 100°, F_2 reacts with $KClO_3$ to yield Cl_2, at 40 to 60°, it gives Cl_2O_6; at -40 to + 20°, ClO_3F results; and at lower temperatures, possibly ClO_4F, is formed. By contrast, reaction of fluorine with $NaClO_3$ to yield Cl_2 first occurs above 200°.[17] Perchloryl fluoride, ClO_3F, possesses the stability and inertness of the perchlorate ion ClO_4^-.[54]

Organic Reactions. Use of chlorates in organic reductions has not been very prevalent due mainly to its too powerful oxidizing action with organic materials, usually resulting in violent explosions. However, under carefully controlled conditions, chlorates have been used to effect oxidation of some organic compounds, for example, unsaturated acids[20, 142] and amino acids.[116] The reader is referred to Reference 16 for some miscellaneous uses of chlorates along this line.

Thermal Decomposition

General Considerations. All chlorates undergo thermal decomposition. At high temperatures a chlorate is converted to a chloride and oxygen and at moderate temperatures into a perchlorate and a chloride. The evolution of oxygen from chlorates is an exothermic reaction and often takes place with explosive violence. On heating, hydrated

decomposition, whereas, the hydrated salts of weak bases hydrolyze.

Pressure as well as temperature has a definite effect upon the decomposition of these compounds. Reduced pressure usually lowers the decomposition temperature, whereas, increased pressure has the converse effect. Many substances, when brought into contact with heated chlorates will accelerate the evolution of oxygen and otherwise influence the course of the reaction. Metallic oxides, metals and radiation will catalyze the decomposition reaction. Recent radiotracer studies have been valuable in determining the mechanism of these reactions.

Sodium and Potassium Chlorates:

Uncatalyzed Decomposition. The chlorates of sodium and potassium can be conveniently discussed together because of the chemical similarities which exist among the elements within a family. The alkali chlorates melt without decomposition but decompose at a slightly higher temperature. There is much disagreement in the literature as to the melting point of sodium chlorate, but it is in the range 250°-260°C.[55, 120, 143] The salt fuses without decomposition, but the latter commences at a temperature just above its melting point. The heat of decomposition of sodium chlorate into chloride and oxygen is 12.3 cal.[143]

Commercially, potassium chlorate is the most important salt of chloric acid. It is commonly employed in the laboratory preparation of oxygen. If this solid is heated considerably above its melting point, oxygen is evolved. Oxygen gas is not liberated until this relatively high temperature is reached and then the process is likely to proceed

rapidly. The method may be modified to advantage by mixing with the chlorate a catalyst which will reduce the decomposition temperature.

The melting point of potassium chlorate, reported in the literature, varies from 350° to 380°C.[55, 120, 143, 225] The salt can be melted in oxygen gas without decomposition. The heat of decomposition of potassium chlorate into potassium chloride and oxygen was found to be 12.1 ± 0.3 kg-cal per mole at constant volume and room temperature.[95]

Recent studies have indicated that a chlorite intermediate is formed in the decomposition of sodium chlorate. Sodium chlorite is unstable, even at low temperatures, yielding chlorate and chloride.[226] A secondary reaction has been found in the chlorite decomposition, namely, $NaClO_2 \longrightarrow NaCl + O_2$. The ratio of these two reactions depends principally on the rate of heating.[173] At moderate temperatures, up to 420°, decomposition of sodium chlorate takes place according to the following equation

$$2NaClO_3 \longrightarrow NaClO_4 + NaCl + O_2$$

Above 420° (examined up to 550°C) the following reactions take place

$$2NaClO_3 \longrightarrow 2NaCl + 3O_2 \text{ and}$$

$$2NaClO_3 \longrightarrow NaClO_4 + NaCl + O_2$$

The perchlorate formed is unstable at these temperatures, yielding chloride and oxygen.[226] Thus, at the higher temperatures, three reactions take place concurrently when sodium chlorate is heated; the larger part is directly decomposed into sodium chloride and oxygen and the remainder is converted into sodium perchlorate. The perchlorate, on further heating, is

decomposed into the chloride and oxygen so that all the oxygen in the chlorate is ultimately evolved. This is evident by the low yields of sodium perchlorate formed at 550°C.(139)

The effect of temperature and pressure on potassium chlorate was investigated. It was found that under a pressure of 5497 atmospheres a transformation into a secondary modification occurred at 0°C. The effect of increasing the pressure is to increase the transition temperature.(143)

Analysis of the decomposition products obtained in a kinetic study of the thermal decomposition of potassium chlorate also indicated the formation of a chlorite intermediate. The weight change during the reaction was followed by use of a thermal balance. The data was analyzed by Andrews equation and a plot of $\log\left(\frac{dw}{dt}\right)$ vs $\frac{1}{T}$ produced two linear portions, whose corresponding energies of activation were 22.1 and 32 kcal for above and below 550°, respectively. The analysis of the decomposition products corresponded with the equation:

$$2KClO_3 \longrightarrow KClO_2 + KClO_4$$

The chlorite and the perchlorate both decompose into chloride and oxygen. The chlorite decomposition predominates in the lower temperature region, whereas the perchlorate decomposition is more pronounced at the higher temperatures.(155) The potassium chlorate decomposition mechanism is somewhat analogous to that postulated for the sodium salt.

Earlier investigators did not propose an intermediate compound in the thermal decomposition mechanism but assumed that potassium chlorate decomposes simultaneously in two ways:

$$2KClO_3 \longrightarrow 2KCl + 3O_2$$

$$4KClO_3 \longrightarrow 3KClO_4 + KCl$$

Potassium perchlorate forms between 270°-310°C and has been reported to decompose at 400°C.[176] However, yields as high as 55% perchlorate have been obtained by heating potassium chlorate as high as 550° for four hours.[139]

Visual observation of the decomposition of a single crystal of potassium chlorate, heated to 223° on a microscope stage, revealed no change for the first six hours. On further heating, rows of dark spots parallel to the edge of the crystal appeared. These developed until they presented the appearance of continuous broad lines. It was concluded that the decomposition is interfacial and proceeds from nuclei on the surface.[38]

Catalytic Decomposition. Many substances, including some trace impurities normally present in commercial chlorate, will affect the rate of thermal decomposition of chlorates, and in some instances may affect the course of the reaction. Catalyzed decomposition yields chloride and oxygen at high temperatures and perchlorate and chloride at moderate temperatures, similar to the termal decomposition. The chloride formed was thought to catalyze one or the other of these reactions. This was substantiated by various investigators[95, 158] who found that potassium chloride accelerated the decomposition into potassium perchlorate, making the reaction autocatalytic. The thermal decomposition of potassium chlorate and chlorate-chlorite mixtures have been studied to

determine the effect of the chloride upon the decomposition. These studies revealed that the activity of the chloride depends on the history of each specimen; certain specimens accelerate the evolution of oxygen, while others favor the formation of the perchlorate. Analytical potassium chloride dried at 110° for two hours catalyzed the decomposition so that the mixture evolved gas at a lower temperature and more quickly than the pure chlorate. Potassium chloride prepared by the thermal decomposition of potassium perchlorate and analytical potassium chloride heated to 600°C for one hour increased the rate of formation of the perchlorate, producing thereby only a slight increase in oxygen. An induced formation of potassium perchlorate was observed in the ternary mixture of $KClO_3$-KCl-$KClO_4$. The results were interpreted to indicate that the formation of the perchlorates was due to the ability of certain specimens of potassium chloride to absorb nascent oxygen. It was suggested that in the various mixtures, a real equilibrium is obtained in which the perchlorate and chlorate are continuously formed and decomposed.[69, 70]

Radiotracer studies have disproved the proposition proposal that formation of potassium perchlorate in the decomposition reaction was due to a transfer of atomic oxygen from the chlorate ion to a chloride ion. No radioactive perchlorate was formed from the thermal decomposition of a mixture of ordinary chlorate and labeled chloride. Further, the chloride was found not to undergo isotropic exchange with chlorate or perchlorate.[18, 26] Other halides beside chlorides, also catalyze the decomposition reaction.[133]

Oxygen is commonly obtained in the laboratory by the thermal decomposition of chlorates. Manganese dioxide is generally added to the chlorate so that the oxygen is liberated more rapidly and at a lower temperature. The evolution of oxygen from mixtures of potassium chlorate and manganese dioxide starts at 70° C and becomes strong at 100° C. (120) Manganese dioxide, as a catalyst for the reaction, undergoes no permanent change during the reaction. Until recently, the way in which manganese dioxide promoted the decomposition of potassium chlorate was not known. It was thought to contribute no oxygen, for the weight of the latter obtained was always 39.2 percent of the weight of the chlorate used, irrespective of the presence of manganese dioxide. Although manganese dioxide is a classical catalyst used in the thermal decomposition of the chlorates, many other compounds will also catalyze this reaction, e.g., Co_2O_3, Cr_2O_3, Fe_2O_3, Ni_2O_3, CuO, TiO_2, etc. Silicon dioxide lowers the decomposition temperature of sodium chlorate by 70°, manganese dioxide lowers the temperature by 180° and potassium chloride lowers the temperature by 60° C. (40)

Oxygen of the highest purity, containing less than 0.25 volume percent chlorine, results from the MnO_2-catalyzed decomposition of potassium chlorate. This is obtained by use of low activity MnO_2, unpulverized MnO_2 and a gram ratio of $KClO_3$: MnO_2 either 5:1 or 1:5. Irradiation of the MnO_2 with ultraviolet light increases the chlorine content of the oxygen. (123)

Recently the mechanism of the catalytic action of manganese dioxide on the decomposition of potassium chlorate was studied by the use of

heavy oxygen as an isotopic tracer.[27, 61, 62] Both oxygen labeled MnO_2 - ordinary $KClO_3$ and ordinary MnO_2 - oxygen labeled $KClO_3$ mixtures were investigated. Heating these mixtures revealed that some portion of the evolved gas was originated from manganese dioxide. The MnO_2 loses some oxygen and then regains oxygen from the chlorate during the decomposition. It appears that the manganese is undergoing a cyclic oxidation and reduction process. It was ascertained that the exchange reaction of oxygen atoms between manganese dioxide and gaseous oxygen is improbable at any temperature below 350°. It was concluded that in the thermal decomposition of potassium chlorate in the presence of manganese dioxide an unstable intermediate compound is formed between the two and that gaseous oxygen is evolved by the decomposition of this intermediate. Comparison of the concentrations of heavy oxygen in the gases evolved at different stages of the decomposition showed that the active part capable of forming the intermediate compound with potassium chlorate is only a limited part of the manganese dioxide catalyst and such an active part readily loses its activity by such a severe treatment as heating it at high temperatures "in vacuo."

Similar evidence for an intermediate has been obtained in susceptibility tests. The results were interpreted as showing that the mechanism of catalyzed decomposition of potassium chlorate by manganese dioxide involves the formation of an intermediate compound. Similar experiments on potassium chlorate and ferric oxide indicate no intermediate is formed.[11]

More recent investigations on the mechanism of manganese catalysts indicate a change in the oxidation state of manganese occurs during reaction. The manganese catalyst, regardless of the oxidation state of manganese at the beginning of a reaction, exists in a mixture of oxidation states at the end of the reaction. Most of the manganese ended with an oxidation state of +3 to +4, although a small fraction of it existed as water soluble permanganate. Potassium permanganate decomposes at 240°, far below the reaction temperatures. Therefore, permanganate must form and decompose in the reaction mixtures. This conclusion is borne out by the fact that when potassium permanganate was used as a catalyst, as much as 14 percent of the manganese could be extracted as permanganate from the reaction residue, even after heating for 21 hours at a temperature 126° above the decomposition point of potassium permanganate. These authors also compared the catalytic action of rhenium compounds in the decomposition reaction. For the rhenium catalysts, regardless of the oxidation state of the rhenium at the beginning of a reaction, at the end of the reaction all the rhenium existed only as a water soluble compound, giving the perrhenate absorption spectrum. All the manganese catalysts, although showing a variety of activity, exibited a continued type catalysis. Rhenium compounds, on the other hand, gave catalytic action for a short time only, and did not cause a continued type of chlorate decomposition. The above facts were explained by the theory that catalytic decomposition of potassium chlorate occurs only during a change in oxidation state of the manganese or rhenium. Since perrhenate is very stable, catalysis stops with the rhenium

compounds as soon as rhenium is oxidized to perrhenate. On the other hand, since MnO_4^- (or MnO_4^{--}) is relatively unstable, it decomposes as formed, and a cyclic oxidation and reduction of the active manganese atoms results so that a continued catalysis occurs. (28)

The concept of the change in oxidation state of the manganese during the decomposition reaction is not new. (10) The following equations have been suggested to represent the reaction:

$$9MnO_2 + 2KClO_3 \longrightarrow 3[Mn(MnO_4)_2] + 2KCl \text{ and}$$

$$3[Mn(MnO_4)_2] \longrightarrow 9MnO_2 + 3O_2.$$

The kinetics of the solid-phase reaction of the system $KClO_3$-MnO_2 has been studied. The amount of oxygen evolved was found proportional to the time of heating below about 335°. Above this temperature, the effect of the diffusion process appeared in such a manner as to decrease the amount of oxygen evolved. The diffusion activation energy was 75 kcal from the experiments with 200-300 mesh powders and the rate, v, was expressed by:

$$v = \left[1 - (1 - x)^{1/3}\right]^2 \frac{r}{t},$$

where r is the average radius of $KClO_3$ powder and x is the fraction decomposed. (225)

Above the melting point of potassium chlorate, 380°, a homogeneous reaction of the second order occurs in the fused phase with the rate proportional to the concentration of both components. The activation energy for this process was found to be 44 kcal. The addition of $KmnO_4$ or K_2MnO_4 in place of MnO_2 made no difference in the kinetic behavior; potassium

perchlorate was not detected. This suggests a different mechanism from the simple decomposition of potassium chlorate. The effect upon the reaction of substances other than manganese dioxide were examined. The rate of reaction with added potassium salts increased in the order:

$$KCl < K_2SO_4 < KBr < K_2CO_3.$$

Other oxide additives were examined, greater reactivity being obtained with additives of stronger acidity. In general, substances which form unstable intermediates were found to be effective catalysts for the decomposition of potassium chlorate.(225)

In another kinetic study, the velocity of decomposition of potassium chlorate was found to be dependent upon the ratio of catalyst, MnO_2, to chlorate. Temperature had little effect on the reaction velocity below 275°; the effect increased gradually above this temperature. The reaction is autocatalytic above 300°. The decomposition is not complete at constant temperature and the completeness of the reaction depends upon the temperature of the experiment and the composition of the mixture.(168)

The catalytic decomposition of potassium chlorate-manganese dioxide mixtures have been studied. Above an upper limit of manganes dioxide, the reaction of velocity was found to become constant. At 300-330°C where the rate was high, examination showed a completely black reaction mixture in which it was impossible to distinguish between potassium chlori and potassium chlorate. With the fused chlorate, the crystals decompose into smaller crystals even at 256° C. The catalysis is not due to fusion of KCl-$KClO_3$ eutectic as this melts at 340° C, a temperature above the

temperature of the experiments. The potassium chloride crystals retain their original form of the potassium chlorate, showing isochromatic rings and hence, an anistropic system. The decomposition occurs at the point of contact of potassium chlorate and manganese dioxide, which move and penetrate the surfaces of the mosaic crystal. Fused chlorate is more reactive because of the higher dispersity of the elementary crystals (6)

The catalytic activity of certain oxides on the decomposition of potassium chlorate has been studied. (124) Mixtures, in which the ratio of potassium chlorate to metal (in catalyst) was ten to one, heated at 275°, showed by measurement of the rate of oxygen evolved the following decreasing order of catalytic activity:

$$Co_2O_3 > Cr_2O_3 > MnO_2 > Fe_2O_3 > Ni_2O_3 > CuO > TiO_2 \ (330^\circ C).$$

No test for chlorine in the evolved gas was obtained. Similar experiments were made with the mixtures of potassium chlorate and vanadium chloride or sulfates of titanium, chromium, manganese, iron, cobalt, nickel and copper at 230-305°. Catalytic activity in decreasing order was found to be: chromium > cobalt > manganese > titanium > iron > nickel > copper > vanadium. Commercial MnO_2 has been found a more effective catalyst than c.p. material in the decomposition of $KClO_3$. This is ascribed to the presence of 8 8% Fe_2O_3 in the former. Experiments with mixtures of these two oxides, show that each oxide is a promoter for the other. The action of CuO and MnO_2 as mutual promoters was also demonstrated. (150)

Of all the substances which catalyze the thermal decomposition of potassium chlorate, Cr_2O_3 is claimed to be the most efficient from the standpoint of low temperature and speed of reaction. As little as one percent by weight will work satisfactorily and it is useless to employ more than five percent. The catalytic cycle involves potassium dichromate, which functions equally well as a catalyst. Contrary to the previous work cited, some chlorine is evolved, but as it is removed by collecting over water, this is no disadvantage. The following advantages are claimed in preparing small quantities of oxygen by this method: The reaction proceeds smoothly at a relatively low temperature and may be stopped at any time by cooling; when all the oxygen is evolved the contents of the tube solidify; more potassium chlorate may be added if desired without more catalyst; the test tube is easily washed out with water. (144)

In an early study, the minimum temperature and the various proportions of ferric oxide for the spontaneous decomposition of potassium chlorate were examined. The history of the specimen is an important factor in making a determination of the spontaneous decomposition temperature. Heat was found to be detrimental to ferric oxide as a catalyst. When iron oxides are heated, they lose their catalytic effect on the decomposition of potassium chlorate. A sudden evolution of chlorine at 120° was attributed to be due to ammonium chloride impurity in the ferric oxide. (24,25)

Considerable disagreement on the effect of water on the decomposition of chlorates has been noted in the literature although no recent work on the subject has been found. Water was found to promote the

manganese dioxide decomposition of potassium chlorate.[141] Water of hydration was found to lower the decomposition temperature also with ferric oxide and ferroso-ferric oxide catalysts. With each degree of dehydration the decomposition temperature was raised a corresponding amount.[25] On the other hand, one investigator found water to exert no definite influence.[5]

Effect of Radiation. Much evidence has been presented to show the decomposition effect on irradiating chlorates. Potassium chlorate exposed to the Heavy Water pile decomposed, liberating oxygen.[86] Irradiated sodium chlorate decomposed into NaClO and NaCl. It appeared likely that sodium perchlorate was produced during radiation from the direct oxidation of sodium chlorate, rather than by direct oxidation of sodium chloride.[180] Solid potassium chlorate evolved oxygen when irradiated by radiation of wavelengths shorter than about 2800 Å. The decomposition was also brought about by the impact of 22-volt electrons.[51] On the other hand, when sodium chlorate was irradiated with amounts of X-rays of up to 24 m. e. v., there was no measurable amount of the chlorate noted by the incident rays.[140] Ultraviolet light promotes the catalytic decomposition of potassium chlorate at room temperature.[167]

Potassium chlorate is converted to CKlO and KCl when subjected to the glow discharge of a Tesla coil in vacuo.[10] The same salt, when subjected to an electrodeless discharge for a period of 7 hours, smelled of chlorine gas and gave a test for KClO.[135] Potassium chlorate,

catalyzed with irradiated manganese dioxide, will also produce some chlorine gas.[123]

Effect of Pressure. No recent work has been uncovered on the effect of pressure upon the thermal decomposition of chlorates. An early review of the effect of pressure on chemical reaction cites the work on the effect of pressure upon the decomposition of potassium chlorate.[22] The effect of pressure is clearly shown in the following results obtained with potassium chlorate: at 125°C, oxygen is evolved from a mixture of manganese dioxide and potassium chlorate if the pressure is below 0.1 mm of mercury but not at atmospheric pressure; at 175°C, oxygen is evolved from the same mixture at 2-3mm pressure of mercury but not at atmospheric pressure; at 300°C, the same mixture decomposes almost explosively at atmospheric pressure but will remain 90 percent undecomposed after 7 hours at 32° if the pressure is above 300 atmospheres.[23] Other investigators attempted unsuccessfully to oxidize potassium chlorate to potassium perchlorate at oxygen pressures as high as 1200 atmospheres; the chlorate began to decompose rapidly at 475°C, the highest temperature tried.[45]

Pressure also has a marked effect on the rate of decomposition of potassium chlorate in the presence of manganese dioxide within the range of 70° to 350°C. At each temperature a pressure exists above which decomposition is very slow or absent. The reaction was not retarded due to approach to equilibrium. When the retarding pressure had been reached at any temperature, a lowering of the temperature did not result in recombination of oxygen with the potassium chloride and the pressure

decreased only as would be expected from the gas laws. The data also shows that potassium chlorate - manganese dioxide mixtures under pressures of 200 to 500 atmospheres, may contain undecomposed potassium chlorate after being held for hours at temperatures much greater than their spontaneous decomposition temperature at atmospheric pressure.(141)

Other Chlorates

Aluminum chlorate occurs as the hexa-or ennea-hydrate. The anhydrous salt has not been obtained on account of its decomposition when heated. The salt explodes at 100°C if slowly heated owing to the evolution of chlorine dioxide. If the salt is heated rapidly, there is no explosion and chlorine is evolved and a basic perchlorate remains.(143)

Solid ammonium chlorate decomposes spontaneously in air. The course of the decomposition is probably very slow autoxidation with the formation of nitric acid, nitrogen, chlorine and water. The nitric acid reacts with more chlorate, forming chloric acid and chlorine peroxide. These products oxidize more chlorate with the formation of more nitric acid and chlorine. The rate of reaction tends to increase unless the acid gases formed are removed quickly. Perchloric acid does not appear to be formed. The relative amounts of the products vary with the conditions under which the decomposition takes place. The solid residue from the decomposition is ammonium nitrate with no chloride.(58) Another investigator gives the decomposition temperature of ammonium chlorate as 102°C. The products of the decomposition are listed as chlorine, nitrogen, water,

hyponitrous acid, a little oxygen and ammonium chloride.[143] The heat of explosion of ammonium chlorate is 537 cal per kg and its temperature of explosion is 1733°.[149]

Barium chlorate monohydrate loses water of hydration at 120°C Some oxygen is evolved if the compound is heated to 250°C and the salt melts at about 400°C. The decomposition residue contained both barium oxide and barium chloride. Other investigators have not found any decomposition below 300°C. Between 378° and 383°C, the decomposition is reported to proceed according to the following equation[143]

$$2Ba(ClO_3)_2 \longrightarrow BaCl_2 + Ba(ClO_4)_2 + 2O_2$$

Dihydrated calcium chlorate melts in its water of crystallization at 100°C, and if heated slowly, all the water can be expelled. Decomposition of the calcium salt proceeds according to the following equations

$$2Ca(ClO_3)_2 \longrightarrow 2CaCl_2 + 6O_2$$

$$2Ca(ClO_3)_2 \longrightarrow 2CaO + 2Cl_2 + 5O_2$$

The first equation greatly predominates.[143]

The literature values for the melting point of $LiClO_3$ $1/2$ H_2O vary from 50° to 65°C. The hydrate becomes anhydrous in dry air at 90°C.[143] The melting point of the anhydrous salt is 124°-129°C and decomposition begins at 270°C.[120, 143] As the temperature is increased, the rate of decomposition reaches a maximum and then gradually decreases This is due to the formation of lithium perchlorate by a side reaction

$$4LiClO_3 \longrightarrow LiCl + 3LiClO_4$$

which accompanies the direct decomposition

$$2LiClO_3 \longrightarrow 2LiCl + 3O_2$$

Magnesium chlorate hexahydrate melts at 35°-40°C. The crystals decompose into water, oxygen, chlorine and a residual magnesium oxide at 120°C, and if heated slowly, some magnesium chloride is formed as well. At 35°C, the hexahydrate passes into tetrahydrate magnesium chlorate At 65°C, the hexa- or tetra-hydrate forms the dihydrate. At 80°C, the dihydrate slowly decomposes, forming a basic salt and hence, the anhydrous magnesium chlorate has not been prepared.(143)

Like potassium chlorate, silver chlorate does not change in dry or moist air. The salt melts at 230°C and decomposes at 270°, leaving a residue of silver chloride. With very rapid heating, the salt may decompose explosively.(143)

Solid Reactions

Potassium chlorate is an excellent oxidizing agent. The reaction is explosive with sulfur or organic material. Large amounts of potassium chlorate are used in the manufacture of matches, pyrotechnics, and certain explosive mixtures.(197)

The catalytic reaction of various forms of carbon with solid potassium chlorate have been studied. Bakelite and potassium chlorate were 15% reacted in 5 hours at 367°C. Novolac and potassium chlorate were 30% reacted in 5 hours at 367°C. Both mixtures ignited on addition of lithium chloride. Carbon black and potassium chlorate at 343°C in the

presence of lithium bromide ignited. LiCl, $BaCl_2$, KCl and NaCl accelerated the reaction; K_2SO_4, Al_2O_3, Li_2SO_4 and talcum had no effect upon the reaction and K_2CO_3 caused a slight inhibition; and Li_2CO_3 and both potassium ortho - and metaphosphates caused a strong inhibition on the reaction. The reaction velocities at temperatures near the ignition points depended on the size of the samples. K_2CO_3 had no effect on the reaction of Nuchar and KClO3 at 320°C; KCl, KBr, KI and K_3PO_4 inhibited, and LiBr accelerated the reaction. With LiCl, the mixture ignited. KCl had no effect on the reactions of graphite and $KClO_3$ at 450°, while KBr, K_2CO_3, potassium ortho-and metaphosphates, LiCl, LiBr and KI accelerated the reaction. Polystyrene and potassium chlorate gave no reaction. Results with carbon black, Nuchar and graphite agree with the parabolic equation, $kt = \left\{1 - [(100-x)/100]^{1/3\ 2}\right\}$ where x is the amount of reaction product, for the first part of each reaction, deviations becoming marked with further reaction. The catalyst may participate in the transition complex of the reactants, thus lowering the energy of activation needed for its formation, or it may participate in the reaction in the form of an unstable oxygenated intermediate, thus serving as an oxygen carrier.(165)

Mixtures of potassium chlorate with various combustible sub stances (carbon black, paraffin wax, starch and asphalt), when heated at relatively low temperatures ignite in most cases, at temperatures at which neither the combustible substance by itself, nor the oxidant by itsel undergoes any appreciable chemical change.(162) (See also under Solid Reactions of Perchlorates).

Mixtures of sulfur and chlorates of silver, potassium and barium ignited at 74°, 160-162° and 108-111°C respectively.[207] Later investigations revealed that mixtures of sulfur and chlorates treated with chlorine dioxide did not react until the chlorine dioxide had begun to decompose. Sulfur dioxide produced an explosion with a mixture of potassium chlorate and sulfur at 100°C whereas sulfur subchloride produced no explosion with the same mixture, even at 140°.[208]

The reduction of potassium chlorate takes place at ordinary temperature with hydrogen, giving potassium chloride and water and at 380° with ammonia with liberation of chlorine and formation of potassium nitrate. By reaction with hydrogen in a silent electric discharge, the following chlorates were converted to the respective chloride and water: $NaClO_3$, $Ca(ClO_3)_2$[148]; $LiClO_3$[147]; and $Ba(ClO_3)_2$[146]. Potassium chlorate acts on phosphorous oxychloride according to the equation[108]

$$KClO_3 + 2POCl_3 \longrightarrow P_2O_5 + KCl + 3Cl_2$$

but has little action on phosphorous pentachloride at room temperature. However, when a mole of PCl_5 is melted with three moles of $KClO_3$, chlorine, and chlorine dioxide, and potassium chloride and phosphoryl chloride are formed.[143]

The explosive mechanism of potassium chlorate and sodium has been investigated. The following equations are presented as indicating the chemical changes taking place on heating these substances

$$2KClO_3 + 4Na_2 \longrightarrow 4Na_2O + K_2O + Cl_2O$$

$$2KClO_3 + Na_2 \longrightarrow Na_2O + K_2O + 2ClO_2$$

$$2KClO_3 + 2Na_2 \longrightarrow 2Na_2O_2 + K_2O + Cl_2O$$

$$2KClO_3 + Na_2 \longrightarrow Na_2O + K_2O_4 + Cl_2O$$

The above four equations may be regarded as taking place simultaneously.(126)

Mixtures of potassium chlorate with ammonium salts and related compounds react violently according to the approximate basic equation:

$$30\,KClO_3 + 20\,NH_4X \longrightarrow 20KX + 4KNO_3 + 6KCl + 24HCl$$
$$+ 18O_2 + 6HNO_2 + 2HNO_3 + 4N_2 + 24H_2O$$

where X is an acid radical.(82) The reaction with ammonium nitrate begins at 120°, proceeds rapidly to 250° and ends at 300°, where the potassium nitrate phase begins.(176)

The system $KClO_3 + AgNO_3 \rightleftharpoons KNO_3 + AgClO_3$ was investigated. The binary system $KClO_3$-$AgNO_3$ was stable whereas the binary KNO_3-$AgClO_3$ was metastable. The exchange reaction proceeded in the direction of the formation of the higher melting component, potassium chlorate.(47)

Thermodynamic calculations have shown the reaction temperature of the system $NaI \cdot 2H_2O + KClO_3 \rightleftharpoons NaClO_3 + KI + 2H_2O$ to be slightly above room temperature. The reaction temperature, as determined experimentally, was found to be 29.8°.(77)

Dusts of nitrates, chlorates and perchlorates of potassium have been investigated as flame extinguishers. Sodium chlorate and potassium chlorate or perchlorate have been found to activate a hot flame but will

extinguish a cool flame. Flames of hydrogen, illuminating gas, methane, and carbon monoxide were used.[48]

Perchlorates

Preparation

Laboratory preparations of the perchlorates covered by this survey are given in this section. Electrolytic methods are now commonly employed in the commercial preparation of perchlorates. The reader is referred to Chapter 2 for industrial production methods.

The most common types of reactions involved in the formation of perchlorates are metathesis and oxidation-reduction reactions. The former is the most widely used in laboratory preparations while the latter is mostly confined to electrolytic and thermal decomposition processes. In the synthesis utilizing metathesis, a readily available perchlorate such as potassium or ammonium perchlorate or more usually, perchloric acid, is reacted with a salt of the desired cation; the new chlorate is isolated by means of physical processes, such as crystallization, solvent extraction, distillation, etc. Preparation by means of thermal decomposition is generally not employed because of the diversity of products and inherent low yields.

Many of the perchlorates are deliquescent and highly hydrated. Since the perchlorates are in general thermally more stable than the chlorates, they can usually be obtained in anhydrous state by careful heating or evaporation in vacuo.

In the following sections, preparations for the individual perchlorates are found. Specific directions for preparation are not given

as most of these compounds are now commercially available in high purity. Reference to the original articles should be made for detailed directions for their preparations.

Aluminum Perchlorate

Colorless, deliquescent cubes of aluminum perchlorate are obtained by evaporating a solution containing aluminum chloride and perchloric acid until all the hydrochloric acid is displaced, and letting the concentrated solution stand over sulfuric acid. (143, 218)

Ammonium Perchlorate

Ammonium perchlorate is prepared commercially by the action of ammonia and hydrochloric acid on electrolytic sodium perchlorate. This compound is most useful in the laboratory preparation of other metal perchlorates by virtue of its ease of formation of perchloric acid upon acidification with a mixture of nitric and hydrochloric acids. (120) Earlier preparations have included metathetical reactions between solutions of the following salt pairs: barium perchlorate-ammonium sulfate; sodium perchlorate-ammonium chloride or nitrate; and magnesium or calcium perchlorate-ammonium chloride. In the first salt pair, barium sulfate is precipitated leaving ammonium perchlorate in solution, while in the other cases, the much higher solubilities of the chlorides allows crystallization of the ammonium perchlorates from the reaction solution on cooling. (143) Another preparation calls for passing ammonia gas into dilute perchloric acid solution, from which the salt is recrystallized and dried at 110°. (221)

Barium Perchlorate

Barium perchlorate is prepared from ammonium perchlorate and barium hydroxide.[196] It can also be made by evaporating a solution containing barium chloride and an excess of perchloric acid. The barium chlorate is recrystallized and dried to constant weight, yielding the dihydrate. When the crystals are dried over sulfuric acid the monohydrate is obtained.[221] The anhydrous salt is prepared by heating to 140° in vacuo.[36] It has also been made by the following reactions: perchloric acid and barium hydroxide or carbonate; potassium perchlorate and hydrofluosilicic acid followed by neutralization with barium carbonate; boiling aqueous solution of potassium chlorate and zinc fluosilicate. On a manufacturing scale it was prepared by evaporating a mixed solution of sodium perchlorate and barium chloride.[143] A good yield of barium perchlorate was obtained by reaction of solid barium carbonate with solid ammonium perchlorate at elevated temperature and pressure.[196]

Calcium Perchlorate

Calcium nitrate is converted into the perchlorate by evaporating with excess perchloric acid. The excess acid is neutralized by pure calcium carbonate, the solution centrifuged and the supernatant liquid decanted. The calcium chlorate crystallized contains four molecules of water of crystallization. The anhydrous compound is obtained by heating and drying to constant weight at 250°.[221]

Lithium Perchlorate

Lithium perchlorate is prepared from the corresponding carbonate and perchloric acid solution.[177] The anhydrous salt is extracted with alcohol[183] or ethyl ether.[8] Another preparation uses lithium fluoride, which is precipitated by the addition of hydrogen fluoride to a lithium nitrate solution. The lithium fluoride is converted to perchlorate by evaporating with perchloric acid. The product from aqueous solution recrystallized from water to give the trihydrate. The trihydrate is dehydrated in a current of air at 250°.[220] Lithium chloride can also be employed in place of the fluoride, the hydrogen chloride and excess perchloric acid being expelled on evaporating to dryness.[143]

Magnesium Perchlorate

Magnesium perchlorate is prepared by adding an excess of magnesium oxide to a 30% perchloric acid solution, filtering, neutralizing the filtrate with perchloric acid to a weakly acid reaction, evaporating and cooling. The crystals obtained are filtered and recrystallized from a small amount of water yielding needle-like crystals of the hexahydrate of magnesium perchlorate. The hexahydrate is converted to the trihydrate and finally the anhydrous compound by heating in vacuo.[2, 194, 219] A good yield of magnesium perchlorate was reported for the reaction of solid magnesium carbonate with solid ammonium perchlorate at elevated temperature and pressure.[196]

Potassium Perchlorate

This compound is available commercially in high purity. It is produced by reaction of potassium chloride with electrolytic sodium perchlorate in a separate step from the electrolysis. Potassium perchlorate is prepared in the laboratory by neutralizing pure potassium carbonate with perchloric acid, recrystallizing, and drying at 250°. It can also be made by the oxidation of the corresponding chlorate. One method requires adding 125 parts of the chlorate to 360 parts of lead dioxide in the form of a paste suspended in sulfuric acid with stirring at 50° and refluxing. The hot filtered solution is cooled, giving potassium perchlorate in the expected yield.[156] Another method oxidizes the chlorate with a concentrated acid. Sulfuric, nitric and phosphoric acids gave yields of potassium perchlorate of 11%, 30% and 15%, respectively.[131] It has also been made by reaction of perchloric acid or a solution of sodium perchlorate with a solution of a potassium salt - chloride, nitrate, acetate, etc. The excess sodium salt is removed by washing with alcohol and the residual sodium perchlorate recrystallized from boiling water.[143]

Silver Perchlorate

Silver oxide reacts with perchloric acid to form silver perchlorate. The solution is filtered and evaporated until crystals begin to appear. After cooling, the material is filtered in a centrifuge, from which crystals can be taken in a condition nearly dry. The silver perchlorate is finally dried in an oven at 110° for two hours.[73, 88] It is also made by a

metathesis reaction between barium perchlorate and silver sulfate.[143]

Sodium Perchlorate

This salt is the basic building block for the synthesis of other perchlorates. It is made by the electrolysis of sodium chlorate. Sodium perchlorate may be prepared in the laboratory from the corresponding carbonate or hydroxide and perchloric acid solution.[143] The anhydrous sodium perchlorate is obtained by crystallizing n aqueous solution above 50° while deliquescent monohydrated crystals are obtained below 50°. The product is dried in a current of dry air at a temperature of 250°.[220]

Reactions in Aqueous Solution

In general, the perchlorates are not as strong oxidizing agents as their corresponding chlorates. In acid solution, the stable perchloric acid is usually formed, which accounts for the stability of perchlorates towards reduction by acids - indeed most of the reactions between perchlorates and acids are of the metathetical type. This is in marked contrast to the analogous situation in acidic chlorate solutions, where due to the inherent instability of chloric acid, these solutions are easily susceptible to reduction by most common reducing agents. Such reducing materials as ferrous sulfate, zinc in the presence of either KOH or dilute mineral acids, Al in the presence of dilute H_2SO_4, and so on, either not at all or only slightly reduce perchlorates.[214] In order to effect a rapid reduction of perchlorate, either severe reaction conditions or a catalyst is required.

Metathesis. Due to the stability of the perchlorate ion, almost all reactions of perchlorates in dilute aqueous solutions are of the metathetical (double decomposition) type. Since a great deal of the work along this line has been carried out prior to 1900, only representative types of reactions will be presented here with no attempt to include all the reactions studied. Most of the reaction types presented below are applicable to any perchlorates whose metallic ions have similar chemical properties.

Metathesis reactions involving perchlorates are of three types: (1) reactions with perchloric acid; (2) reactions forming perchloric acid; and (3) reaction of perchlorate salts. All three types have been used in the preparation of perchlorates (Section entitled "Perchlorates") or perchloric acid (Section entitled "Perchloric Acid"). There is a certain interrelation between types (1) and (2) as pointed out below.

In the first type, perchloric acid reacts with a metal oxide, base or salt to form the corresponding metal perchlorate and either water or the acid of the salt. Typical examples of this type of metathesis are:

$$MgO + 2HClO_4 \longrightarrow Mg(ClO_4)_2 + H_2O$$

$$Ba(OH)_2 + 2HClO_4 \longrightarrow Ba(ClO_4)_2 + 2H_2O$$

$$AgNO_3 + HClO_4 \longrightarrow AgClO_4 + HNO_3$$

The second type of reaction is the reverse of the salt plus perchloric acid reaction given above, namely, a strong acid acting on a metal perchlorate. Obviously, these two types represent a single system in equilibrium. As to which direction the reaction will take depends upon the specific nature of the

salt and the reaction conditions, such as concentration, temperature, etc.

An example of the second type of metathesis reaction is

$$Ba(ClO_4)_2 + H_2SO_4 \longrightarrow 2HClO_4 + BaSO_4$$

In this case, the reaction proceeds readily due to the insolubility of the barium sulfate formed; the removal of the barium sulfate from the reaction phase shifts the equilibrium to the right in the equation shown until the concentration of barium ion in solution approaches the solubility product of the barium sulfate.

The third type of metathesis reaction is a simple double decomposition involving a perchlorate and another salt, as given in the following examples

$$NaClO_4 + NH_4NO_3 \rightleftharpoons NH_4ClO_4 + NaNO_3$$

$$Ca(ClO_4)_2 + Na_2CO_3 \rightleftharpoons 2NaClO_4 + CaCO_3$$

Again, this type of reaction is strictly an equilibrium reaction and many times the reaction can be reversed by a change in the reaction conditions.

Oxidation-Reduction. Potassium perchlorate has been reduced by hydrogen generated in an external vessel and passed into solution through filter-paper or parchment.[143] Perchlorates are acted upon by fluorine as given by the following sequence of reactions[60]

$$2HClO_4 + F_2 \longrightarrow Cl_2O_8 + 2HF$$

$$Cl_2O_8 + H_2O \longrightarrow HClO_4 + HClO_5$$

$$HClO_5 + H_2O \longrightarrow HClO_4 + H_2O$$

Bromine also reduces perchloric acid with the liberation of chlorine according to the equation[107]

$$2HClO_4 + Br_2 \longrightarrow 2HBrO_4 + Cl_2$$

A similar reaction occurs with an aqueous solution of iodine when heated[104], viz.,

$$2HClO_4 + 4H_2O + I_2 \longrightarrow 2H_5IO_6 + Cl_2$$

Whereas the reduction of a chlorate with a metal in acid solution occurs preferentially with practically no evolution of hydrogen in most cases, with a perchlorate, the metal perchlorate is formed and hydrogen is liberated in all cases with dilute solutions.[143] Examples of this are zinc and magnesium in dilute acid perchlorate solutions. The heavy metals dissolve slowly if at all. The rate of dissolution of silver in ferric perchlorate is hindered by adsorption of the silver perchlorate formed in the reaction on the silver.[118]

The action of acids on perchlorates usually results in a metathetical reaction with formation of perchloric acid, as discussed above. However, under more severe reduction conditions, such as boiling 40 percent sulfuric acid or boiling concentrated nitric acid, perchlorates are converted to chlorine and oxygen.[143] Chromium is oxidized to chromic acid by 72 percent perchloric acid at 180-200°.[120] A nitrosyl salt $NO(ClO_4)$, made by heating concentrated perchloric acid with nitrous fumes, has been reported.[183] Perchloryl fluoride is formed by reaction of $KClO_4$ with HSO_3F.[224]

Perchlorate ion is reduced by trivalent titanium in acid solution, by some of the lower valencies of vanadium and molybdenum, and

slowly by chromous salts.[175] Perchlorates are also easily reduced by thiosulfate.[183] Titanium trichloride is one of the few substances found that will reduce perchlorates but not chlorates. This fact was the basis of a procedure for the estimation of perchlorate.[122]

Kinetic measurements of the reduction of aqueous $HClO_4$ by trivalent Ti and Mo, and divalent Cr in solutions containing HCl and H_2SO_4, showed that in dilute solutions, the concentration of the HCl or H_2SO_4 has only a slight influence on the velocity of the reaction; but above a definite acid level, its influence increases almost linearly with concentration. Titanium was found to react faster than molybdenum and chromium under similar reaction conditions. For titanium, the form of the rate equation is of a lower order than that required by the reaction

$$8Ti^{+++} + ClO_4^- + 8H^+ \longrightarrow 8Ti^{++++} + Cl^- + 4H_2O$$

being first order in both $[Ti^{+++}]$ and $[HClO_4]$.[21] The addition of chloride ion retards the reaction, apparently owing to the formation of $TiCl^{++}$ ion. At high perchlorate concentrations (above 1M), the reaction rate becomes more than linear in $[ClO_4^-]$, probably due to the increased activity coefficient of the perchlorate ion. A four-step mechanism has been proposed to explain the data.[49]

The kinetics of the molybdenum catalyzed reduction of perchlorate by stannous ions in sulfuric acid solution follows a complex rate equation involving the concentrations of tin, perchlorate and molybdenum to fractional powers. Neither stannic nor chloride ions influence the kinetics.

Evidence for a direct bivalent reduction of molybdate is presented.[79] A similar study, catalyzed by tungstate, in hydrochloric acid, shows the reaction to be zero order with respect to stannous and first order with respect to perchlorate and tungstate. Catalysis is attributed to complex formation between tungstate and perchlorate. Apparently, chloride ions inhibit the catalysis by complexing with tungstate, thus competing with perchlorate ions for sites on the tungstate.[78]

Addition Compounds. A number of stable addition compounds are formed with perchlorates. Many perchlorates form stable insoluble ammines or ammoniates in aqueous solution, for example $[Ni(NH_3)_6](ClO_4)_2$ and $Ba(ClO_4)_2 \cdot 3NH_3$. Magnesium forms two ammines, $[Mg(NH_3)_2](ClO_4)_2$ and $[Mg(NH_3)_6](ClO_4)_2$.[5] The $LiClO_4$-NH_3 system has been studied in detail.[191] In general, these compounds are formed in those cases where definite hydrates of the perchlorate exist - the amine group replacing the hydrate group. Basic perchlorates such as insoluble $BiOClO_4$, $Ba(OH)ClO_4$ and $Cu(ClO_4)_2 \cdot Cu(OH)_2$ have also been reported.[120]

Irradiation and Exchange. Perchlorate ions are not decomposed in dilute solution when irradiated by X-rays. However, in concentrated solutions both ClO_3^- and Cl^- are obtained at the same rate over a range of temperature from -80° to + 20°. The decomposition energy of a ClO_4^- ion is 24.7 ev.[39]

There is no exchange of chlorine atoms in aqueous solution between perchlorate ion and chloride ions[41], chlorine dioxide[46] or

chlorate ions.[129] Oxygen does not interchange between perchlorate ions and water.[90, 222]

Reactions in Non-Aqueous Media

Inorganic Reactions. Potassium perchlorate reacts with liquid sulfur trioxide according to the equation[130]

$$3SO_3 + 2KClO_4 \longrightarrow K_2S_3O_{10} + Cl_2O_7$$

Potassium perchlorate can be isolated from a solution of silver perchlorate in hydrogen cyanide when treated with potassium cyanide, or if traces of moisture are present; but in the absence of either the equilibrium

$$AgClO_4 + HCN \rightleftharpoons AgCN + HClO_4$$

lies far to the left.[113] An ethyl ether solution of $LiAlH_4$ can be titrated quantitatively with $AgClO_4$, with formation of $AgAlH_4$. The reaction is probably ionic, involving the AlH_4^- ion.[114] Potassium perchlorate reacts with ammonia gas forming mainly nitrogen and water with a small amount of potassium nitrate.[94]

The most remarkable example in this category is the reaction of iodine with an ethereal solution of silver perchlorate. The silver is removed and a stable solution containing ClO_4, or probably the dimer $(ClO_4)_2$ is obtained. The latter reacts quantitatively with zinc and magnesium, forming perchlorates; with iron, tin and copper, forming salts of the metals of lower and of higher valence; it acts slowly and incompletely upon cadmium, bismuth and silver.[73]

In nitrobenzene or carbon tetrachloride, silver perchlorate reacts with iodine monochloride to precipitate silver chloride and form iodine perchlorate, $IClO_4$.[7] The $IClO_4$ cannot be isolated due to its immediate reaction with the solvent. For instance, with CCl_4 the following reaction occurs:

$$IClO_4 + CCl_4 \longrightarrow ICl + CCl_3ClO_4$$

With solvents containing hydrogen attached to carbon, the hydrogen is replaced by iodine:

$$-C-H + IClO_4 \longrightarrow -C-I-HClO_4$$

This reaction is a basis of iodination of organic compounds; calcium or magnesium is usually added to remove the perchlorate as the insoluble metal perchlorate as well as water produced in the reaction.[12, 183]

Organic Reactions. A large wealth of data is available in the literature on the use and reactions of perchlorates and perchloric acid with organic substances. This material is beyond the scope of this investigation - only a few characteristic examples of these reactions will be discussed here. The reader is referred to References 31, 120 and 183 for further examples and details.

Owing to the exceptional ability of perchloric acid to ionize, it can form normal salts even with very weak organic bases, e.g., triaryl amine perchlorate, $[Ar_3NH]\cdot(ClO_4)$, the only known salts of these amines[183]. Perchlorate salts of normal amines are well-known, for instance, with aniline, $C_6H_5NH_2\cdot HClO_4$.[198] There is also a series of

abnormal "tetravelent" nitrogen salts of the type $[Ar_3N]\cdot(ClO_4)$, which are odd molecules.[183] The perchlorates of carbonium, oxonium and diazonium bases can be readily made.[120]

Metal perchlorate addition compounds are formed with many organic substances. The most remarkable along this line is the silver salt. For instance, it forms addition complexes with pyridine[183], acetylene[66, 213], dioxane[37] and polystyrene[57] to name a few. The pyridine-$AgClO_4$ complex can further react with bromine or iodine to form $[Br, py_2](ClO_4)$ or $[I, py_2](ClO_4)$, respectively.[183] With pyridine, many bivalent perchlorates form addition compounds of the type: $M(ClO_4)_2\cdot npy$, where n varies from 4 to 8 moles of pyridine per mole of metal perchlorate.[187, 188, 189]

In organic oxidation reactions, again silver perchlorate stands in a peculiar class of its own, not shared by the other perchlorates. It may act in three ways: (1) by replacing halide by ClO_4; (2) by forming with nucleophilic substances and catalyzing reactions of the Freidel-Crafts type; (3) by oxidation in which Ag and not ClO_4 is the oxidant.[33] It reacts with MeI and $PhCH_2Br$ to give the respective perchlorates.[29, 170] In the catalytic acetylation[34] and alkylation[30] of aromatic compounds, only $AlCl_3$, $SbCl_3$ and $FeCl_3$ are superior to AgClO as a catalyst.[35] Silver perchlorate reacts with silanes of the type R_3SiH to give R_3SiClO_4, silver and hydrogen.[50]

Perchloric esters have been prepared by distillation of the barium alkyl sulfate with barium perchlorate. They are one of the most violent chemical explosives known.(183)

It is again emphasized that there are many more and other types of organic perchlorate compounds mentioned in the literature, which have not been listed here.

Thermal Decomposition

General Considerations. Perchlorates decompose at a much higher temperature than the corresponding chlorate. The perchlorate ion is more stable than the chlorate ion, presumably due to symmetry. The thermal stabilities of the salts of oxyacids of chlorine increase in the order: $MOCl<MOClO<MOClO_2<MOClO_3$.

All perchlorates are hydrated when crystallized from water, except the potassium salt. The products formed when perchlorates are thermally decomposed depend on the presence of any water of hydration as well as the basicity of the salt. Salts of strong bases dehydrate upon heating, followed by decomposition of the anhydrous salt, yielding oxygen and the metal chloride. Chlorates may be formed as an intermediate reaction product. Generally, hydrated salts of the heavy metals decompose to form oxides or hydroxides and perchloric acid. Ammonium perchlorate is unique in that it decomposes into only gaseous products.

Techniques of differential thermal analysis and thermogravimetry have been instrumental in studying the decomposition of perchlorates. Differential thermal analysis indicates that the alkali metal perchlorates (except lithium) undergo transition from rhombic to the cubic lattice. Rapid decomposition occurs immediately after melting. The alkaline earth perchlorates do not undergo crystalline transition while heating and generally decompose considerably above their melting point. The transition and fusion temperatures for various perchlorates are presented in Table 1.[74]

Table 1

Transition Temperatures		Fusion Temperatures	
Formula	Transition Temp, °C	Formula	Fusion, °C
NH_4ClO_4	240	$LiClO \cdot 3H_2O$	90
$NaClO_4$	313	$NaClO_4$	473
$KClO_4$	300	$KClO_4$	588
$AgClO_4$	157	$Mg(ClO_4)_2$	246
		$Ca(ClO_4)_2$	123
		$Ba(ClO_4)_2$	469

Sodium and Potassium Perchlorate

Uncatalyzed Decomposition. Sodium perchlorate exists as the anhydrous, mono- and tri-hydrate. Hydrated salts, when heated, lose their water of crystallization, a temperature of 130°C being sufficient to produce the anhydrous salt. Sodium perchlorate slowly decomposes at its melting point. The melting point reported in the literature varies from

432° to 482°C.[120, 143] The over-all decomposition reaction is

$$NaClO_4 \longrightarrow 2O_2 + NaCl$$

The heat of reaction into chloride and oxygen is 3.0 cal.[138, 143]

Potassium perchlorate cannot be fused without comparatively rapid decomposition.[143] The melting point of potassium perchlorate is dependent on previous decomposition and for pure potassium perchlorate is probably above 600°C. The "beginning decomposition" temperature ranges from 470° for impure material to 580°C for purified samples.[185] Other investigators have found decomposition to commence as low as 400°C.[143] The heat of decomposition of potassium perchlorate into chlorate and oxygen was found to be 1.73 ± 0.07 kg-cal per mole at constant volume and room temperature.[95]

Thermal decomposition of potassium perchlorate in vacuo, at temperatures from 570° to 620°C, shows complete fusion after 120 minutes with 14.3 to 43.5% potassium chloride in the residue after gas evolution ceases. In the pressure range, one micron to atmospheric, and up to 630°C, there is no instantaneous fusion and no fusion without decomposition. At atmospheric pressure, and even in vacuo, if 0.001% heavy metal is present, decomposition is complete. Below 530° to 570°C, depending on the source of the sample, no phase change occurs in 2 to 3 hours of heating except about 1 percent weight loss by sublimation and irregular crystal growth; above a limiting temperature, progressive melting with gas release occurs.[184]

Potassium perchlorate shows four distinct breaks in the differential thermal analysis curve, the exothermic break being attributed to the decomposition reaction.[74] It was pointed out that decomposition of an inorganic compound, which yields at least in part, gaseous products would be endothermic. The exothermic break was interpreted as due to crystallization of reaction product. Thermodynamic calculations made on the decomposition of potassium perchlorate substantiate an endothermic reaction[137], viz:

	Observed DTA Temp, °C	Equation	Process	ΔH kcal/mole
(1)	300	$KClO_4(s, II) \rightarrow KClO_4(s, I)$	Transition	3.29
(2)	588	$KClO_4(s, I) \rightarrow KClO_4(l)$	Fusion	1.7-2.6
(3)	610	$KClO_4(l) \rightarrow KCl(l) + 2O_2(g)$	Decomposition	1.7-0.8
(4)	660	$KCl(l) \rightarrow KCl(s)$	Crystallization	-6.1

The decomposition rate of potassium perchlorate from 480° to 540°C was determined at pressures under 0.15 mm Hg. Curves of oxygen release versus time exhibit two maxima. At 480°C, the second maximum is one-half the first, but at higher temperatures, the two maxima are equal. The last of the oxygen is released very slowly. Release of oxygen from potassium chlorate formed during decomposition, or fusion of the salts, is not thought responsible for the second maximum. The reaction is dependent upon mass rather than surface. There is ample space in the potassium perchlorate crystal lattice for free oxygen circulation. It is

postulated that the chloride, formed at the surface by spontaneous decomposition, catalyzes the reaction in a chain manner, attracting oxygen atoms from the interior of the crystals and bathing the surface in an oxygen "flux." A random chloride path to the interior is thus set up, giving a rapid increase in oxygen release. The second maximum is said to result from the breakdown of the potassium perchlorate crystal structure, further accelerating oxygen release. The minimum in the curves occurs at the maximum chloride content of the salt residue.(67)

Experimental studies have indicated that potassium perchlorate at 480° retains its lattice structure until at least 15% potassium chloride is present. These investigators used X-ray diffraction techniques to study the progress of decomposition. The X-ray diffraction pattern of a sample of potassium perchlorate that had been partially decomposed into potassium chloride and potassium chlorate in vacuo was found to be qualitatively different from that of a mechanical mixture of the three salts in the same ratio.(185)

Quantitative studies were made to verify the hypothesis that the perchlorate lattice, on losing oxygen, persists for a measurable time before changing into the lattice of the chloride. Lines of potassium chloride did not appear in the partially decomposed perchlorate up to a chloride content of 15% and became conspicuous only at 37% chloride content. The lines of the perchlorate fade out gradually with the progress of decomposition. Differences in the pattern of the thermal and corresponding mechanical mixtures may arise from the fact that the potassium chloride

crystals, when first formed, are very small, affecting the intensities of their diffraction lines.(186)

An eutectic mixture of $KClO_4$, $KClO_3$ and KCl was found to be formed during the thermal decomposition of potassium perchlorate between 530° and 550°C. The results were poorly reproducible owing to the splattering of the reaction mixture by the oxygen bubbling from the viscous melt. A slow evolution of oxygen was observed initially. This evolution became more rapid when melting began, reaching a maximum when the melting had ended and the liquid had become homogenous. The melt finally solidified because of the formation of the chloride and the rate of reaction became slower.(15)

A study was undertaken to establish the relationship of the physical state of the system to the isothermal decomposition rate of potassium perchlorate. The data for the isothermal decomposition of potassium perchlorate at constant volume and under pressure of the evolved oxygen at 556° to 582°C was correlated with the temperature-composition phase diagram for the system $KClO_4$-$KClO_3$-KCl. The results show that the decomposition proceeds by two 1st-order reactions: a solid phase decomposition prior to the appearance of a liquid phase and a liquid-phase decomposition which occurs after the melting of the sample is complete. The rates of these reactions are dependent upon the concentration of potassium chlorate. In the transition phase, the rate of reaction changes continuously from the rate of the solid phase reaction to that for the reaction in the liquid

phase. The fact that the rate of reaction in the solid phase is less than that in the liquid phase is attributed to the slower diffusion of the oxygen through the crystal lattice. This slow diffusion of oxygen might permit a micro-reversible reaction of the type $ClO_4^- \rightleftharpoons ClO_3^- + (O)$ to exist. The addition of a catalyst, like magnesium oxide, causes the rate of reaction in both phases to become approximately equal. It is postulated that magnesium oxide prevents the reverse reaction by forming a complex with the oxygen. The mechanism of the reaction as proposed, involves the stretching and rupture of the Cl-O bond, forming chlorate as an intermediate. This in turn, decomposes into more oxygen and the chloride.(83)

Catalyzed Decomposition. Halides greatly influence the thermal decomposition of potassium perchlorate. The reduction of perchlorate by ammonium halides is apparently due to a catalytic effect of the anion which increases with the atomic weight of the halogen ion. At 525°, the bromide is more effective than the chloride in effecting oxygen release; with the iodide, the rate is too fast to be measured. At 400°C, very little oxygen is given off in the presence of iodide, and the mixture is converted quantitatively into iodate, chlorate, and chloride in a short time.(68)

The kinetics of the pyrolysis of potassium perchlorate and its mixtures with potassium halides were studied at atmospheric pressure. The rates of reaction were determined by analytical and gasometric techniques. The curves representing the oxygen evolved versus time are of the sigmoid type characteristic for many reactions of solids. The

potassium perchlorate decomposition proceeds stepwise, and potassium chlorate is formed as an intermediate. The induction period, which exists with pure perchlorate, is greatly reduced and the rate of decomposition is accelerated by the addition of a halide. The reaction is accelerated by the halides in the order of increasing atomic weights. At comparatively low temperatures, the reaction mixtures may retain considerable amounts of oxygen. It is suggested that oxygen may diffuse through the partially decomposed perchlorate and establish a state of equilibrium. (71)

Past investigators considered the decomposition of potassium perchlorate into potassium chloride and oxygen to proceed according to a unimolecular reaction. No chlorine was liberated from the reaction. Particles of ferric oxide, used as catalysts, increased five-fold in diameter during the reaction. The velocity coefficient increased in proportion to the weight concentration of the catalyst. It was concluded that addition of a catalyst did not accelerate the reaction already proceeding, but initiated concomitant reaction with the probable formation of intermediate compounds. (157)

A thermogravimetric study indicated that barium nitrate catalyzes the decomposition of potassium perchlorate to potassium chloride. Decomposition temperatures of pure potassium perchlorate and pure barium nitrate are about 600°C and 650°C, respectively. The mixture decomposes at 520°C, significantly lower than that observed for the individual pure components. The decomposition of potassium perchlorate in the presence of the

nitrate was found to proceed smoothly. Thermogravimetric curves of ternary mixtures (potassium perchlorate-aluminum-barium nitrate) exhibited weight losses equivalent to the quantitative decomposition of perchlorate and of nitrate. The area under the potassium perchlorate transition peak at 300°C on the differential thermograms, for a constant sample weight, was found to be linearly proportional to the amount of potassium perchlorate present. (97)

Thermal analytical techniques were used to determine the composition of the eutectic mixture found above as well as to elucidate the major thermal phenomena occurring in this system. Fusion at 465°C of a eutectic mixture immediately preceded the barium nitrate catalyzed decomposition of potassium perchlorate. A eutectic composition, nominally 2 to 1 potassium perchlorate-barium nitrate, was obtained from the integrated areas of the fusion endotherms on the DTA curves for a series of mixtures. It is noted that the presence of potassium ions, in addition to that of barium ions, provides increased thermal stability for the nitrate ion. (96)

Sodium nitrite has also been used as a catalyst in the decomposition of potassium perchlorate. When the mixture is heated at 444.5° and 520°C, the decomposition is 90 percent complete in 25 and 38 minutes, respectively. Without sodium nitrite, decomposition in 65 minutes was 2.3 and 24.9 percent, respectively. In 7 minutes at about 600°C, the decomposition was 78.3 percent with sodium nitrite and 75 percent without the catalyst. The decreased decomposition in the presence of the catalyst was probably due to the instability of sodium nitrite at these temperatures.

Increased temperatures increased auto-decomposition, but had no effect on decomposition in the presence of sodium nitrite.(210)

The effect of carbonate upon the decomposition of sodium and potassium perchlorate has been investigated. Complete decomposition of pure sodium perchlorate occurs at about 460-540°C in 300 minutes. The addition of 10-15 mol percent sodium carbonate reduces the time of decomposition to 130 minutes. Complete decomposition of pure potassium perchlorate occurs at about 550-580°C and proceeds more rapidly than the corresponding sodium salt. Addition of potassium carbonate, in the above amount, lowers the temperature of decomposition to 500-520°.(100) Earlier investigators also found carbonate to accelerate the decomposition of the perchlorates.(101)

Effect of Radiation. The characteristics of a chemical reaction may be changed by exposure of the system to radiation. Reactions of many types, such as decomposition, can be brought about by exposure to light of suitable wave length.

Pure potassium perchlorate crystals are decomposed by 50-kilovolt X-rays. The main products of the primary decomposition are potassium chlorate and potassium chloride. The potassium chlorate formed decomposes by a secondary reaction into potassium chloride. These reactions are approximately first order. The average amount of X-ray energy absorbed by the salt per perchlorate decomposed was 19 ± 2 e. v.(85)

Ammonium Perchlorates. Ammonium perchlorate is stable at 110°C, but begins to decompose when heated in a vacuum to 150°C, and deflagrates at 400°C with the evolution of light. Decomposition in air is slow below about 300°C. Some of the material sublimes at this temperature, but a greater part decomposes according to the equation:[44, 120]

$$4NH_4ClO_4 \longrightarrow 2Cl_2 + 8H_2O + 2N_2O + 3O_2$$

Small quantities of oxides of chlorine, probably chlorine dioxide and traces of nitrogen and nitrous gases are also formed. Above 350°C, the following equation is reported as more representative of the decomposition reaction:

$$2NH_4ClO_4 \longrightarrow 4H_2O + [\,Cl_2, O_2, 2NO\,]$$ plus a complex mixture of chlorine, oxygen, nitrogen dioxide, nitrogen trioxide and nitrogen oxychloride being formed.[44] The heat of reaction is given by the following equation is 38.3. cal:[143]

$$NH_4ClO_4 \longrightarrow Cl + O_2 + N + 2H_2O(g)$$

The thermal decomposition of ammonium perchlorate has been studied recently in the temperature range 220-280° and 380-450°, both in vacuum and under small initial pressures of nitrogen to suppress sublimation. This work agrees with the equations given above for the low and high temperature decomposition of ammonium perchlorate. In the low temperature range, only 30 percent decomposition occurred, although the "residue" was still ammonium perchlorate. The "residue" was found to be porous in nature and could be rejuvenated by exposure to solvent vapors. Decomposition begins at surface nuclei whose numbers increase with time. The decomposition then spreads into the interior of the crystal in a hemispherical

shape until the reaction zones meet. The resulting common reaction zone then continues slowly towards the center of the crystal. This type of reaction indicates that the rate of decomposition is strongly influenced by the condition of the surface of the crystal and by the presence of impurities.[13]

The kinetics of the decomposition have been determined from pressure-time curves, over the temperature range 215° to 275°C. The mean value for the energies of activation are reported as 27.8 kcal for the orthorhombic form and 18.9 kcal for the cubic form. The rate of decomposition was found to increase to a maximum with decreasing particle size and then decrease again with continued diminishing sizes. An electron transfer mechanism is tentatively advanced to explain some of the observed decomposition results. In a vacuo or in a gas stream, between 215° and 280°C, only about 30 percent decomposition occurred, although the residue was chemically the same as before heating. Though no solid products are formed, decomposition does take place at a solid/solid interface.[14]

Other Perchlorates. Two general types of reactions can take place when a hydrated perchlorate is heated: dehydration, followed by decomposition to yield chloride and oxygen, or hydrolysis of the hydrated compounds to yield the oxide (or hydroxide) and perchloric acid. Salts of weak bases are more easily hydrolyzed than those of strong bases.

Aluminum perchlorate hexahydrate melts at 82°C. Dehydration occurs at 178°C simultaneously with hydrolysis, to yield $Al(OH)(ClO_4)_2$. At 262° and 264°C, the final stages of decomposition occur in rapid

succession, yielding aluminum oxide, chlorine and oxygen.[228] Other investigators have found that the aluminum salt, upon heating, begins to lose weight at about 110-120°C. As the temperature is raised, the salt gradually hydrolyzes, yielding aluminum oxide.[138]

Differential thermal analysis of aluminum perchlorate nonahydrate shows two endotherms, the first corresponding to the fusion by dissolution from 50° to 90°C. With the onset of decomposition, evidenced by slight chlorous fuming at about 165°C, a broad endotherm is produced from 165° to 330°C, with rapid fuming occurring at 185°C. The endotherm levels off at about 500°C.[32]

Much disagreement exists in the literature as to the effect of heat on barium perchlorate. The trihydrate loses two-thirds of its combined water over concentrated sulfuric acid and the remaining one-third at 100°C. The salt begins to decompose at 400°C when 0.09% oxygen is lost in 70 minutes. At 460°C, all the oxygen is lost in about 9-1/2 hours. The anhydrous perchlorate melts at 505°C.[143] Other workers found that barium perchlorate trihydrate dehydrates at 174°C, undergoes polymorphic transformation at 284° and again at 360°C, and decomposes above 520° to yield barium chloride and oxygen.[228] However, in another investigation, no evidence of visible reaction was observed until vigorous decomposition at 504°.[74]

Calcium perchlorate tetrahydrate melts at 57°C and loses water at 256°C. About 340°C, the anhydrous salt appears to undergo an

endothermic change, suggesting polymorphic transformation. Decomposition begins at 470° to 478°C which yields calcium chloride and oxygen, with traces of calcium oxide and chlorine.[228] Some researchers indicate that the hydrated calcium salt loses water as low as 220°C and decomposition occurs at 405°C.[138] Differential thermal analysis curves indicate that fusion of the calcium salt occurs at 123°C, slight bubbling at 258°C and vigorous bubbling at 285°C. The calcium salt decomposes exothermally at a temperature of 565°C.[74]

Anhydrous lithium perchlorate is extremely deliquescent. The anhydrous salt fuses at 300°C, decomposes slightly at 400° and vigorously at 450°C.[172] Other investigators have reported the melting point of the anhydrous salt as low as 236°C.[120]

The melting point of the trihydrate of lithium perchlorate is 95°C. The monohydrate is formed upon heating to 100°C and the anhydrous salt at 130°C. The anhydrous salt melts at 236°C and loses no oxygen at 300°C; this gas is evolved at about 368°C. At 380°, the speed of decomposition is rapid - lithium chlorate and chloride are first formed, and the speed of decomposition at 368° is greatest when the ratio $LiClO_4$: $LiClO_3$ is approximately 1:3.[143]

Lithium perchlorate, unlike the other alkali perchlorates, does not undergo crystalline transition. Differential thermal analysis indicated that the trihydrate fused at 90°C. Visual phenomena occurring during decomposition have indicated that slight bubbling occurs at 310°C, rapid bubbling at

412°C and vigorous bubbling at 504°C.[74] The curve of weight loss versus time for hydrated lithium perchlorate indicates that the salt loses its water of crystallization very slowly, beginning at about 115°C. Lithium is a sufficiently strong base to withstand the action of water. The anhydrous salt decomposes at about 440°C.[138] A somewhat controversial discussion on the above study has been reported.[80]

Magnesium perchlorate hexahydrate, $Mg(ClO_4)_2 \cdot 6H_2O$ or $[Mg(H_2O)_6](ClO_4)_2$, melts at 147°C. Anhydrous, di-tri- and tetra-hydrates of magnesium perchlorate have been prepared.[120, 194] Magnesium perchlorate hydrates lose water when heated and the hydrates above the dihydrate melt on heating and probably hydrolyze to some extent according to the equation:

$$Mg(ClO_4)_2 \cdot 6H_2O \longrightarrow Mg(OH)_2 + 2HClO_4 + 4H_2O$$

The hexahydrate of magnesium perchlorate dehydrates in two stages, 141° and 185°C, respectively. At 410°, a three stage series of exothermic decomposition reactions were reported involving an intermediate compound of the formula, $[Mg(ClO_4)]_2O$.[228]

The decomposition of magnesium perchlorate was studied by means of a thermal balance. On decomposition, the residue was found to be magnesium oxide. The hydrated salt, when heated, gradually lost weight, starting at a temperature slightly above room temperature, wherein dehydration and hydrolysis occurred.[138]

The hexahydrate of magnesium perchlorate, when stored over P_2O_5 in vacuo, converts to the trihydrate at 25°C but not at 0°C.(194, 219) When either the trihydrate or hexahydrate was completely melted, and allowed to cool slowly, it solidified at 145-147°C, possibly indicating the eutectic point of these two hydrates. Heating the hexahydrate to 170°C removes most of the water of crystallization and the remainder of the water is removed at 250°C. The anhydrous salt is stable at 250°C and begins to decompose at a slightly higher temperature. When anhydrous magnesium perchlorate was gradually raised in temperature from 250° to 400°C, it decomposed, leaving a residue consisting principally of magnesium oxide.(219)

The hexahydrate melts at 145-7°C in its crystalline water. On heating, part of the water of crystallization is removed and the trihydrate is formed. Heating the trihydrate at 170-200°C in vacuo produces the anhydrous magnesium perchlorate. Heating the anhydrous salt above 250°C causes decomposition into magnesium chloride, magnesium oxide and chlorine monoxide.(2)

Differential thermal analysis shows that anhydrous magnesium perchlorate fuses at 246°C. This salt does not undergo crystalline transition while heating. It decomposes exothermally at a temperature of 525°C.(74)

The melting point of silver perchlorate is given as 486°C and it decomposes suddenly just below red heat.(143) Differential thermal

analysis of this salt shows a color change on decomposition (white to brown) at 277°C and vigorous bubbling at 473°C. The thermal reactions are completed at about 550°C.[74]

Solid Reactions

The reaction between potassium perchlorate and carbon black has been studied with varying initial amounts of reactants. The reaction was found to take place considerably below the decomposition temperature of pure potassium perchlorate. In the temperature range 320-385°C, the reaction was found to proceed according to the equation

$$KClO_4 + C \longrightarrow 2CO_2 + KCl$$

No induction period was noted in contrast to the decomposition of pure potassium perchlorate.[71] The rate of reaction, as measured by carbon dioxide build-up, is first order in both reactants and inhibited in the later stages by the potassium chloride formed.[160] A subsequent investigation was concerned with the influence of various physical factors upon the reaction. Some of the factors which were considered were: wetting, pressure in preparation, aging of tablets, particle size of components, temperature of reaction, relative quantities of reactants and different forms of carbon. Standard samples in tablet form were prepared by wetting the powder mixture and pressing into tablets under a pressure of 2250 kg/sq cm. Reaction rates were found to be lower than the rate of the standard sample if water was not added, the samples were prepared with a pressure of 1125 kg/sq cm, or the samples were allowed to age. At 343°,

the rate increased with increasing available surface area (smaller particle sizes).[91]

The effect of potassium perchlorate, as a catalyst, upon the air oxidation of carbon black has been determined. At an air pressure of 200 mm, a slow reaction occurs between carbon black and atmospheric oxygen in the presence of the perchlorate. Heating at 367°C for 1-2 hours, consumes almost all the oxygen in the oxidation of the carbon to carbon dioxide. The following reaction also occurs concurrently:

$$KClO_4 + 2C \longrightarrow KCl + 2CO_2$$

Potassium chloride produces the same effect in this reaction as the perchlorate. The carbon was pressed into tablets under 600 atm pressure and dried at 120° and 150°, under vacuum. The reaction rate is first order both in carbon black and oxygen and depends upon the absolute quantities of the reactants.[161] The catalytic action of perchlorates is explained by the formation of an oxygenated intermediate from the perchlorate ion, which acts as an oxygen carrier.[163]

The effect of heating various solid inorganic oxidants (potassium chlorate, perchlorate and nitrate) on combustible substances (carbon black, paraffin wax, starch and asphalt) was determined. In most cases, ignition was initiated at temperatures below which the combustible substance by itself, or the oxidant by itself, would undergo any appreciable chemical change. In some cases, a solid-solid type of reaction occurs according to the equation:

$$\text{oxidant} + \text{fuel} \longrightarrow \text{products} + \text{heat}$$

The heat liberated raises the temperature of the sample so that the following reactions take place:

oxidant ⟶ oxygen

and

oxygen + fuel ⟶ products + heat

Besides the above reactions, combustion of the organic substance above its ignition temperature by atmospheric oxygen also occurs. The oxidants, in order of their increased reactivity are: $KNO_3 < KClO_4 < KClO_3$. A plot of the natural logarithm of the time needed for ignition at various initiation temperatures, against 1/T resulted in a straight line. The critical increment E' of the Arrhenius equation was evaluated from this plot. Although the value of E' is not the real activation energy of the pre-ignition reaction, it is expected that there should be some simple relationship between the values of E' and the real activation energies of the primary process of the pre-ignition reaction.(162)

Mixtures of aromatic hydrocarbons and potassium perchlorate are practically unchanged on heating to 440°C, but at temperatures approaching the decomposition temperature of potassium perchlorate (510°C), very rapid reaction occurs, resulting in the explosion of the glass ampules used. Tetrahydronaphthalene yielded 94% $C_{10}H_8$, decahydronaphthalene yielded 58% $C_{10}H_8$, cyclohexane yielded 5% C_6H_6, cyclohexanol yielded 4.8% phenol, cyclohexanone yielded 2.5 grams of phenol, and methylcyclohexanone yielded 17% metacresol. No attempt was made to obtain maximum yields.(164)

Tetralin has been dehydrogenated by potassium perchlorate at 200°C in the presence of certain oxidation-reduction catalysts of the electron-carrying type. One and a half moles of perchlorate were used for each mole of Tetralin and 5 percent of the weight of potassium perchlorate was taken of each catalyst. Catalysts found effective were $FeSO_4$, ferric salts, $VOSO_4$, $Ce(NH_4)SO_4$, and $TiCl_3$. Other electron transfer catalysts (manganous, cupric and cobaltous salts), oxygen-carrier catalysts (Cr_2O_3, BaO, PbO_2) and basic salts (K_2CO_3) were totally ineffective. The desired reaction did not occur in the presence of catalysts at reduced pressures.(159)

Mixtures of potassium perchlorate, zinc and hexachlorobenzene in various formulations have been used for the production of smokes. Binary, ternary and quaternary mixtures of the three ingredients and carbon (a reduction product of hexachlorobenzene) were studied by means of (1) differential thermal analysis, (2) determinations of ignition temperatures and the energy of activation for ignition, and (3) the determination of the closed bomb heat of combustion and gas evolution in inert atmospheres. The results obtained are presented in the following table:

Composition	Energy of Activation Kcal/mole	Ignition Temperatures °C	Heat of Combustion cal/gm
61.1% Zn, 22.2% $KClO_4$, 16.7% C_6Cl_6	14.9, 29.3	325	516
64.5% Zn, 34.6% $KClO_4$	25.4	520	815
74.3% $KClO_4$, 25.7%C	13.9	360	---
54.5% Zn, 41.2% $KClO_4$, 4.3%C	9.9	335	---
50.9% Zn, 30.9% $KClO_4$, 13.9% p3.9% C_6Cl_6, 4.3%C	11.8	320	---

It is concluded from this investigation that three reactions are responsible for the pre-ignition, ignition and combustion phases of the ternary system, viz.,

$$3Zn + C_6Cl_6 \longrightarrow 3ZnCl_2 + 6C$$

$$4C + KClO_4 \longrightarrow KCl + 4CO(+CO_2)$$

$$4Zn + KClO_4 \longrightarrow KCl + 4ZnO$$

The first reaction is a slow exothermal reaction which takes place at, and above, the boiling point of hexachlorobenzene, producing carbon. The reaction of carbon with potassium perchlorate, together with the first reaction, raises the temperature of the system above 500°. At temperatures above the melting point of zinc, the pre-ignition reaction (third equation) becomes highly exothermal and propagation ensues in the range of 520°. Therefore, the production of carbon by the first reaction is an important factor in the sensitivity of this composition to thermal ignition.(75)

Alkali perchlorates are reduced upon ignition with glucose, oxalic acid, sodium carbonate or ammonium iodide. Ignition of percholorate with boric acid at 800° produces complete conversion to borate, providing the mixing is adequate.(178) Potassium perchlorate is reduced by hydrogen under ordinary conditions to give the chloride and water.(109)

Perchlorates can be fused with zinc chloride to quantitatively liberate chlorine.(143) Fusion of sodium perchlorate with sodium sulfite produces the chloride and sulfate.(112)

Hydrogen was found to react with potassium perchlorate in an electric discharge of 15,000 volts. The reaction products were potassium chloride and water.[145]

The reactions between perchlorates and numerous organic and inorganic substances which take place during the combustion of solid propellants have been the subject of much study and speculation. Numerous hypotheses have been proposed but the true mechanism of burning is not yet well understood. The complex reactions common to combustion processes in general are found to be made even more difficult to analyze because of the large number of ingredients used in formulating these propellants. A review of this subject has been included in Chapter 3 of Volume 2.

BIBLIOGRAPHY

1. Aktiebolag, Mo och Domsjo, C. A. 44, 9126[i].

2. Alimarin, I, P., C. A. 37, 4315[7].

3. Amiel, J., Compt. rend., 198, 1033 (1934).

4. Amiel, Jean, C A. 29, 66[8].

5. Balareff, D., C. A. 19, 1526[5].

6. Balarev, D., C. A. 28, 3648[1].

7. Bennett, F. W., and Sharpe, A. G., J. Chem. Soc. 1383 (1950).

8. Berglund, Ulla, and Sillen, Lars Gunnar, C. A. 43, 2075[i].

9. Bethell, D. E., and Sheppard, N., J Chem. Phys., 21, 1421 (1953).

10. Bhatnager, S. S., Shayma, Rama Krishna, and Mitra, N. G., C. A. 22, 4378[2].

11. Bhatnager, S. S., Prakash, Brahm, and Singh, Jarnail, C. A. 34, 4972[4].

12. Birckenbach, Lothar, and Goubeau, Josef, C. A. 26, 3198[8].

13. Bircumshaw, L. L., and Newman, B. H., C. A. 49, 5789[a]

14. Bircumshaw, L. L., and Newman, B. H., C. A. 49, 7343[g].

15. Bircumshaw, L. L., and Phillips, T. R., J. Chem. Soc., 703 (1953).

16. Blatt, John Wiley and Sons, Inc., New York, 1948.

17. Bode, Hans, and Klesper, Ernest, C. A. 46, 2946[h]

18. Bosch, A. Varden, and Aten, Jr., A. H. W., J. Am. Chem. Soc., 75, 3835 (1953).

19 Bouket, Charles, and Lafont, Robert, C. A. 42, 7123[f].

20. Braun, Giza, J. Am. Chem. Soc., 51, 228 (1929).

21. Bredig, G., and Michel, J., C.A. 16, 1896[6].

22. Brown, F. E , Proc. Iowa Acad. Sci., 33, 145 (1926).

23. Brown, F. E., and McLaughlin, H. M., Proc. Iowa Acad. Sci., 31 277 (1924).

24. Brown, F. E., and White, W. C. O., Proc. Iowa Acad, Sci., 31, 276 (1924).

25. Brown, F. E., and White, W. C. O., Proc. Iowa Acad. Sci., 31, 291 (1924).

26. Brown, F. E., and Woods, J. D., Proc. Iowa Acad. Sci., 61, 250 (1954).

27. Brown, F. E., and Woods, J. D., Proc. Iowa Acad. Sci., 62, 258 (1955).

28. Brown, F. E., and Woods, J. D., Proc. Iowa Acad. Sci., 63, 410 (1956).

29. Burton, H., and Praill, P. F. G., Chemistry and Industry, 939 (1951).

30. Burton, H., and Praill, P. F. G., J. Chem. Soc., 827 (1953).

31. Burton, H., and Praill, P. F. G., Analyst, 80, 4 (1955).

32. Campbell, Clement, and Gordon, Saul, Technical Report 2200, Samuel Feltman Ammunition Laboratories, Picatinny Arsenal, Dover, N. J., July 1955.

33. Cauquil, Germaine, and Barrera, Héribert, C.A. 46, 917[b]

34. Cauquil, Germaine, Barrera, Héribert, and Barrera, Renee, C.A. 46, 6102[b].

35. Cauquil, Germain, Barrera, Héribert, and Barrera, R., C.A. 49, 3038[d].

36. Chaney, Albert L., and Mann, Charles A., J. Phys. Chem., 35, 2289 (1931).

37. Comyns, Alan E., and Lucas, Howard J., J. Am. Chem. Soc., 76, 1019 (1954).

38. Coppock, J. B. M., Colvin, J., and Hume, J., Trans. Faraday Soc, 27, 283 (1931).

39. Cottin, M., Ann. Review of Phys. Chem. 9, 144 (1958).

40. Crespi, M., and Caamaño, J. L. G., C.A. 31, 5701[5].

41. Dandel, Raymond, Dandel, Pascaline, and Martin, Monique, C.A. 40, 1707[6].

42. Davies, Richard L., C.A. 36, 351[3].

43. Deshmukh, G. S., and Vunugopalan, M., C.A. 50, 16504[h].

44. Dodé, Maurice, C.A. 29, 1348[1].

45. Dodé, Maurice, and Basset, James, C.A. 29, 3617[9].

46. Dodgen, Harold, and Taube, Henry, J. Am. Chem. Soc., 71, 2501 (1949).

47. Drozdov, B. N., C.A. 37, 4959[9].

48. Dufraisse, Charles, and Geman, Manuel, C.A. 33, 1499[4].

49. Duke, Frederick R., and Quinney, Paul R., J. Am. Chem. Soc., 76, 3800 (1954).

50. Eaborn, C., J. Chem. Soc., 2517-19 (1955).

51. Ellis, Carleton, and Wells, Alfred A., Reinhold Pub. Corp., New York, N Y., 1941.

52. Emeléus, H. J., and Woolf, A. A., J. Chem. Soc., 164 (1950).

53. Engelbrecht, Alfred, C.A. 48, 14134[i].

54. Engelbrecht, A., and Atzwanger, H., C.A. 47, 991[h].

55. Ephraim, F., Inorganic Chemistry, Interscience Publishers, Inc., New York, 1947.

56. Epik, P. A., and Tolstikov, V. P., C.A. 44, 8210[d].

57. Evans, D. F., J. Chem. Phys., 24, 1244 (1956).

58. Fairbrother, Fred, J. Am. Chem. Soc., 44, 2419 (1922).

59. Farkas, L., and Klein, F. S., J. Chem. Phys., 16, 886 (1948).

60. Fichter, Fr., and Brunner, Ernst, Helv. Chim. Acta, 12, 305 (1929).

61. Fukushima, Shouzow, and Horibe, Yoshio, C. A. 48, 1786[a].

62. Fukushima, Shouzow, Horibe, Yoshio, and Titani, Toshizo, C. A. 47, 5781[i].

63. Gall, H., and Manchot, W., C. A. 19, 1995[6].

64. Gehar, J., C. A. 11, 1302[5].

65. Gilbert, P., and Durand-Garrelin, A., C. A. 31, 3361[3].

66. Gilbert, Jr., T. W., Meyer, Jr., A. S., and White, J. C., Anal. Chem. 29, 1627 (1957).

67. Glasner, A., and Simchen, A. E., C. A. 45, 8861[b].

68. Glasner, A., and Weidenfeld, L., C. A. 44, 9291[i].

69. Glasner, A., and Weidenfeld, L., C. A., 46, 4941[h].

70. Glasner, A., and Weidenfeld, L., J. Am. Chem. Soc., 74, 2464 (1952).

71. Glasner, A., and Weidenfeld, L., J. Am. Chem. Soc., 74, 2467 (1952).

72. Gleason, E. H., Mino, G., and Thomas, W. M., J. Phys. Chem., 61, 447 (1957).

73. Gornberg, M., J. Am. Chem. Soc., 45, 398 (1923).

74. Gordon, Saul, and Campbell, Clement, Anal. Chem., 27, 1102 (1955).

75. Gordon, S., and Campbell, C., Fifth Symposium on Combustion, Reinhold Publishing Corp., New York, 1955, Paper No. 21.

76. Grieger, Philip F , J. Am Chem. Soc., 70, 3045 (1948).

77. Güntelberg, E., C. A. 9, 1463[7].

78. Haight, Jr., G. P., J. Am. Chem. Soc., 76, 4718 (1954).

79. Haight, Jr., G. P., and Sager, W. F., J. Amer. Chem. Soc., 74, 6056 (1952).

80. Hall, Wm. T., C. A. 40, 531[7].

81. Halperin, Joseph, and Taube, Henry, C. A. 46, 6910[h].

82. Hantke, C. A. 31, 5703[3].

83. Harvey, Jr., Aubrey E., Edmison, Marvin T., Jones, Eric D., Seybert, Robert A., and Catto, Keith A., J. Am. Chem. Soc., 76, 3270 (1954).

84. Harvey, Cecil O., C. A. 20, 1042[8].

85. Heal, H. G., C. A. 47, 4758[f, g].

86. Hennig, Gerhart, Lees, Robert, and Matheson, Max S., J. Chem. Phys., 21, 664 (1953).

87. Herschkowitsch, M., C. A. 17, 1393[4].

88. Hill, A. E., J. Am. Chem. Soc., 43, 254 (1921).

89. Hodgkinson, W. R., C. A. 9, 571[4].

90. Hoering. T: C., Ishimori, F. T., and McDonald, H. O., J. Am. Chem. Soc., 80, 3876 (1958).

91. Hoffman, Eliahu, and Patai, Saul, J. Chem. Soc., 1797 (1955), cf. C. A. 45, 2806[g].

92. Hofmann, K. A., C. A. 7, 999[5]

93. Hofmann, K. A., Ehrhart, O., and Schneider, Otto, C. A. 7, 3088[8].

94. Hofmann, K. A., and Linnman, W., C. A. 18, 2115[1].

95. Hofmann, K. A., and Marin, P. H., C. A. 27, 1264[1, 2].

96. Hogan, Virginia, and Gordon, Saul, J. Phys. Chem., 62, 1433, (1958).

97. Hogan, Virginia, D., Gordon, Saul, Campbell, Clement, C.A. 51, 6432g.

98. Holst, Gustaf, C.A. 40, 3069[5]

99. Il'inskii, Vl. P., C.A. 18, 1416[5].

100. Ishikawa, Fusao, and Hagisawa, Hiroshi, C.A. 26, 4231[9].

101. Ishikawa, Fusao, Murooka, Toyosaku, and Hagisawa, Hiroshi, C.A. 28, 1615[2-4]

102. Jacobson, C. A., Encyclopedia of Chemical Reactions, Reinhold Publishing Corp., New York, 1948, Vol. I.

103. Ibid, Vol. II, Reaction No. 2685.

104. Ibid, Vol. II, Reaction No. 2800.

105. Ibid, Vol. II, Reaction No. 2822, Vol. V, Reaction No. 2033.

106. Ibid, Vol. II, Reaction No. 2790.

107. Ibid, Vol. II, Reaction No. 2798.

108. Ibid, Vol. V, Reaction No. 2045.

109. Ibid, Vol. V, Reaction No. 2053.

110. Ibid, Vol. VI, Reaction No. 1234.

111. Ibid, Vol. VI, Reaction No. 1235.

112. Ibid, Vol. VI, Reaction No. 1241.

113. Jander, Gerhart, and Gauttner, Barbara, C.A. 43, 516[h], 517[c].

114. Jander, Gerhart, and Kraffczyk, Karl, C.A. 50, 11155[d, e]

115. Kailan, Anton, C.A. 16, 2806[6].

116. Katsuda, Tsuneyoshi, C.A. 45, 3881[h].

117. Kepinski, Jozef, and Blaszkiewicz, Genowefa, C.A. 52, 12339[e].

118. King, Cecil, V., and Lang, Frances S., J. Electro. Chem. Soc., 99295 (1952).

119. Kiriyama, Ryôichi (V); Kiriyama, Ryôichi, and Yamada, Minoru (VI), C. A. 45, 6468c, a.

120. Kirk, R. E., and Othmer, D. F., Interscience Encylclopedia, Inc., New York, 1949, Vol. III.

121. Klinger, C. A. 5, 3547[4].

122. Knecht, E., C. A. 4, 2246[7].

123. Kolarov, N., C. A. 49, 765c.

124. Kolhatkar, G. B., and Sant, U. A., C. A. 37, 3325[5].

125. Kubina, Hans, C. A. 17, 1599[5].

126. Kunz-Krause, Hermann, C. A. 25, 5861[3].

127. Lamb, A. B., Bray, W. C., and Geldard, W. J., J. Am. Chem. Soc., 42, 1636 (1920).

128. Lee, F. S., and Carpenter, G. B., J. Phys. Chem., 63, 279 (1959).

129. Lee, D. A., J. Am. Chem. Soc., 76, 2590 (1954).

130. Lehmann, Hans A., and Krüger, Günther, C. A. 48, 6897c.

131. Lenher, V., Stone, H. W., and Skinner, Helen H., J. Am. Chem. Soc., 44 143 (1922).

132. Levi, G. R., and Ghiron, D., C. A. 25, 654[7].

133. Lydén, Ragnor, C. A. 23, 50[5].

134. Lydén, Ragnor, C. A. 31, 5292[6].

135. Magidson, O. Yu, Baichikov, A. G., C. A. 24, 5588[5]

136. Mahant, Sampuran D., C. A. 24, 1013[3].

137. Markowitz, Meyer Melvin, J. Phys. Chem., 61, 505 (1957).

138. Marvin, George G., and Woolover, Lawrence B., Ind. Eng. Chem., Anal. Ed., 17, 474 (1945).

139. Mathers, Frank C., and Aldred, Jacob W. H., C. A. 16, 3822[1]

140. McCallum, K. J., and Holmes, O. G., C. A. 46, 363[e].

141. McLaughlin, H. M., with Brown, F. E., J. Am. Chem. Soc., 50, 782 (1928).

142. Medvedev, S. S., and Alekseeva, E. N., C. A. 22, 3132[9].

143. Mellor, J. W., Inorganic and Theoretical Chemistry, Longmans, Green and Co., London, 1952, Vol. II.

144 Meyer, Martin, J. Chem. Education, 17, 494 (1940).

145. Miyamoto, Susumu, C. A. 28, 4319[9].

146. Miyamoto, Susumu, C. A. 29, 1019[4].

147. Miyamoto, Susumu, C. A. 29, 5753[2].

148. Miyamoto, Susumu, C. A. 31, 7341[6].

149. Naoum, P., and Aufschläger, R., C. A. 18, 3721[3].

150. Neville, H. A., J. Am. Chem. Soc., 45, 2330 (1923).

151. Nicholson, D. G., and Holley, Jr., Charles E., C. A. 40, 6009[6].

152. Nixon, A. C., Krauskopf, K. B., J. Am. Chem. Soc., 54, 4606 (1932).

153. Offord, H. R., Ind. and Eng. Chem., Anal. Ed., 7, 93 (1935).

154. Okada, Shinzo, Yoshizawa, Shiro, Nakagawa, Kyoichi, and Matsuoka, Akira, C. A. 51, 14222[d].

155. Osada, Hideyo, C. A. 49, 10712[f].

156. Ott, Erwin, C. A. 48, 1639[b, c].

157. Otto, C. E., and Fry, H. S., C. A. 17, 2089[8].

158. Otto, C. E., and Fry, H. S., J. Am. Chem. Soc., 46, 269 (1926).

159. Patai, S., and Freitzg. N., C. A. 49, 13751[a].

160. Patai, Saul, and Hoffmann, E., J. Am. Chem. Soc., 72, 5098 (1950).

161. Patai, Saul, and Hoffmann, Eliahu, C. A. 46, 5414[b].

162. Patai, Saul, and Hoffmann, E., J. Applied Chem. (London), C. A. 46, 4797[e].

163. Patai, Saul, Hoffmann, E., and Rajbenbach, L., J. Applied Chem. (London), 2, 306 (1952).

164. Patai, Saul, and Rajbenbach, Leon, J. Am. Chem. Soc., 73, 862 (1951).

165. Patai, S., and Rajabenbach, L., C. A. 48, 5628[h].

166. Pauling, L., Cornell University Press, Ithaca, New York, 1945.

167. Pisavchevskii, L. V., C. A. 22, 2512[3].

168. Polyakov, M. V., Nosenko, D. S., C. A. 34, 5730[5].

169. Putochin, N., C. A. 24, 1113[1].

170. Rodies, M. F., and Iredale, T., C. A. 38, 6169[4].

171. Ricci, John E., and Offenback, Jack A., C. A. 45, 6916[i].

172. Richards, T. W., and Cox. M. W., C. A. 7, 1999[1].

173. Riolo, Carla B., C. A. 49, 6710[a]

174. Riskin, I. . and Pugacheva, G., C. A. 33, 1616[4].

175. Rothmund, V., C. A. 3, 2277[4].

176. Salvadori, R., C. A. 10, 3041[7].

177. Scatchard, G., Prentiss, S. S., Jones, P. T., J. Am. Chem. Soc., 56, 805 (1934).

178. Schulek, E., and Koros, E., C. A. 48, 6895[d].

179. Seipel, Burton B., C. A. 44, 2400[f].

180. Sharman, L. J., and McCallum, K. J., C. A. 49, 10087[f, g].

181. Shchegol, Sh. S., C. A. 52, 15209[f].

182. Shraibman, S. S., C.A. 31, 5111[9].

183. Sidgwick, N. V., The Chemical Elements and Their Compounds, Oxford University Press, London, 1950, Vol. II.

184. Simchen, A. E., and Glasner, A., C.A. 47, 5229[g].

185. Simchen, A. E., Glasner, A., and Frankel, B., C.A. 48, 7965[b]

186. Simchen, A. E., Merhav, Y., Frankel, B., C.A. 49, 15354[b].

187. Sinka, P. C., and Ray, R. C., C.A. 37, 6580[3, 4, 5].

188. Sinka, P. C., and Ray, R. C., C.A. 43, 2114[a].

189. Sinka, P. C., and Ray, R. C., C.A. 43, 3699[f].

190. Skrabel and Schreiner, C.A. 29, 4247[5].

191. Smeets, C., C.A. 30, 2129[9].

192. Smith, G. Frederick, C.A. 21, 1579[7].

193. Smith, G. F., J. Am. Chem. Soc., 75, 184 (1953).

194. Smith, G. F., Brown, M., and Ross, J. F., Ind. Eng. Chem., 16, 20(1924).

195. Smith, G. Frederick, and Freidman, Bernard S., C.A. 28, 6650[5]

196. Smith, G. Frederick, and Hardy, V. R., C.A. 29, 5033[2, 3].

197. Snead, M. C., Maynard, J. L., and Brasted, R. C., Comprehensive Inorganic Chemistry, D. Van Nostrand Co., Inc., New York, 1954, Vol. III.

198. Spallino, R., C.A. 8, 2701[8].

199. Stargardter, Albert R., C.A. 45, 10186[f].

200. Stauff, J., C.A. 35, 3144[9].

201. Stefanovskiĭ, V. F., C.A. 34, 3570[5].

202. Stefanovskiĭ, V. F., and Zan'ko, A. M., C.A. 33, 4856[8]

203. Stefanovskiĭ, V. F., and Zan'ko, A. M., C.A. 37, 2644[1].

204. Suryanavayana, K., C.A. 18, 3548[8].

205. Tabadoire, F., C.A. 28, 7191[7].

206. Taradoire, F., C.A. 31, 5702[7,8].

207. Taradoire, F., C.A. 32, 1455[6].

208. Taradoire, F., C.A. 38, 525[6].

209. Taube, Henry, and Dodgen, Harold, J. Am Chem. Soc., 71, 3330 (1949).

210. Tian, A., and Svilarich C.A. 24, 5657[4].

211. Titani, Tosizo, and Goto, Kokiti, C.A. 33, 8095[1].

212. Van Valkenburg, H. B., J. Am. Chem Soc., 42, 757 (1920).

213. Vestin, Ragnar, and Ralf, Elisabeth, C.A. 44, 69[a].

214. Vitali, D., C.A. 5, 645[5].

215. Weber, K., Liszt, F., and Balzer, I., C.A. 33, 4498[4].

216. Weber, Karl, and Pichler, Maria, C.A. 34, 6155[2].

217. Weber, Karl, and Valić, Ramiza, C.A. 34, 17[9].

218. Weinland, R. F., and Ensgraber, Fr., C.A. 8, 878[8].

219. Willard, H. H., and Smith, G. F., J. Am. Chem. Soc., 44, 2255 (1922).

220. Willard, H. H., and Smith, G. F., J. Am. Chem. Soc., 44, 2816 (1922).

221. Willard, H. H., and Smith, G. F., J. Am. Chem. Soc., 45, 286 (1923).

222. Winter, E. R. S., Carlton, M., and Briscoe, H. V. A., C.A. 34, 3570[2].

223. Woolf, A. A., Chemistry and Industry, 346 (1954).

224. Woofl, A. A., C. A. 51, 2444[c].

225. Yamamoto, Sukenori, and Asaba, Tetsuro, C. A. 49, 6761[a].

226. Yoshida, Ginjiro, and Osada, Hideyo, C. A. 49, 11480[a].

227. Zan'ko, A. M., and Stefanovskii, V. F., C. A. 32, 2413[8].

228. Zinov'ev, A. A., and Chudinova, L. I., C. A. 51, 2439[e].

CHAPTER 4. USES OF CHLORATES AND PERCHLORATES

CHAPTER 4. USES OF CHLORATES AND PERCHLORATES

A difference in chemical stability, or reactivity, is the chief reason for differing major uses of chlorate and perchlorate compounds. The chlorates, as chemical intermediates, may be oxidized further to perchlorates, or as sensitive oxidizing agents, for example, they provide a ready source of chlorine dioxide, the bleach currently preferred in the pulp and paper industry.[10] As a group, the perchlorates are more stable than the chlorates. They are powerful oxidizing agents, sufficiently stable to be widely used in the field of propellants. In this use, they offer reasonable safety in storage and handling while in intimate contact with certain oxidizable materials.

Sodium Chlorate for Bleaching

The superior characteristics of chlorine dioxide as a bleaching agent, especially for paper pulps, was known for a long time before industrial use was commenced in 1946 in foreign areas and in 1952 in the United States. The delay in this application was occasioned by the cost and danger associated with the shipment and handling of this toxic, explosive, corrosive substance [8] Development of economical processes for generating chlorine dioxide at the use site by the reduction of sodium chlorate led to its widespread use and provided the major outlet for sodium chlorate. In the United States, three processes are used by the pulp industry: (1) the Solvay process which reduces sodium chlorate with methyl alcohol in the presence of sulfuric acid; (2) the Olin-Mathieson process which uses sulfur dioxide in

sulfuric acid solution to reduce the chlorate; and (3) the Day-Kesting process which produces both sodium chlorate and chlorine dioxide, once the process is underway; sodium chlorate is regenerated electrolytically from the sodium chloride formed when the chlorate is reduced to chlorine dioxide with hydrochloric acid.(8, 27)

Chlorine dioxide is used also in other bleaching operations, such as the bleaching of flour, and in water purification. It appears, however, that in these uses it is generated, ordinarily, from starting materials other than sodium chlorate.(9, 44, 50)

Pyrotechnics Application

General

Pyrotechnics have played an important role in the history of the world. In the siege of Delium in 424 B.C., vats of pitch, sulfur and burning charcoal were hurled against the enemy and went down in history as "Greek Fire." In 54 B.C. the Britons used hot clay balls to set Caesar's camp on fire, while four hundred years later, Vegetius used incense, naphtha, pitch, and sulfur packed in a tube, ignited and thrown on the decks of enemy ships to burn their fleet. In the days of Marco Polo, firecrackers and bombs were used for their demoralizing effect on the enemy by the Chinese. Sky rockets were first supposed to have been used by the Tartars during the Mongol siege of Peking. In more recent times we have the "Rocket's red glare" from the action at Ft. McHenry by the British. It was British rockets

that won the victory that allowed the city of Washington to be burned during the War of 1812.

Today, pyrotechnics are often thought of as the display of fireworks seen on the Fourth of July. Militarily, they encompass a group of weapons and tools that can be used to obtain an advantage over the enemy. Included in military pyrotechnics are signal flares, parachute flares, tracer bullets, smoke screens and smoke grenades. Igniters as well as the propellants used in rockets and missiles are covered in Volume 2.

Primers, Matches, and Signals

Primers, receiving their activating energy through some physical action such as impact or friction, provide the flame, hot gas, and hot particles necessary to ignite a propellant, fuze, or initial detonating charge. They are mixtures for, as yet, no single substance has been found which satisfies all of the requirements of their uses. Potassium chlorate is frequently a component because it makes the mixture sensitive to friction and provides the oxygen required for combustion. However, one of the products of combustion of a chlorate composition is chloride which is very corrosive to firearms. Noncorrosive priming compositions, containing an oxygen source such as a barium nitrate, instead of a chlorate, are known and used. A typical priming mix is composed of mercury fulminate or lead azide, antimony sulfide, potassium chlorate, and particles of glass or silicon carbide. Many chlorate-containing primer compositions are possible, and the quantity of potassium chlorate they contain varies from about 15 to 60 percent. (33, 58, 98)

Potassium chlorate-containing compositions, with a similarity to priming compositions, are used for matches, toy caps, pull-wire igniters, electric squibs and matches, railroad torpedoes and fuses, smokes, flares, and various pyrotechnics. In fact, the match industry is the largest consumer of potassium chlorate, using about 6200 tons in 1953 which was about 80 percent of the amount produced.[41] Barium chlorate is used to some extent in fireworks.

Potassium perchlorate, which has generally replaced the chlorates in colored lights and illuminating flares, and ammonium perchlorate find important but small tonnage use in smoke puff generators, gas gencrators, flash powder, colored flares, sulfur dioxide generators pistol rocket-fired distress signals, and railway fusees. Strontium and barium perchlorates have been used in the dual role of oxidizer and coloring agent in flares.*

The representative formulas for several compositions employing potassium chlorate or perchlorate which follow were furnished by Kilgore, Inc:

RED SIGNAL COMPOSITION

	Percentage
Potassium Perchlorate	12.46
Asphaltum (Gilsonite)	5.67
Hexachlorobenzene	5.67
Strontium Nitrate	40.80
Magnesium	34.00
Graphite	1.40

* From private communications from U.S. Flare Corp. and Universal Match Corp., Armament Div., and Kilgore, Inc.

ORANGE SMOKE COMPOSITION

	Percentage
Paratoner Dark Dye	48.31
Potassium Chlorate	21.74
Lactose	13.53
Filler (Asbestos Sheets)	16.42

GREEN SIGNAL COMPOSITION

Barium Nitrate	51.95
Barium Chloride	4.90
Magnesium	21.56
Potassium Perchlorate	4.90
Linseed Oil	1.95
A-4 Black Powder	2.00
Hexachlorobenzene	12.74

IGNITER COMPOSITION

Potassium Chlorate	53.70
Burnt Umber	6.30
Strontium Carbonate	1.88
Airfloat Charcoal	3.12
Shellac (3 lb. in 1 gal. Ethyl Alcohol)	14.14

IGNITER COMPOSITION

Potassium Chlorate	88
Powdered Charcoal	10
Dextrin	2

Smoke Grenades

The use of different colored smoke grenades to mark targets for artillery and aircraft plays an important role in today's warfare, especially for close ground-air support. The smoke grenade consists of a container with four small holes through which the smoke escapes. The smoke is created by the incomplete burning of a composition containing an aniline dye of the desired color and an oxidizer usually potassium chlorate.

This composition is set burning by a fuse such as those used in regular explosive hand grenades. To obtain the various colors, the following formulas have been developed by the Chemical Warfare Service.[95]

Yellow #1	Percent
Auramine O	38
Sodium Bicarbonate	28.5
Potassium Chlorate	21.4
Sulfur	9.4
Other	2.7

Yellow #2	
Beta-Naphthalene Azodimethylaniline	50.0
Potassium Chlorate	30
Sugar	20

Red #1	
Diethylaminorosidone	48
Potassium Chlorate	26
Sugar	26

Red #2	
Methylaminoanthraquinone	42.5
Potassium Chlorate	27.4
Sodium Bicarbonate	19.5
Sulfur	10.6

Orange #1	
1-Amino-8-Chloroanthraquinone	39.0
Auramine O	6.0
Sodium Bicarbonate	24
Potassium Chlorate	22.3
Sulfur	8.7

Orange #2	Percent
a-Aminoanthraquinone	24.6
Auramine O	16.4
Sodium Bicarbonate	24.0
Potassium Chlorate	25.9
Sulfur	10.1
Violet	
1-Methylaminoanthraquinone	18.0
1,4-Diamino-2,3-dihydroanthraquinone	26.0
Sodium Bicarbonate	14.0
Potassium Chlorate	30.2
Sulfur	11.8
Green	
Auramine O	11.7
1,4-Di-p-toluidinoanthraquinone	28.3
Sodium Bicarbonate	24.0
Potassium Chlorate	25.9
Sulfur	10.1
Blue	
1,4-Dimethlaminoanthraquinone	50.0
Potassium Chlorate	25.0
Sugar	25.0

Smoke Shells

Smoke shells are made by filling the inside of the shell with finely divided powder of the desired color. The colors in general use are: (1) red, American Vermillion; (2) blue, Ultramarine; (3) green, Paris green; (4) yellow, chrome yellow; (5) white, chalk; and (6) black, ivory black. These colors are loaded into the shell case with enough explosive charge to burst the case and spread the finely divided powders giving observers an easy method of spotting and correcting artillery fire.

Parachute Flares

Parachute flares are used to illuminate battlefields. These flares are made in many sizes varying from small trip flares to the large ones dropped from airplanes for night photography. One of the smaller flares is the trip flare, a mine that is actuated by a trip wire on a pull fuse. Anyone hitting the wire would cause the flare to go off revealing his position. This type is generally placed in front of defensive positions to give the alarm in case of an enemy attack. The airplane flare gives about 350,000 candle power and when dropped from about 5,000 feet will burn for approximately five minutes allowing ample time for reconnaisance photographs or for bomb runs by the planes. In the intermediate range there are parachute flares that can be fired by the infantry from 60mm mortars or from larger guns by the artillery. A flare composition usually contains a mixture of chlorates, or perchlorates, aluminum or magnesium powder and a binder. Flares are packed into a case containing the parachute that is released at a predetermined time by a small charge allowing it to open and drop the flare slowly back to earth.

Signal Flares

Signal flares and Very pistol flares were developed as a visual signal to be used either at night or by day. The Very pistol is a hand gun that fires a shotgun type shell containing a colored star or cluster. The star or cluster rises to a height where it can be seen before igniting and usually there is assigned some meaning for each color. Very pistol flares are

quite frequently for signalling when radio or telephone communications might fail or do not exist, such as distress signals for transoceanic airplane emergency kits.

These flares are usually composed of an oxidizer, a binder and some metal that gives off a characteristic color when it burns. The oxidizers most frequently used are potassium chlorate, potassium perchlorate and sodium chlorate. The colors are produced by the following materials: (1) red, strontium nitrate or carbonate; (2) pink, calcium carbonate or sulfate; (3) green, barium nitrate or chlorate and ammonium chloride or calomel; (4) blue, copper sulfate or other copper compound and ammonium chloride; (5) yellow, sodium compounds.

There are other additives used to give brilliance to the colors.

Tracer Bullet

Tracers are used to direct the fire of machine guns as an aid to getting on target. Usually every fifth bullet is a tracer and the gunner watches them and moves his gun just as a fireman directs a stream of water on a fire. Tracers have a small pyrotechnic charge inside the jacket. This charge consists of potassium chlorate, strontium nitrate or other colorant, fine charcoal and a shellac binder and is ignited by the propellant charge, burning on the way to the target. It gives a glow that can be seen by night or by day.

Smoke Screens

Smoke screens are used to conceal troop movements from enemy observation. Once used extensively in naval warfare, the effectiveness

has been hampered by modern advances such as radar. In land warfare, smoke screens are still used to cover the advance of infantry or armor. These screens are usually laid down by the artillery firing smoke shells or by smoke generators. These smoke generators contain zinc dust, hexachloraethane, ammonium perchlorate, ammonium chloride, and calcium carbonate. On igniting the generator, the reaction of zinc dust and hexachloraethane produces zinc chloride and free carbon which pass off in the smoke. Ammonium perchlorate acting as an oxidizer helps keep the reaction going. The calcium carbonate stabilizes the reaction by absorbing any hydrogen chloride that may be formed.

Explosives Applications

Use of chlorates and perchlorates in the explosives field is limited almost entirely to primers and rocket propellants (see Section on Pyrotechnics). Explosive mixtures containing chlorates are characterized by extreme sensitivity to friction. This property, ideal for priming material, renders chlorate mixtures undesirable for use as propellants or noninitiating explosives. Perchlorates, while more stable than chlorates, do not have a satisfactory record in the field of explosives except as the oxidizing agent in solid rocket propellants Failure of chlorates and perchlorates to become dependable, practical agents for noninitiating high high explosive and blasting explosive uses may be attributed to their inherent dangerous and erratic sensitivity, which as yet has not been satisfactorily controlled for general use, and to the formation of irritating and toxic fumes

when detonated.[30, 58, 98] Even so, literature of the explosives field contains many records of their use, attempted use, and incorporation into explosive formulations. Because this past activity is of historical interest in the explosives field and of significance to those who would develop desirable chlorate and perchlorate explosives in the future, it has been surveyed and included in this chapter.

General Uses

The first recorded use of a chlorate as an explosive was in 1788 when an attempt to prepare a more potent gunpowder resulted in an unwanted explosion which was fatal to two people.[33] Although this did not prevent subsequent work with chlorates and perchlorates as explosives, it did establish a pattern which has since dogged the manufacture and use of explosives employing these substances.[30, 58] However, several types of chlorate and perchlorate high explosives were developed and used rather widely during the latter part of the 19th century and World War I.[33]

The first of these were the Sprengel explosives, patented in 1871 by Herman Sprengel.[98] This type of explosive consisted of an oxidizing agent and a combustible substance which were combined at the demolition site. This practice permitted the safe transport of the ingredients and avoided certain storage and deterioration problems. When a chlorate was used as the oxidizing agent, it was combined with combustible liquids such as carbon disulfide, nitrobenzene, and various petroleum fractions. A combination of nitrobenzene and potassium chlorate in a 1:4 ratio was called

Rack-a-Rock.[16] It was a very efficient underwater explosive and was used for blasting the entrance to New York Harbor.

Sprengel explosives were used in the United States, France, Italy, Russia, and China but were forbidden in England and other countries as being contrary to the explosives manufacturing laws.[33] They were successfully employed in general demolition work, in artillery ammunition, and in aerial bombs, but they have been replaced by more desirable explosives.

One of the early dynamites used in England was called Ajax Powder.[16] It contained wood flour, potassium perchlorate, nitroglycerin, ammonium oxalate and small quantities of collodion cotton and nitrotoluene. Another blasting agent, Blastine, used in World War I for mining, had the following formula:

Ammonium Perchlorate	60%
Sodium nitrate	22%
Paraffin Wax	7%
TNT	11%

Other blasting compositions used at varous times include the following:

Coronite was a German blasting powder based on chlorates and was used in quarries and mines. It had the formula:

Sodium chlorate	72%
Vegetable meal	1%
Tri and dinitrotoluene	20%
Paraffin	4%
Nitroglycerine	3%

Gelatin Dynamite is a waterproof plastic dynamite that can be loaded into bore holes and gives off very little toxic gas. It is suitable for underground work. It gives a maximum shattering effect and is useful in underwater work. Its composition is:

Nitroglycerine	36%
Nitrocellulose	2%
Vegetable meal	2%
Nitrotoluene or naphthalene	8%
Nitrates or perchlorates	52%

Percoronite is a German blasting powder based on perchlorates and is used in mines and quarries. Its composition is:

Potassium perchlorate	65%
Nitroglycerine	5%
Aromatic Nitro Compounds	25%
Vegetable meal	5%

Cheddites is the name which was given to certain chlorate explosives manufactured first in Chedde, France, under patents held by Street.[97] A cheddite was composed of a chlorate, a desensitizing fatty oil such as castor oil, and a nitroaromatic compound such as nitrobenzene. Other composition variations included the addition of nitrocellulose and nitroglycerin to give a more plastic, more brisant, but less sensitive preparation. Cheddites were used in grenades, mortar shells, and in demolition work.[33]

The perchlorate explosives, such as those above and others employing the sodium, potassium or ammonium compounds have thus found some use for blasting and in mortar ammunition. It should be noted that in addition to the perchlorate component, these explosives usually contained

variable quantities of an inorganic nitrate, a nitroaromatic compound, paraffin, and perhaps a metal powder.[21] The formation of objectionable gaseous products, high cost, deterioration during storage, and the lack of any exceptional explosive quality have discouraged the use of perchlorate explosives in general applications.[33,98]

The use, interest in, and development of chlorate and perchlorate explosives continued after the close of World War I, although mostly outside of the United States.[30,67] For instance, in 1921, chlorate explosives were being used in the potash, salt, and iron ore mines in Germany[71], and the patents issued since that time are predominantly foreign. The salient features of some of these patents are as follows:

(1) Producing a more intimate mixture of ammonium perchlorate and sodium nitrate

(2) A method for producing solid, porous blocks of a chlorate

(3) A mixture of potassium chlorate, sugar or antimony, sulfur, sodium bicarbonate, and a combustion-controlling agent such as wood flour[24,75,76,92]

(4) A mixture of potassium chlorate, sugar, wood pulp or sawdust, aromatic compounds, and petrolatum[66]

(5) Incorporation of salt as a cooling agent and absence of any nitrogen compounds[52]

(6) Method of dispersing a sensitizing agent with the chlorate in anhydrous ammonia[5]

(7) The incorporation of shredded wood into a chlorate explosive mix[23]

(8) A mixture of chlorate or perchlorate with starch or gum, cellulose, etc., plus a stabilizing oily substance such as castor oil[64]

(9) A mixture similar to those above but made to explode with thermite in a closed space[19]

(10) The addition of a chlorinated hydrocarbon and rosin or tar to a chlorate or perchlorate explosive mixture[65]

(11) A variable density perchlorate explosive[101]

(12) A chlorate explosive specifying chestnut wood extract as an essential additive[81]

(13) A chlorate mixture incorporating protein substances, several inorganic compounds, and formaldehyde[79]

(14) A mixture of a chlorate-nitrate explosive similar to those above but containing hexamethylene tetramine[47]

(15) A mixture of sodium chlorate, organic explosives, and polyvinyl acetate which can be used in water[11]

(16) A mixture of ammonium perchlorate, nitrocellulose, and ammonium nitrate useful for blasting[12].

Chlorates as Herbicides

The use of chlorates to kill weeds is well documented.[46,48,68,69,86,90] They are toxic to almost all plant life, in contrast to the recently developed selective-action organic compounds. Because chlorate is readily translocated from one part of the plant to the other, the toxic solution may be applied effectively to the soil or directly onto the plants.[48,96] Some investigators claim that application of the proper amounts of chlorates stimulates nitrogen and humus formation in the soil, increasing plant growth.[34,35,49,61] The results obtained with chlorates as weed killers have varied widely with changes in soil type, rainfall amounts, mode of application, quantity applied, and time of application with respect to the life cycle of the plant.[39,68,90,96] The most widely used chlorate for this purpose is sodium chlorate which was being consumed in this use at a rate of about 12,000 tons per year immediately following World War II.* Magnesium perchlorate is used as a cotton defoliant.[57]

Contact of chlorates with organic matter, particularly dried vegetation, constitutes a genuine fire hazard.[6] To lessen this hazard, fire retardants such as calcium chloride[48], alkali metal carbonates or bicarbonates[87], sodium stannate, and borates[4,29,60,86] have been added to weed killing mixes.

* Kirk, R. E., and Othmer, D. F., Encyclopedia of Chemical Technology, Vol. 3, The Interscience Encyclopedia, Inc., N. Y. (1949).

Additional action, synergistic in some cases, is developed when chlorates are mixed with other toxic or herbicidal compounds such as 4, 6-dinitro-o-cresol[45], borates[4, 29, 60, 86, 88], trichloracetates[91] and zinc sulfate.[39]

To give chlorate solutions increased retention time and better wetting action on plants, emulsifying agents[45] and other materials* have been added.

Although chlorates are classified as nonselective herbicides, some selectivity of action has been claimed in a French patent employing chlorates and additives of potassium, magnesium, or ammonium salts in very dilute solutions[7], and wheat and oats may be treated with amounts which will not injure them but which will destroy the weeds.[46]

Perchlorates as Drying and Absorptive Agents

The first comprehensive study of magnesium perchlorate as a desiccant was reported by Willard and Smith[99] in 1922 who found that this perchlorate was about as efficient as phosphorus pentoxide as a drying agent and had the following advantages:

(1) Higher absorptive capacity for water per unit weight

(2) Nonsticky in use

(3) Easier to recover and to reactivate

(4) Chemical neutrality

* Kirk, R. E., and Othmer, D. F., Encyclopedia of Chemical Technology, Vol. 3, The Interscience Encyclopedia, Inc., N. Y. (1949).

The trihydrate was observed to be nearly as effective as the anhydrous form. This was verified by later investigators, Moles and Roquero[70], who found that the absorptive power did not diminish until the amount of water taken up became equivalent to the composition $Mg(ClO_4)_2 \cdot 4.5\ H_2O$. A commercial application for magnesium perchlorate as a final stage dryer for oxygen during the fractional distillation of liquid air was described by Smith in 1934.[84] More recently, the rate at which laboratory desiccators are dehydrated by magnesium perchlorate and other dessiccants has been investigated[85], and the use of this compound as a quantitative absorbent for many organic vapors has been reported[15], along with the suggestion that it is probably effective for all polar vapors. Although no explosions occurred in the organic vapor absorption work, adequate safety precautions are recommended. Other workers[37, 38, 62, 100] have reported activities relating to the use of magnesium perchlorate as a drying absorption agent.

Barium perchlorate is a good drying agent, also, although not quite so efficient as the magnesium compound. Its use as a desiccant and reversible absorbent for ammonia has been studied and reported by Smith.[82, 83]

Miscellaneous Uses

Assorted minor uses have been found for chlorates and perchlorates. In metallurgical and related fields, chlorates and perchlorates have been used as oxygen source additives[51, 93], corrosion inhibitors[77], and in metal phosphating preparations.[63]

Perchlorates have been used as a polymerization promoter[42] and inhibitor[56], gel coagulation agent[18], and the silver compound has been

reported to exhibit catalytic activity of the Friedel-Crafts type.[25, 26] Such catalytic activity has been questioned, however.[22] Other uses are as a laboratory reagent[17, 36], and electrolyte (magnesium compound) in a primary cell.[28]

Chlorates have been used as oxidizing agents for dyes and other organic compounds[2], as sources of oxygen for physiological, workshop, and laboratory use[53, 80], laboratory reagent and primary standard[59, 73, 78], and polymerization catalyst for vinyls.[55]

BIBLIOGRAPHY

1. Abbott, Frederick C., C. A. 44, 8312c.

2. Alexander, T. J. R., C. A. 23, 28275.

3. Aktiebolaget, Finska Elektrokemiska, C. A., 11773.

4. Anon., C. A. 51, 8395b (1957).

5. Anon., C. A. 36, 11809

6. Anon., C. A. 34, 71108.

7. Anon., C. A. 28, 11348, (P).

8. Anon., Chem. Eng. 63, 7, 134-36 (July 1956).

9. Anon., Oil, Paint, and Drug Reporter 170,11, 7 (Sept. 10, 1956).

10. Anon., Chem. Week, 83, 3, 91-94, (July 19, 1958).

11. Anon., C. A 45, 3599c.

12. Anon., C. A. 47, 7779g.

13. Anon., C. A. 29, 38425.

14. Anon., C. A. 46, 9311f (P).

15. Bacarella, A. L., Dever, David F., and Greenwald, Ernest, C. A. 50, 2368b.

16. Bebie, Jules, Manual of Explosives, Military Pyrotechnics and Chemical Warfare Agents, MacMillan Co., New York, 1943.

17. Biedermann, Geo., C. A. 50, 16296e.

18. Biget, Anne M., C. A. 44, 5186a.

19. Billwiller, John, C. A. 42, 9180a.

20. Bjorkman, P. O., C. A. 28, 63119.

21. Burrows, Edwin H., C. A. 27, 20368.

22. Burton H., and Praill, P. F. G., C.A. 48, 7582[f].

23. Byers, Laud S., C.A. 31, 5583[5].

24. Corta, Fazzoro, C.A. 33, 2339[4].

25. Cauquil, G., Barrera, H., and Barrera, R., C.A. 49, 3038[d]. cf. C.A. 46, 6102[b]

26. Cauquil, Germaine, Barrera, Héribert, Barrera, Renée, C.A. 50, 2487[a].

27. Chilton, C.H., Chem. Eng., 64, 11, 142-4 (Nov. 1957).

28. Coleman, Joseph J., Lauzos, Demetrios V., C.A. 46, 8547[i] (P).

29. Connell, George A., C.A. 50, 13361[a] (P).

30. Cook, Melvin A., Reinhold Pub. Corp., New York (1958), 14.

31. Cook, W. H., C.A. 27, 5140[2].

32. Darmois, Eugene, Epelboin, Israël, and Amine, Djafar, C.A. 45, 2336[h].

33. Davis, Tenny L., John Wiley and Sons, Inc., New York, Vol. I and II, 354-367 (1953).

34. Dekatov, N. E., C.A. 44, 3645[e].

35. Dekatov, N. E., C.A. 44, 2156[e].

36. Deniger, G., C.A. 11, 2309[6].

37. Druce, J. G. F., C. A. 29, 5948[2].

38. Druce, J. G. F., C.A. 29, 2257[2].

39. Eglite, A., C.A. 47, 6592[e].

40. Epelboin, Israël, C.A. 52, 8786[e].

41. Faith, W. L., Keyes, D. B., and Claric, R. L., Industrial Chemicals, 2nd ed., John Wiley and Sons Inc. (1957).

42. Feldman, Isaac, and Havill Jean R., C.A. 46, 8460[h].

43. Fieldner, A. C., and Brewer, R. E., C.A. 40, 5899[2] (1946).

44. Fisher, N., Ritchie, M. L., Williams, J., and Coppock, J. B. M., Chem. and Ind., 35, 1179-80 (Aug. 31, 1957).

45. Fogg, Gordon E., and Warburg, James W., C.A. 45, 6792[h].

46. Fron, G., C.A. 28, 4822[5].

47. Garcia, Alvaro H., C.A. 35, 898[4].

48. Godchaux, Leon, C.A. 43, 9351[d].

49. Gordienko, M., C.A. 47, 7143[e].

50. Granstrom, M. L., and Lee, G. Fred, Am. Water Works Ann. J., 50, 11, 1453-66 (Nov. 1958).

51. Griffiths, Frederick J., C.A. 45, 2843[b].

52. Hallett, Charles S., C.A. 36, 272[7].

53. Harukaze, Udaka, C.A. 18, 796[7].

54. Heyes, Josef, and Fischer, Wilhelm, C.A. 52, 10770[c].

55. Hill, Archie, C.A. 48, 14297[d].

56. Jones, James R., C.A. 52, 674[h].

57. Kirk, Othmer, Ency. of Chem. Technol., Interscience Pub., Inc., New York, 15, 18 (1956).

58. Kirk, R. E., and Othmer, D. F., Ency. of Chem. Technol., The Interscience Encylopedia, Inc., New York, 6, 1-90 (1951).

59. Kling, A., and Lassieur, A., C.A. 17, 1396[6].

60. Knight, Harold P., C.A. 49, 5794[e].

61. Kotlyar, M. L., C.A. 50, 9671[c].

62. Lenher, Sam, and Taylor, Guy B., C.A. 24, 2342[3].

63. Ley, Helmut, Stenger, Walter, and Werner, Willy, C.A. 46, 14278.

64. Lorenzini, Ettore, C.A. 36, 1496[4].

65. Matter, Oskar, C.A. 43, 2437[d].

66. McMeans, Dewitt C., C.A. 32, 3156[1].

67. Medard, Louis, C.A. 47, 9013[i].

68. Minshall, W. H., C.A. 44, 3656[b].

69. Minshall, W. H., C.A. 42, 6982[e].

70. Moles, E., and Roquero, C., C.A. 27, 1555[7].

71. Muhlcfeld, Bergass, C.A. 16, 496[3].

72. Neumark, Aug. S., C.A. 6, 535[9].

73. Nutten, A. J., C.A. 44, 3395[a].

74. Osakcyhtio, Kymin, C.A. 43, 3159[h]

75. Pert, Henry G., C.A. 35, 8299[4].

76. Pert, Henry G., C.A. 33, 8993[1]

77. Robertson, W. D., C.A. 46, 7403[a].

78. Roth, Fritz, C.A. 39, 3184[6] (1945).

79. Schliemann, Martin, C.A. 52, 14172[d].

80. Schnechter, William H., Miller, R. R., Bovard, Robert M., Jackson, C. B., and Pappenheimer, John R., C.A. 45, 285[i].

81. Simoncini, Alberto, C.A. 52, 15910[g] (1958).

82. Smith, G. Frederick, C.A. 23, 53[1].

83. Smith, G. Frederick, C.A. 23, 2612[6].

84. Smith, G. Frederick, C.A. 28, 4139[3].

85. Smith, G. Frederick, Bernhart, D. U., and Wiederkehr, V. R., C.A. 46, 7253[b].

86. Spon, F. S., C.A. 45, 7739[f].

87. Stockholms Superfostat Fabriks Aktiebolag, C.A. 31, 5109.

88. Stone, J. D., and Smith, L. M., C.A. 48, 8464g.

89. Streijffert, Peter W., C.A. 44, 2246[f].

90. Sven, L. Jansson, Jacobson, Georg, and Jägerstahl, Gustav, C.A. 46, 5246[e].

91. Taylor, Jack P., C.A. 46, 5252[f].

92. Tremblay, Guy, and Carta, Lazzaro, C.A. 31, 2824[3].

93. Vignos, James C., C.A. 47, 7426g.

94. Virgili, Juan Tages, C.A. 5, 1724[8].

95. Weingart, George W., Pyrotechnics, Chemical Publishing Co., Brooklyn, N. Y. (1947).

96. Whiteley, M. A., Thorpe's Dictionary of Applied Chemistry, Fourth Ed., XI, 947 (1954).

97. Whiteley, M. A., Thorpe's Dictionary of Applied Chemistry, II, 525 (1946).

98. Whiteley, M. A., Thorpe's Dictionary of Applied Chemistry, IV, 453-552 (1946).

99. Willard, H. H., and Smith, G. F., J. Am. Chem. Soc., 44, 2255-9 (1922).

100. Yoe, J. H., C.A. 19, 2430[6].

101. Yoshihara, Ko, C.A. 51, 13400[a] (1957).

102. Zuber, Claude, and Jomain, Bernard, C.A. 47, 8376[a].

APPENDIXES

APPENDIX A

PROPERTIES OF CHLORATE AND PERCHLORATE COMPOUNDS

APPENDIX A

PROPERTIES OF CHLORATE AND PERCHLORATE COMPOUNDS

CONTENTS

Section		Page
A1	INTRODUCTION	220
A2	GENERAL PROPERTIES	223
A3	PROPERTIES OF SOLIDS	229
A4	PROPERTIES OF AQUEOUS SOLUTIONS	257
A5	PROPERTIES OF NONAQUEOUS SOLUTIONS	431
A6	THERMODYNAMIC PROPERTIES	533
A7	EXPLOSIVE PROPERTIES	568
A8	TOXIC PROPERTIES	574
BIBLIOGRAPHY		587

A1. INTRODUCTION

Property data are presented in seven major groupings as follows: General Properties, Properties of Solids, Properties of Aqueous Solutions, Properties of Nonaqueous Solutions, Thermodynamic Properties, Explosive Properties, and Toxic Properties.

In the General Properties Section, which consists of often-used information, tables are arranged in handbook style. The data in these tables are taken from the Handbook of Chemistry and Physics, 39th Edition, except where otherwise noted. Single values are given and these values do not appear in the individual property tables which follow, except where they are the sole source of information or are at variance with data obtained from different sources.

At the beginning of the sections on Properties of Solids and Thermodynamic Properties, and at the beginning of each subsection of the Properties of Nonaqueous Solutions, a list is given of the contents within the section or subsection. The data are tabulated under particular property headings, with the tables containing the data for chlorates always preceding the ones for perchlorates. For the Properties of Solids and Thermodynamic Properties, units are given immediately following the table title. The volume of data for the Properties of Aqueous Solutions and for the Properties of Nonaqueous Solutions was such that a symbol system was used for identification of certain units within each category, or subsection, of data. The key to the symbols used is presented immediately before the contents list of a category of data to which it applies, except in the Miscellaneous Subsections where the symbols are explained on each page.

Most of the data acquired in the literature search has been presented. An effort has been made to avoid duplication of the values of an original work with the same values taken from a secondary source. Occasionally, data were omitted because they were confusing, definitive units or temperature were not given, tabulation was not practical, or procurement of the pertinent journal was not possible under the limits of the work. In these instances, references to the sources are given within the section concerned. Where data were presented in original articles in units other than those chosen for this work, they were converted to the chosen units for the sake of uniformity. Omission of a compound from a particular property table means that data were not found for that compound.

Some narrative material was required to describe certain properties adequately, particularly in the sections on Explosive Properties and Toxic Properties, and it has been inserted where judged advisable. However, wherever possible, presentation of information in Appendix A has been made in tabular form.

A2. GENERAL PROPERTIES

TABLE OF CONTENTS

Table		Page
A2-1	GENERAL PROPERTIES - CHLORATES	225
A2-2	GENERAL PROPERTIES - PERCHLORATES	227

TABLE A2-1. GENERAL PROPERTIES - CHLORATES[a]

No.	Name	Formula	Molecular Weight	Crystalline Form and Color	Sp. Gravity or Density	Melting Point °C	Solubility, g/100 ml of Cold H_2O	Hot H_2O	Alcohol, Acids, etc.
1.	Aluminum chlorate	$Al(ClO_3)_3 \cdot 6H_2O$	385.44	rhbdr. col., deliq.		d.	vs	vs	S. dil. HCl
2.	Ammonium chlorate	NH_4ClO_3	101.50	monocl. need. col.		exp. 102	vs	vs	sl. s. al.
3.	Barium chlorate	$Ba(ClO_3)_2$	304.27	col.(169)		414(308)	20.35 at 0° (1-169)	84.8 at 80° (1-169)	
4.	Barium chlorate	$Ba(ClO_3)_2 \cdot H_2O$	322.29	monocl. col.	3.18	$-H_2O$ at 120	27.4	111.2	sl. s. al., acet., HCl
5.	Calcium chlorate	$Ca(ClO_3)_2 \cdot 2H_2O$	243.03	monocl. wh-yelsh., deliq.	2.711	$-H_2O$ >100	177.7 at 8°	vs	s. al., acet.
6.	Lithium chlorate	$LiClO_3$	90.40	rhomb. need. col.		124-9.	18° 313.5	vs	
7.	Lithium chlorate	$LiClO_3 \cdot 1/2H_2O$ or $1/3H_2O$	99.41	tetr., deliq.		65	s.	∞	vs. al.
8.	Lithium chlorate	$LiClO_3 \cdot H_2O$	108.42	Long, flat platelets, probably tetragonal(19)		+22(19)			
9.	Lithium chlorate	$LiClO_3 \cdot 3H_2O$	144.45			$-H_2O$ m+8.1°(19)			
10.	Magnesium chlorate	$Mg(ClO_3)_2$	191.23			d. 120(198)			

NAVORD REPORT 7447 (VOLUME 1)

TABLE A2-1. GENERAL PROPERTIES - CHLORATES[a] (Cont'd)

No.	Name	Formula	Molecular Weight	Crystalline Form and Color	Sp. Gravity or Density	Melting Point °C	Solubility, g/100 ml of Cold H_2O	Hot H_2O	Alcohol, Acids, etc.
11.	Magnesium chlorate	$Mg(ClO_3)_2 \cdot 2H_2O$	227.27			d. 80[198]			
12.	Magnesium chlorate	$Mg(ClO_3)_2 \cdot 4H_2O$	263.30	Rhombohedral[198]		$-2H_2O$ at 65 [198]			
13.	Magnesium chlorate	$Mg(ClO_3)_2 \cdot 6H_2O$	299.33	wh. cr. or powder. deliq.	$1.80^{25°}$	35	$56.5^{18°}$	$73.7^{93°}$	s. al. acetone[198]
14.	Potassium chlorate	$KClO_3$	122.55	monocl. col	2.32	368.4	$7.1^{20°}$	$57^{100°}$	0.831 al. s. alk.
15.	Silver chlorate	$AgClO_3$	191.34	tetr. wh.	4.430	230	$10^{15°}$	$50^{80°}$	sl. s. al.
16.	Sodium chlorate	$NaClO_3$	106.45	cub. or trig. col.	$2.490^{15°}$	248-261	$79^{0°}$	$230^{100°}$	s. al. glyc.

[a] Values in this table are from Handbook of Chem. and Physics, 39th Ed., C. D. Hodgman, Ed-in-Chief, Chem. Rubber Co., Cleveland (1957)[115] unless otherwise noted.

TABLE A2-2. GENERAL PROPERTIES - PERCHLORATES[a]

No.	Name	Formula	Molecular Weight	Crystalline Form and Color	Sp. Gravity or Density	Melting Point °C	Solubility, g/100 ml of Cold H_2O	Hot H_2O	Alcohol, Acids, etc.
1.	Aluminum perchlorate	$Al(ClO_4)_3$	325.34		2.209[10]				
2.	Aluminum perchlorate	$Al(ClO_4)_3 \cdot 6H_2O$	433.44		2.020[10]	120.8[205]			
3.	Aluminum perchlorate	$Al(ClO_4)_3 \cdot 9H_2O$	487.49		1.924[10]	85.3[205]			
4.	Ammonium perchlorate	NH_4ClO_4	117.50	rhomb. col.	$1.95\frac{20°}{4}$	d.	$10.74^{0°}$	$42.54^{85°}$	s. acet., sl. s. al.
5.	Barium perchlorate	$Ba(ClO_4)_2$	336.27	hex. col.		505	$198.5^{25°}$	vs	v. s. al.
6.	Barium perchlorate	$Ba(ClO_4)_2 \cdot 3H_2O$	340.32	hex.	2.74	d. 400	s	s	v. s. al.
7.	Calcium perchlorate	$Ca(ClO_4)_2$	238.99	col. deliq. prisms[198]		123[96]	vs.		$166.2\frac{25}{25}$ al. $237.4^{25°}$ m. al. s. acet., v. sl. s. eth
8.	Lithium perchlorate	$LiClO_4$	106.40	col. deliq.	2.429	236	$59.7^{25°}$		s. al.
9.	Lithium perchlorate	$LiClO_4 \cdot 3H_2O$	160.45	hex. col.	1.841	95[308]	s	s	v. s. al.
10.	Magnesium perchlorate	$Mg(ClO_4)_2$	223.23	wh. deliq.[169] long prisms[198]	$2.60\frac{25°}{4}$ [308]	251 d.	$49.90^{25°}$	v. s.	$24^{25°}$ al. $51.8^{25°}$ m. al. [169]

TABLE A2-2. GENERAL PROPERTIES - PERCHLORATES[a] (Cont'd)

No.	Name	Formula	Molecular Weight	Crystalline Form and Color	Sp. Gravity or Density	Melting Point °C	Solubility, g/100 ml of Cold H_2O	Hot H_2O	Alcohol, Acids, etc.
11.	Magnesium perchlorate	$Mg(ClO_4)_2 \cdot 3H_2O$	277.28		$2.044^{(319)}$				
12.	Magnesium perchlorate	$Mg(ClO_4)_2 \cdot 6H_2O$	331.33		$1.970^{25°}$	147	$s^{(169)}$		s. al.$^{(169)}$
13.	Potassium perchlorate	$KClO_4$	138.55	rhomb. col.	$2.52^{10°}$	610 ± 10	$0.75^{0°}$	$21.8^{100°}$	i. al., eth.
14.	Silver perchlorate	$AgClO_4$	207.34	wh. cr., deliq. cubic	$2.806^{25°}$	d. 486	$525^{25°}$	s.	s. al., tol
15.	Sodium perchlorate	$NaClO_4$	122.45	rhomb. deliq.		482 d.	s.	vs.	s. al.
16.	Sodium perchlorate	$NaClO_4 \cdot H_2O$	140.47	rhbdr. col., deliq.	2.02	130	$209^{15°}$	$284^{50°}$	s., al.

[a] Values in this table are from Handbook of Chem. and Physics, 39th Ed., C. D. Hodgman, Ed-in-Chief, Chem. Rubber Co., Cleveland (1957)[115] unless otherwise noted.

NAVORD REPORT 1147 (VOL. 1)

A3. PROPERTIES OF SOLIDS

TABLE OF CONTENTS

Section or Table		Page
A3-1	DENSITY, g/cc, OR SPECIFIC GRAVITY OF CHLORATES	232
A3-2	DENSITY, g/cc, OR SPECIFIC GRAVITY OF PERCHLORATES	233
A3-3	MELTING POINT OF CHLORATES, °C	234
A3-4	MELTING POINT OF PERCHLORATES, °C	236
A3-5	BOILING POINT OF CHLORATES, °C	237
A3-6	BOILING POINT OF PERCHLORATES, °C	237
A3-7	REFRACTIVE INDEX OF CHLORATES	238
A3-8	REFRACTIVE INDEX OF PERCHLORATES	239
A3.1	RAMAN SPECTRA	240
A3-9	INFRARED ABSORPTION FREQUENCIES OF CHLORATES, cm^{-1}	241
A3-10	INFRARED ABSORPTION FREQUENCIES OF PERCHLORATES, cm^{-1}	242
A3.2	OPTICAL ACTIVITY	243
A3-11	CRYSTALLOGRAPHY OF CHLORATES	244
A3-12	CRYSTALLOGRAPHY OF PERCHLORATES	245
A3-13	TRANSITION TEMPERATURE OF CHLORATES, °C	246
A3-14	TRANSITION TEMPERATURE OF PERCHLORATES, °C	246
A3-15	THERMAL CONDUCTIVITY OF CHLORATES, cal/cm sec, °C	247

TABLE OF CONTENTS (Cont'd)

Section or Table		Page
A3-16	LINEAR COEFFICIENT OF EXPANSION FOR CHLORATES	247
A3-17	ELECTRICAL CONDUCTIVITY OF CHLORATES, $ohm^{-1}\ cm^{-1}$	247
A3-18	DIELECTRIC CONSTANT FOR CHLORATES	248
A3-19	DIELECTRIC CONSTANT FOR PERCHLORATES	248
A3-20	MOLAR AND IONIC MAGNETIC SUSCEPTIBILITY OF CHLORATES, x, c.g.s.e.m.u.	249
A3-21	MOLAR AND IONIC MAGNETIC SUSCEPTIBILITY OF PERCHLORATES, x, c.g.s.e.m.u.	250
A3-22	COMPRESSIBILITY OF SOME CHLORATES IN THE SOLID STATE	250
A3-23	FREEZING POINT OF SOME SOLID SOLUTIONS OF KNO_3-$KClO_3$	251
A3-24	FREEZING POINT OF SOME SOLID SOLUTIONS OF $KClO_3$- $NaClO_3$	252
A3-25	FREEZING POINT OF SOME SOLID SOLUTIONS OF $NaNO_3$-$NaClO_3$	253
A3-26	FREEZING POINT OF SOME SOLID SOLUTIONS OF $NaNO_3$-$KClO_3$	254
A3-27	FREEZING POINT OF SOME SOLID SOLUTIONS OF $NaClO_3$-KNO_3	255
A3.3	MISCELLANEOUS	256

TABLE A3-1. DENSITY, g/cc, OR SPECIFIC GRAVITY OF CHLORATES

Compound	Value	Reference
$Ba(ClO_3)_2 \cdot H_2O$	$3.18,\ 3.179\ \frac{20°}{4}$	308
	2.988, 3.179	198
$Ca(ClO_3)_2 \cdot 2H_2O$	2.711	115
$Mg(ClO_3)_2 \cdot 6H_2O$	$1.80^{25°}$	115
	$1.80\ \frac{20°}{4}$	308
	2.3	89
$KClO_3$	2.32	115
	$2.32\ \frac{20°}{4}$	308
	2.3467	309
	2.3385	5
	2.3383	50
	2.32	196
	2.344 (molar vol = 52.2cc)	108
	$2.326^{3.9°}$, $2.35^{17.5°}$, 2.246, 2.364	198
$AgClO_3$	4.430	115
	$4.430\ \frac{20°}{4}$	308
	4.42-4.44; $4.401^{23°}$, 4.21	198
$NaClO_3$	$2.490^{15°}$	308
	2.289, $2.490^{15°}$, 2.996, 2.488, 2.467	198
	2.307	233
	2.29	89

TABLE A3-2. DENSITY, g/cc, OR SPECIFIC GRAVITY OF PERCHLORATES

Compound	Value	Reference
$Al(ClO_4)_3$	2.209	10
	$1.95\ \frac{20°}{4}$	308
$Al(ClO_4)_3 \cdot 6H_2O$	2.020	10, 205
$Al(ClO_4)_3 \cdot 9H_2O$	1.924	10, 205
NH_4ClO_4	1.952	11, 198
	1.89	89
$Ba(ClO_4)_2 \cdot 3H_2O$	$2.74\ \frac{20°}{4}$	308
$LiClO_4$	$2.429\ \frac{20°}{4}$	308
	2.4284	309
$LiClO_4 \cdot 3H_2O$	$1.841\ \frac{20°}{4}$	308, 198
$Mg(ClO_4)_2$	$2.60\ \frac{25°}{4}$	308, 319
$Mg(ClO_4)_2 \cdot 3H_2O$	$2.044\ \frac{25°}{4}$	319
$Mg(ClO_4)_2 \cdot 6H_2O$	$1.970\ \frac{25°}{4}$	308, 319
$KClO_4$	$2.52\ \frac{20°}{4}$	308
	$2.524\ \frac{11°}{4}$	169
	$2.52^{10°}$	115
	2.54	89
	2.53574 ± 0.00014	2
$AgClO_4$	$2.806^{25°}$	115
$NaClO_4 \cdot H_2O$	$2.02\ \frac{20°}{4}$	308

TABLE A3-3. MELTING POINT OF CHLORATES, °C

Compound	Value	Reference
$Al(ClO_3)_3 \cdot 6H_2O$	d.	115
NH_4ClO_3	Exp. 102	115
	Exp. 100	169
	d. 102	198
$Ba(ClO_3)_2$	414	308
	400	198
$Ba(ClO_3)_2 \cdot H_2O$	$-H_2O$ at 120	308
$Ca(ClO_3)_2 \cdot 2H_2O$	$-H_2O$ above 100	115
	$-H_2O$ at 50	102
	$-H_2O$ at 50	198
	$-H_2O$ at 100	198
$LiClO_3$	124-129	115
	129	308
	129	198
	127.6	250
$LiClO_3 \cdot 1/2H_2O$	$-H_2O$ at 55	18
or	65	
$\cdot 1/3H_2O$	50, 63-65	198
	+50	
$LiClO_3 \cdot H_2O$	+22	19
$LiClO_3 \cdot 3H_2O$	+8.1	19
$Mg(ClO_3)_2$	d. 120	198
$Mg(ClO_3)_2 \cdot 2H_2O$	d. 80	198
$Mg(ClO_3)_2 \cdot 4H_2O$	$-2H_2O$ at 65	198
$Mg(ClO_3)_2 \cdot 6H_2O$	$-2H_2O$ at 35	198
	35, 40	198
	35	308

TABLE A3-3. MELTING POINT OF CHLORATES, °C (Cont'd)

Compound	Value	Reference
$KClO_3$	365	225
	368	169
	368.4	308
	357.1	34
	372, 370, 351, d. 352	198
	334, d. 352	89
$AgClO_3$	231	250
	230	308
	230	198
$NaClO_3$	248	308
	245	16
	255	94
	202, 248, 255, 261	198
	356, d. 350	304
	258	225
	302	89

TABLE A3-4. MELTING POINT OF PERCHLORATES, °C

Compound	Value	Reference
$Al(ClO_4)_3 \cdot 6H_2O$	120.8	205, 10
$Al(ClO_4)_3 \cdot 9H_2O$	85.3	205, 10
NH_4ClO_4	d.	115
$Ba(ClO_4)_2$	505	309, 198
	469	96
$Ba(ClO_4)_2 \cdot 3H_2O$	d. 400	198
$Ca(ClO_4)_2$	123	96
$LiClO_4$	236	308, 198
$LiClO_4 \cdot 3H_2O$	90	96
	95	308, 198
$Mg(ClO_4)_2$	246	96
	d. 251	308
$Mg(ClO_4)_2 \cdot 6H_2O$	147	308
	193	17
$KClO_4$	d. <400	265
	d. 400	308, 198
	588	96
	610	198
	610 ± 10°	115
	525 - 30	115
	610	89
$AgClO_4$	480	33
	d. 486	115
	486	198
$NaClO_4$	432	198
	473	96
	d. 482	308
$NaClO_4 \cdot H_2O$	130	115
	d. 130	308, 198

TABLE A3-5. BOILING POINT OF CHLORATES, °C

Compound	Value	Reference
$LiClO_3$	d. 270	308
	d. 290	198
$LiClO_3 \cdot 1/2H_2O$	$-1/2H_2O$ at 90	198
or $1/3H_2O$	$-H_2O$ at 55	18
$LiClO_3 \cdot H_2O$	$-H_2O$ at 55	18
$KClO_3$	d. 400	115
$AgClO_3$	d. 270	198
$NaClO_3$	d. 265	198

TABLE A3-6. BOILING POINT OF PERCHLORATES, °C

Compound	Value	Reference
$LiClO_4$	d. <300	265
	d. 368	198
	d. 380	115
	d. 410	308
$LiClO_4 \cdot 3H_2O$	$-2H_2O$ at 98-100	204
	$-3H_2O$ at 130-150	204
$Mg(ClO_4)_2 \cdot 6H_2O$	$-6H_2O$ at 250	169
$KClO_4$	d. 653	69
$NaClO_4$	d. 471 to 620	69
$NaClO_4 \cdot H_2O$	$-H_2O$ at 130	69

TABLE A3-7. REFRACTIVE INDEX OF CHLORATES

Compound	Value	Reference
$Ba(ClO_3)_2 \cdot H_2O$	ω 1.562	308
	ϵ 1.577	308
	α 1.635	308
	β 1.5622	308
$KClO_3$	1.409	115
	1.517	115
	1.524	115
	1.440	308
	1.515	308
	1.525	308
	1.5167	169
	α 1.4099	227
	β 1.5174	227
	γ 1.5241	227
	α 1.410	328
	β 1.517	328
	γ 1.524	328
	1.484 (avg)	196
	α 1.415	196
	β 1.517	196
	γ 1.523	196
$NaClO_3$	B line 1.51163 at 23°C	198
	D line 1.51267 at 23°C	198
	Cd line 1.58500 at 23°C	198

Note: ω = ordinary ray
ϵ = extraordinary ray
α = least index of refraction
β = intermediate index of refraction
γ = greatest index of refraction

B line = 6870 Å
D line = 5893 Å
Cd line = 6438 Å

TABLE A3-8. REFRACTIVE INDEX OF PERCHLORATES

Compound	Value	Reference
$Al(ClO_4)_3$	1.482	115
	ω 1.4818	115
	ϵ 1.4833	115
	α 1.4881	115
NH_4ClO_4	1.482	115
	β 1.486	308
	1.4833	169
$Ba(ClO_4)_2 \cdot 3H_2O$	1.5330	169
$KClO_4$	ω 1.4731	115
	ϵ 1.4737	115
	α 1.4769	115
$NaClO_4$	1.4617	169

Note: ω = ordinary ray
ϵ = extraordinary ray
α = least index of refraction
β = intermediate index of refraction
γ = greatest index of refraction

A3.1 Raman Spectra

The chlorate ion in the free state possesses four fundamental vibrations active in Raman effect. A number of investigations have concluded that the ClO_3 ion is of pyramidal structure of the point group C_{3v} type.[303, 264] The pyramidal structure gives rise to two nondegenerate A_1 type and two doubly degenerate E type Raman frequencies. For chlorate ion these frequencies are: A_1 - 625 and 933 and, E - 480 and 963.[303] The frequencies of these Raman shifts are unchanged in the crystalline state, however, a number of additional Raman lines are observed which are due to lattice structure.[167] The fact that the doubly degenerate frequencies (480 and 963) of the free chlorate ion are not split in crystals of $KClO_3$ suggests that the K ion has little influence on vibrations of the ClO_3 ion in the crystalline state.[167] Heating of a $KClO_3$ crystal causes a shift in the Raman lines of 98, 136, 975 and 930 cm^{-1} [167]

Molecules of the type xy_4 and having T_d symmetry give rise to 1 nondegenerate type a_1 vibration, 1 doubly degenerate type e vibration, and 2 triply degenerate type t_z vibrations.[302] The frequencies of these vibrations for ClO_4 ion have been determined to be: a_1 1 932 cm^{-1}, e = 460 cm^{-1}, t_z = 1110 cm^{-1} and 626 cm^{-1} [302]

Other investigators who have reported similar studies and data are: 23, 44, 59, 164, 165, 166, 168, 185, 186, 187, 188, 192, 190, 191, 248, 251, 258, 301, and 314.

TABLE A3-9. INFRARED ABSORPTION FREQUENCIES OF CHLORATES, cm^{-1}

Compound	Value	Reference
$Al(ClO_3)_3$	625, 930-980, 1600-1700	70
$Ba(ClO_3)_2$	977, 510	311
	625, 930-980, 1600-1700	70
	483, 503, 605, 921, 955, 972	247
	913, 953, 1610, 3540, 3570	201
$Ca(ClO_3)_2$	478, 493, 626, 938, 959, 984; 625, 930-980, 1600-1700	247, 70
$Mg(ClO_3)_2$	478, 499, 609, 915, 958 975, 625, 930-980, 1600-1700	247, 70
$KClO_3$	988, 617	311
	ω_1 = 930, ω_2 = 975, ω_3 = 620, ω_4 = 486	238
	1087-833, 1887	237
	625, 930-980, 1600-1700	70
$KClO_3$	479, 619, 933, 968, 989	247
	935, 962	201
$AgClO_3$	929, 611	311
	625, 930-980, 1600-1700	70
	470, 493, 612, 935, 697, 987	967

TABLE A3-9. INFRARED ABSORPTION FREQUENCIES OF CHLORATES, cm^{-1} (Cont'd)

Compound	Value	Reference
$NaClO_3$	996, 623	311
	400 is the characteristic absorption frequency. Absorption occurs between 250 and 83, with the maximum at 120.	171
	625, 930-980, 1600-1700	70
	478, 619, 933, 968, 989	247
	935, 965, 990	201

TABLE A3-10. INFRARED ABSORPTION FREQUENCIES OF PERCHLORATES, cm^{-1}

Compound	Value	Reference
NH_4ClO_4	1060, 1135, 1420, 3330	201
$Mg(ClO_4)_2$	652, 945, 962, 1060, 1130, 1625, 2100, 3540	201
$KClO_4$	1000 (strong motion of oxygen atoms)	287
	637, 940, 1075, 1140, 1990	201
$NaClO_4 \cdot H_2O$	1100, 1630, 2030, 3570	201

A3. 2 " Optical Activity

No information is available on the optical activity of perchlorates, and only a small amount of information is available for chlorates, as the Na or K crystal. $NaClO_3$ has a structure similar to that ascribed by Bragg to calcite, the Ca atoms being replaced by Na and the C by Cl.[14] The structural difference between $NaClO_3$, $NaBrO_3$(both optically active) and the nitrates of Pb (optically inactive) is in the position of the oxygen atoms.[299] In the nitrates the 3 oxygen atoms form a triangle in a plane normal to the line joining the atom centers of the metal and the nitrogen but placed between these two centers. In $NaClO_3$, the halogen atom lies between the metal and a plane similar to that in the nitrates containing the oxygen atoms.[299] Other investigators reporting on the optical activity of the chlorate crystal structure are: 41, 42, 95, 112, 215, 222, 223, and 234.

TABLE A3-11. CRYSTALLOGRAPHY OF CHLORATES

Compound	System Structure Type	Space Group	Lattice Constants a	b	c	Ax. Ang.	Molecules per Unit Cell	Reference
$Ba(ClO_3)_2 \cdot H_2O$	Monoclinic	C_{2h}	8.9 8.6	7.8 7.8	9.3 9.35		4	143
	Monoclinic		Axial Ratios, a:b:c = 1.1416 : 1 : 1.1981			β = 93° 94'		198
$Ca(ClO_3)_2 \cdot 2H_2O$	Monoclinic							198
$LiClO_3$	Cubic							198
$LiClO_3 \cdot H_2O$	Long, flat platelets, probably tetragonal							19
$Mg(ClO_3)_2 \cdot 4H_2O$	Rhombohedral							198
$KClO_3$	Monoclinic	C_{2h}^5	4.647	5.585	7.085	β = 109° 38'	2	196, 326
			4.6569 ±0.0001	5.59089 ±.00005	7.0991 ±.0001			121
			4.6478	5.57962	7.0848			122
		T, °C						
		20	4.647	5.585	7.085			235
		90	4.665	5.600	7.122			
		150	4.679	5.611	7.152			
		200	4.692	5.621	7.180			
		259	4.706	5.632	7.209			
$AgClO_3$	Tetragonal	V_d^{11} or D_4^{17}	8.47 8.49	--- ---	7.9 7.91		8 8	75 106
	Tetragonal	C_{4h}	(7.486)	---	7.89		8	226
		C_{4h}^5	8.48	---	7.91		14	80
	Tetragonal labile cubic		axial ratio a:c = 1.010:.9325					198
$NaClO_3$	Cubic	T^4	6.570				4	326
			6.559 (avg.)				*	22
			6.76				4.4	323
	Cubic; unstable rhombic isomorphous with $NaNO_3$ > unstable monoclinic isomorphous with $KClO_3$; pseudocubic in presence of other salts.	D-line = 43.120° (13°); rotational dispersion, a, at 13°, when wave length λ, is in μμ and a is in degrees, is: a = 11683001λ^{-2} − 0.3514 + 0.000000306λ^2. B-line = 2.38°; D-line = 3.16°; max. angle = 14.727° Cd line; right hand and left hand crystal = h(100), p(210), d(1$\bar{1}$0), and o(1$\bar{1}$1)						198

* Square of the number of the atoms in the face of cubic crystal : 64, 18, 110/3, 64/5, and 6

TABLE A3-12. CRYSTALLOGRAPHY OF PERCHLORATES

Compound	System, Structure Type	Space Group	Lattice Constants a	b	c	Ax. Ang.	Molecules per Unit Cell	Reference
NH_4ClO_4	Orthorhombic	V_h^{16}	9.202	5.816	7.449		4	97
	Cubic at 270°C			7.63			1	115
	Cubic	T_h^2 or T^2		7.63(avg.)			4	113
	Rhombic to isotropic at 240°C							305
			axial ratios, a:b:c = 0.7932:1:1.2808					198
$Ba(ClO_4)_2 \cdot 3H_2O$	Hexagonal		7.28	--	9.64		2	115
		C_6^6 or C_{6h}^2	7.28	--	9.64		2	316
	Hexagonal		axial ratio, a:c = 1:0.6625					198
$Ca(ClO_4)_2$	Deliquescent Prisms							198
$LiClO_4 \cdot 3H_2O$	Hexagonal	C_{6v}^4	7.71	--	5.42		2	115
		C_{6v}^4	7.71	--	5.42		2	316
	Hexagonal		axial ratio, a:c = 1:0.7039					198
$Mg(ClO_4)_2$	Deliquescent, Long Prisms							198
$KClO_4$	Rhombic ($BaSO_4$)	V_h^{16}	8.834	5.65	7.24		-	115
	Cubical at 340°C	T_d^2 or T^2		7.47				115
		V_h^{16}	8.84	5.65	7.23			12
	Orthorhombic	V_h^{16}	8.834	5.650	7.240		4	97
	Cubic	T_a^2 or T^2		7.47			4	113
	Rhombic		8.85	5.67	7.26			294
	Rhombic to isotropic at 299-300°C							305
	Rhombic, bipyramidal		axial ratios, a:b:c = 0.7817:1:1.2792					198
$AgClO_4$	Cubic at 200°C ($KClO_4$)	T_d^1		6.92			4	115
	Cubic	T_a^2 or T^2		6.92			4	113
	Goes to isotropic form at 155-159°C						-	305

TABLE A3-13. TRANSITION TEMPERATURE OF CHLORATES, °C

Compound	Value	Reference
$LiClO_3$	c, III to c, III at 41.5	250
	c, II to c, I at 99	250
	c, I to liq at 127.6	250
	982 ± 5°	310
$KClO_3$	255 ± 5°	310

TABLE A3-14. TRANSITION TEMPERATURE OF PERCHLORATES, °C

Compound	Value	Reference
NH_4ClO_4	240 (rhombic, c, II to cubic, c, I)	310, 250 96
$Ba(ClO_4)_2$	284 ± >5° (c, II to c, I)	310 250
$KClO_4$	299.5 c, II to c, I	116, 250,
	300 ± <5°, rhombic to cubic	310, 96
$AgClO_4$	158 ± >5°	310
	157 rhombic to cubic	96
$NaClO_4$	158 ± >5°	310
	308 c, II to c, I	250
	313 rhombic to cubic	96

TABLE A3-15. THERMAL CONDUCTIVITY OF CHLORATES AND PERCHLORATES

a. Chlorates

Compound	Thermal Conductivity, cal/cm sec °C x 10^3	Reference
$KClO_3$	1.153	198
$NaClO_3$	2.68 (between -80 and 0°C)	311
	2.65 (at 0°C)	311
	2.665 (at 0°C)	73
	3.77 (at -78°C)	73

b. Perchlorates

Compound	Thermal Conductivity
NH_4ClO_4	This value for NH_4ClO_4 was estimated from thermal diffusivity, density, thermal conductivity and specific heat data for AN-525J propellant, assuming a weight additive relationship. *

thermal diffusivity = $k/\rho C_v$

Material	Wt %	Density, ρ g/cm^3	Specific Heat, C_v cal/g/°C	Thermal Conductivity, k cal/(sec)(cm^2)(°C/cm)
AN-525J Propellant	100	1.67	0.301	7.5×10^{-4} **
GS-2 Fuel	25	1.13	.412	1.57×10^{-4} ***
NH_4ClO_4 Oxidizer	75	1.95	.264	9.48×10^{-4} (estimated)

TABLE A3-15. THERMAL CONDUCTIVITY OF CHLORATES AND PERCHLORATES (Cont'd)

*Thermal diffusivity for NH_4ClO_4 was estimated from diffusivity data on propellant composition AN-525J assuming a weight additive relationship as follows:

Material	Wt %	Thermal Diffusivity, cm^2/sec	Reference
AN-525J Propellant	100	1.49×10^{-3}	**
GS-2 Fuel	25	3.16×10^{-4}	**
NH_4ClO_4 Oxidizer	75	1.88×10^{-3}	estimated

**Data obtained from Aerojet-General Corp. QPR No. 649. "Thermal Properties of Aeroplex Propellants," Contract NOa(s) 52-359, 24 Feb 1953, Confidential.

***Estimated from diffusivity, density, thermal conductivity and specific heat data for propellant AN-525J.

TABLE A3-16. COEFFICIENTS OF EXPANSION FOR CHLORATES AND PERCHLORATES

a. Chlorates

Compound	Linear Coefficient x 10^6	Reference
$NaClO_3$	47.7 at 25°C	95
	44.92 at 34.2°C	262
	49.5 at 100°C	95
	51.4 at 125°C	95
	53.4 at 150°C	95
	55.5 at 175°C	95
	59.50 at 225.9°C	262

b. Perchlorates

Compound	Specific Volume	Reference
NH_4ClO_4	$V_t = a + bt + ct^2$ where: $a = 0.5074\ cm^3/g$, $b = 0.819 \times 10^{-4}\ cm^3/g/°F$, $c = 0.704 \times 10^{-7}\ cm^3/g/(°F)^2$	*

Cubical Expansion

NH_4ClO_4 Equation: $\beta = (1/V)dV/dt$,

Temp., °F:	-25	0	25	50	75	100	125	150	175
$\beta \times 10^{-4}$/°F:	1.690	1.613	1.538	1.462	1.389	1.316	1.244	1.172	1.101

*Data from Aerojet-General Corp. QPR No. 492. Contract NOa(s) 51-328-C, Items 1 and 2. 13 Feb 1951, Confidential.

TABLE A3-17. ELECTRICAL CONDUCTIVITY OF CHLORATES, $ohm^{-1}\ cm^{-1}$

Compound	Value	Reference
$KClO_3$	4.19 at 359°C (liq)	312
	0.238 at 359°C	198
	0.125×10^{-4} at 352°C	198
	0.268×10^{-12} at 145°C	198
$AgClO_3$	321.9×10^{-3} at 200°C (liq)	312
	352.7×10^{-3} at 210°C (liq)	312
	367.6×10^{-3} at 215°C (liq)	312
	382.9×10^{-3} at 220°C (liq)	312
	413.4×10^{-3} at 230°C (liq)	312
	444.4×10^{-3} at 240°C (liq)	312
	474.3×10^{-3} at 250°C (liq)	312

TABLE A3-18. DIELECTRIC CONSTANT FOR CHLORATES

Compound	Value	Reference
$KClO_3$	5.1 at 18°C, freq = 6.3×10^7	312
	6.2 at 15°C, freq = 1×10^8	312
	5.27	141
	4.96 at 10-23°C	142
$NaClO_3$	5.28 at 3000 kc	147
	5.9	240

TABLE A3-19. DIELECTRIC CONSTANT FOR PERCHLORATES

Compound	Value	Reference
$KClO_4$	5.9	277
$NaClO_4$	5.4 at 19 (freq 6.3×10^7)	312

TABLE A3-20. MOLAR AND IONIC MAGNETIC SUSCEPTIBILITY OF CHLORATES, x, c.g.s. e.m.u.

Compound	Value x 10^6 Molar	Value x 10^6 Ionic	Reference
ClO_3		30.2	292
NH_4ClO_3	42.1		221
$Ba(ClO_3)_2$	87.5		221
	-87.74		229
$Ba(ClO_3)_2 \cdot H_2O$	-104.3		207, 208
	99.2		221, 230
$KClO_3$	-96.7		312
	-48.7		207, 208
	-42.8		221
	-36.81		229
	44.3	29.4	292
$NaClO_3$	34.7		221
	-33.27		229
	37.8	31.0	292

TABLE A3-21. MOLAR AND IONIC MAGNETIC SUSCEPTIBILITY OF PERCHLORATES, x, c.g.s.e.m.u.

Compound	Value x 10^6		Reference
	Molar	Ionic	
ClO_4		32.0	292
NH_4ClO_4	46.3		219
$Ba(ClO_4)_2$	94.7		219
$LiClO_4$	32.8		219
$LiClO_4 \cdot 3H_2O$	Value of $LiClO_4 + H_2O$		219
	Disputed		230
$Mg(ClO_4)_2$	65.0		219
$Mg(ClO_4)_2 \cdot 6H_2O$	Value of $Mg(ClO_4) + H_2O$		219
	Disputed		230
$KClO_4$	47.4		219
	45.1, 48.1	30.2, 33.2	292
$NaClO_4$	37.6		219

TABLE A3-22. COMPRESSIBILITY OF SOME CHLORATES IN THE SOLID STATE[a]

Electrolyte	$\beta \times 10^6$
$NaClO_3$	4.85
$KClO_3$	6.25
$Ca(ClO_3)_2$	4.5
$Ba(ClO_3)_2$	3.0

(a) Reference 39. β = compressibility coefficient

TABLE A3-23. FREEZING POINT OF SOME SOLID SOLUTIONS OF KNO_3-$KClO_3$[a]

Melt No.	Mole % KNO_3	Mole % $KClO_3$	Temp. of First Appearance of Crystals, °C	Melt No.	Mole % KNO_3	Mole % $KClO_3$	Temp. of First Appearance of Crystals, °C
1	100	-	340	15	43	57	314
2	95	5	334	16	41	56	316
3	80	10	327	17	39	61	320
4	85	15	318	18	37	63	322
5	80	20	312	19	35	65	323
6	75	25	305	20	33	67	326
7	70	30	301	21	31	69	328
8	65	35	298	22	29	71	331
9	60	40	296	23	27	73	335
10	55	45	301	24	25	75	338
11	50	40	308	25	20	80	343
12	49	51	305	26	15	85	347
13	47	53	308	27	10	90	350
14	45	55	312	28	15	95	357
				29	-	100	365

(a) Reference: 225

TABLE A3-24. FREEZING POINT OF SOME SOLID SOLUTIONS OF $KClO_3$-$NaClO_3$ [a]

Melt No.	Mole % $KClO_3$	Mole % $NaClO_3$	Temp. of First Appearance of Crystals, °C	Melt No.	Mole % $KClO_3$	Mole % $NaClO_3$	Temp. of First Appearance of Crystals, °C
1	100	0	365	24	54	46	293, 5
2	98	2	363	25	52	48	288
3	96	4	360	26	50	50	286
4	94	6	356	27	46	54	282
5	92	8	351	28	42	58	277
6	90	10	349	29	38	62	271
7	88	12	347	30	34	66	266
8	86	14	346	31	30	70	260
9	84	16	348	32	26	74	248
10	82	18	338	33	22	78	243
11	80	20	335	34	20	80	241
12	78	22	331	35	18	82	239
13	76	24	329	36	16	84	237
14	74	26	327, 5	37	14	86	237
15	72	28	323	38	12	88	237
16	70	30	320	39	10	90	236 5
17	68	32	320	40	8	92	237
18	66	34	314	41	6	94	238
19	64	36	310	42	4	96	241
20	62	38	307	43	2	98	246
21	60	40	303	44	0	100	258
22	58	42	299				
23	56	44	296. 5				

(a) Reference: 225

TABLE A3-25. FREEZING POINT OF SOME SOLID SOLUTIONS OF $NaNO_3$-$NaClO_3$[a]

Melt No.	Mole % $NaNO_3$	Mole % $NaClO_3$	Temp. of First Appearance of Crystals, °C	Melt No.	Mole % $NaNO_3$	Mole % $NaClO_3$	Temp. of First Appearance of Crystals, °C
1	100	-	308	11	50	50	218
2	95	5	302	12	45	55	218
3	90	10	292	13	40	60	222
4	85	15	284	14	35	65	225
5	80	20	272	15	30	70	230
7	75	25	268	16	25	75	237
7	70	30	257	17	20	80	241
8	65	35	245	18	15	85	246
9	60	40	236	19	10	90	250
10	55	45	228	20	5	95	257
				21	-	100	261

(a) Reference: 225

TABLE A3-26. FREEZING POINT OF SOME SOLID SOLUTIONS OF $NaNO_3$-$KClO_3$[a]

Melt No.	Mole % $NaNO_3$	Mole % $KClO_3$	Temp. of First Appearance of Crystals, °C	Melt No.	Mole % $NaNO_3$	Mole % $KClO_3$	Temp. of First Appearance of Crystals, °C
1	100	-	308	12	45	55	236
2	95	5	293	13	40	60	252
3	90	10	275	14	35	65	269
4	85	15	260	15	30	70	283
5	80	20	246	16	25	75	298
6	75	25	222	17	20	80	312
7	70	30	210	18	15	85	323
8	65	35	207	19	10	90	335
9	60	40	209	20	5	95	350
10	55	45	213	21	-	100	365
11	50	50	220				

(a) Reference: 225

TABLE A3-27. FREEZING POINT OF SOME SOLID SOLUTIONS OF $NaClO_3$-KNO_3[a]

Melt No.	Mole % KNO_3	Mole % $NaClO_3$	Temp. of First Appearance of Crystals, °C	Melt No.	Mole % KNO_3	Mole % $NaClO_3$	Temp. of First Appearance of Crystals, °C
1	100	-	337	12	45	55	217
2	95	5	320	13	40	60	215
3	90	10	298	14	35	65	214
4	85	15	277	15	30	70	212
5	80	20	257	16	25	75	215
6	75	25	243	17	20	80	218
7	70	30	233	18	15	85	228
8	65	35	226	19	10	90	237
9	60	40	222	20	5	95	245
10	55	45	220	21		100	258
11	50	50	218				

(a) Reference: 225

A3.3 Miscellaneous

The information contained in the following references did not lend itself well to tabulation and inclusion with the data presented previously nor did it exist in sufficient quantity to warrant treatment in separate sections:

(1) Force constants for perchlorates[224]

(2) Bond lengths and structure of the perchlorate ion[105]

(3) X-ray K absorption spectra for chlorates and perchlorates[272, 273]

(4) X-ray diffraction powder pattern for sodium chorate[284]

(5) Proton resonance in barium chlorate monohydrate[271]

(6) Radio-frequency absorption in barium chlorate[161]

(7) New absorption lines of barium chlorate in the sub-microwave region[162]

(8) Quadrupole resonance of Cl^{35} in magnesium chlorate hexahydrate[25]

(9) Elastic constants and piezoelectric coefficients of sodium chlorate[15, 20, 110, 128]

(10) Paramagnetic resonance in X-irradiated potassium chlorate[120]

A 4. PROPERTIES OF AQUEOUS SOLUTIONS

TABLE OF CONTENTS

			Page
1.	SOLUBILITY AND SOLUBILITY PRODUCTS		269
	A4-1	SOLUBILITY OF $Ba(ClO_3)_2$ IN WATER	271
	A4-2	SOLUBILITY OF $Ca(ClO_3)_2$ IN WATER	272
	A4-3	SOLUBILITY OF $LiClO_3$ IN WATER	274
	A4-4	SOLUBILITY OF $Mg(ClO_3)_2$ IN WATER	277
	A4-5	SOLUBILITY OF $KClO_3$ IN WATER	278
	A4-6	SOLUBILITY OF $AgClO_3$ IN WATER	280
	A4-7	SOLUBILITY OF $NaClO_3$ IN WATER	280
	A4-8	SOLUBILITY OF $Al(ClO_4)_3$ IN WATER	281
	A4-9	SOLUBILITY OF NH_4ClO_4 IN WATER	281
	A4-10	SOLUBILITY OF $Ba(ClO_4)_2$ IN WATER	282
	A4-11	SOLUBILITY OF $Ca(ClO_4)_2$ IN WATER	283
	A4-12	SOLUBILITY OF $LiClO_4$ IN WATER	284
	A4-13	SOLUBILITY OF $Mg(ClO_4)_2$ IN WATER	286
	A4-14	SOLUBILITY OF $KClO_4$ IN WATER	287
	A4-15	SOLUBILITY OF $AgClO_4$ IN WATER	288
	A4-16	SOLUBILITY OF $NaClO_4$ IN WATER	289
	A4-17	SOLUBILITY PRODUCT OF SOME CHLORATES AND PERCHLORATES	290

TABLE OF CONTENTS (Cont'd)

			Page
2.		DENSITY OF SATURATED SOLUTIONS	291
	A4-18	DENSITY OF SATURATED SOLUTIONS OF $Ba(ClO_3)_2$ IN WATER	293
	A4-19	DENSITY OF SATURATED SOLUTIONS OF $Ca(ClO_3)_2 \cdot H_2O$ IN WATER	293
	A4-20	DENSITY OF SATURATED SOLUTIONS OF $LiClO_3$IN WATER	293
	A4-21	DENSITY OF SATURATED SOLUTIONS OF $Mg(ClO_3)_2$ IN WATER	294
	A4-22	DENSITY OF SATURATED SOLUTIONS OF $KClO_3$ IN WATER	294
	A4-23	DENSITY OF SATURATED SOLUTIONS OF $NaClO_3$ IN WATER	295
	A4-24	DENSITY OF SATURATED SOLUTIONS OF NH_4ClO_4 IN WATER	296
	A4-25	DENSITY OF SATURATED SOLUTIONS OF $Ba(ClO_4)_2$ IN WATER	297
	A4-26	DENSITY OF SATURATED SOLUTIONS OF $Ca(ClO_4)_2$ IN WATER	297
	A4-27	DENSITY OF SATURATED SOLUTIONS OF $LiClO_4$ IN WATER	297
	A4-28	DENSITY OF SATURATED SOLUTIONS OF $LiClO_4 \cdot 3H_2O$ IN WATER	298
	A4-29	DENSITY OF SATURATED SOLUTIONS OF $Mg(ClO_4)_2 \cdot 6H_2O$ IN WATER	298
	A4-30	DENSITY OF SATURATED SOLUTIONS OF $KClO_4$ IN WATER	299

TABLE OF CONTENTS (Cont'd)

		Page
A4-31	DENSITY OF SATURATED SOLUTIONS OF $AgClO_4 \cdot H_2O$ IN WATER	300
A4-32	DENSITY OF SATURATED SOLUTIONS OF $NaClO_4$ IN WATER	300
A4-33	DENSITY OF SATURATED SOLUTIONS OF $NaClO_4 \cdot H_2O$ IN WATER	301
3.	DENSITY OF UNSATURATED AQUEOUS SOLUTIONS	302
A4-34	DENSITY OF NH_4ClO_3 IN AQUEOUS SOLUTIONS	304
A4-35	DENSITY OF $LiClO_3$ IN AQUEOUS SOLUTIONS	305
A4-36	DENSITY OF $LiClO_3 \cdot 3H_2O$ IN AQUEOUS SOLUTIONS	307
A4-37	DENSITY OF $Mg(ClO_3)_2$ IN AQUEOUS SOLUTIONS	308
A4-38	DENSITY OF $KClO_3$ IN AQUEOUS SOLUTIONS	309
A4-39	DENSITY OF $AgClO_3$ IN AQUEOUS SOLUTIONS	311
A4-40	DENSITY OF $NaClO_3$ IN AQUEOUS SOLUTIONS	312
A4-41	DENSITY OF $Al(ClO_4)_3$ IN AQUEOUS SOLUTIONS	313
A4-42	DENSITY OF $Al(ClO_4)_3 \cdot 9H_2O$ IN AQUEOUS SOLUTIONS	313
A4-43	DENSITY OF NH_4ClO_4 IN AQUEOUS SOLUTIONS	314
A4-44	DENSITY OF $Ba(ClO_4)_2$ IN AQUEOUS SOLUTIONS	315
A4-45	DENSITY OF $Ca(ClO_4)_2$ IN AQUEOUS SOLUTIONS	315
A4-46	DENSITY OF $LiClO_4$ IN AQUEOUS SOLUTIONS	316
A4-47	DENSITY OF $KClO_4$ IN AQUEOUS SOLUTIONS	317

TABLE OF CONTENTS (Cont'd)

			Page
	A4-48	DENSITY OF $AgClO_4$ IN AQUEOUS SOLUTIONS	318
	A4-49	DENSITY OF $NaClO_4$ IN AQUEOUS SOLUTIONS	320
4.	VAPOR PRESSURE		323
	A4-50	VAPOR PRESSURE OF $Ba(ClO_3)_2$ SOLUTIONS	325
	A4-51	VAPOR PRESSURE OF $KClO_3$ SOLUTIONS	326
	A4-52	VAPOR PRESSURE OF $NaClO_3$ SOLUTIONS	328
	A4-53	VAPOR PRESSURE OF $Mg(ClO_4)_2$ HYDRATES	330
	A4-54	VAPOR PRESSURE OF $KClO_4$ SOLUTIONS	330
5.	VISCOSITY AND TEMPERATURE COEFFICIENT OF VISCOSITY		331
	A4-55	VISCOSITY OF $LiClO_3$ SOLUTIONS	333
	A4-56	VISCOSITY OF $LiClO_3 \cdot 3H_2O$ SOLUTIONS	335
	A4-57	VISCOSITY OF $KClO_3$ SOLUTIONS	336
	A4-58	VISCOSITY OF $NaClO_3$ SOLUTIONS	337
	A4-59	VISCOSITY OF $AgClO_4$ SOLUTIONS	338
	A4-60	VISCOSITY OF $NaClO_4$ SOLUTIONS	339
6.	INDEX OF REFRACTION AND MOLAR REFRACTION		340
	A4-61	INDEX OF REFRACTION OF $Al(ClO_4)_3$ SOLUTIONS	342
	A4-62	INDEX OF REFRACTION OF $Ba(ClO_3)_2$ SOLUTIONS	342
	A4-63	INDEX OF REFRACTION OF $Ca(ClO_3)_2$ SOLUTIONS	343

TABLE OF CONTENTS (Cont'd)

		Page
A4-64	INDEX OF REFRACTION OF $LiClO_3$ SOLUTIONS	343
A4-65	INDEX OF REFRACTION OF $Mg(ClO_3)_2$ SOLUTIONS	344
A4-66	INDEX OF REFRACTION OF $KClO_3$ SOLUTIONS	344
A4-67	INDEX OF REFRACTION OF $NaClO_3$ SOLUTIONS	345
A4-68	INDEX OF REFRACTION OF $Ba(ClO_4)_2$ SOLUTIONS	346
A4-69	INDEX OF REFRACTION OF $KClO_4$ SOLUTIONS	346
A4-70	INDEX OF REFRACTION OF $NaClO_4$ SOLUTIONS	347
A4-71	MOLAR REFRACTION OF CHLORATE SOLUTIONS	348
A4-72	IONIC AND MOLAR REFRACTION OF PERCHLORATE SOLUTIONS	349
7.	CONDUCTIVITY	351
A4-73	IONIC CONDUCTANCE IN AQUEOUS SOLUTIONS	353
A4-74	EQUIVALENT CONDUCTANCE OF $Ba(ClO_3)_2$ IN WATER	353
A4-75	EQUIVALENT CONDUCTANCE OF $Ca(ClO_3)_2$ IN WATER	354
A4-76	SPECIFIC CONDUCTANCE OF $LiClO_3$ IN WATER	355
A4-77	EQUIVALENT CONDUCTANCE OF $LiClO_3$ IN WATER	357

TABLE OF CONTENTS (Cont'd)

		Page
A4-78	SPECIFIC CONDUCTANCE OF $LiClO_3$ $3H_2O$ IN WATER	358
A4-79	EQUIVALENT CONDUCTANCE OF $Mg(ClO_3)_2$ IN WATER	358
A4-80	SPECIFIC CONDUCTANCE OF $KClO_3$ IN WATER	359
A4-81	EQUIVALENT CONDUCTANCE OF $KClO_3$ IN WATER	360
A4-82	EQUIVALENT CONDUCTANCE OF $AgClO_3$ IN WATER	361
A4-83	SPECIFIC CONDUCTANCE OF $NaClO_3$ IN WATER	362
A4-84	EQUIVALENT CONDUCTANCE OF $NaClO_3$ IN WATER	363
A4-85	EQUIVALENT CONDUCTANCE OF NH_4ClO_4 IN WATER	364
A4-86	EQUIVALENT CONDUCTANCE OF $Ba(ClO_4)_2$ IN WATER	364
A4-87	SPECIFIC CONDUCTANCE OF $LiClO_4$ IN WATER	365
A4-88	EQUIVALENT CONDUCTANCE OF $LiClO_4$ IN WATER	366
A4-89	EQUIVALENT CONDUCTANCE OF $Mg(ClO_4)_2$ IN WATER	367
A4-90	SPECIFIC CONDUCTANCE OF $KClO_4$ IN WATER	368
A4-91	EQUIVALENT CONDUCTANCE OF $KClO_4$ IN WATER	369

TABLE OF CONTENTS (Cont'd)

			Page
	A4-92	SPECIFIC CONDUCTANCE OF $AgClO_4$ IN WATER	370
	A4-93	EQUIVALENT CONDUCTANCE OF $AgClO_4$ IN WATER	371
	A4-94	SPECIFIC CONDUCTANCE OF $NaClO_4$ IN WATER	371
	A4-95	EQUIVALENT CONDUCTANCE OF $NaClO_4$ IN WATER	372
8.		ACTIVITY COEFFICIENTS	373
	A4-96	ACTIVITY COEFFICIENTS FOR $LiClO_3$	375
	A4-97	ACTIVITY COEFFICIENTS FOR $KClO_3$	376
	A4-98	ACTIVITY COEFFICIENTS FOR $NaClO_3$	377
	A4-99	ACTIVITY COEFFICIENTS FOR $Ba(ClO_4)_2$	378
	A4-100	ACTIVITY COEFFICIENTS FOR $Ca(ClO_4)_2$	379
	A4-101	ACTIVITY COEFFICIENTS FOR $LiClO_4$	381
	A4-102	ACTIVITY COEFFICIENTS FOR $Mg(ClO_4)_2$	383
	A4-103	ACTIVITY COEFFICIENTS FOR $KClO_4$	384
	A4-104	ACTIVITY COEFFICIENTS FOR $AgClO_4$	384
	A4-105	ACTIVITY COEFFICIENTS OF $NaClO_4$	385
9.		BOILING POINT ELEVATION	387
	A4-106	BOILING POINT ELEVATION BY CHLORATES IN SOLUTION	389
	A4-107	BOILING POINT ELEVATION BY PERCHLORATES IN SOLUTION	389

TABLE OF CONTENTS (Cont'd)

		Page
10.	FREEZING POINT LOWERING	390
A4-108	LOWERING OF FREEZING POINT BY $Al(ClO_3)_3$ IN AQUEOUS SOLUTIONS	392
A4-109	LOWERING OF FREEZING POINT BY $Ba(ClO_3)_2$ IN AQUEOUS SOLUTIONS	392
A4-110	LOWERING OF FREEZING POINT BY $Ca(ClO_3)_2$ IN AQUEOUS SOLUTIONS	393
A4-111	LOWERING OF FREEZING POINT BY $LiClO_3$ IN AQUEOUS SOLUTIONS	394
A4-112	LOWERING OF FREEZING POINT BY $Mg(ClO_3)_2$	395
A4-113	LOWERING OF FREEZING POINT BY $KClO_3$ IN AQUEOUS SOLUTIONS	396
A4-114	LOWERING OF FREEZING POINT BY $NaClO_3$ IN AQUEOUS SOLUTIONS	397
A4-115	LOWERING OF FREEZING POINT BY $Ba(ClO_4)_2$ IN AQUEOUS SOLUTIONS	398
A4-116	LOWERING OF FREEZING POINT BY $Ca(ClO_4)_2$ IN AQUEOUS SOLUTIONS	398
A4-117	LOWERING OF FREEZING POINT BY $LiClO_4$ IN AQUEOUS SOLUTIONS	399
A4-118	LOWERING OF FREEZING POINT BY $Mg(ClO_4)_2$ IN AQUEOUS SOLUTIONS	399
A4-119	LOWERING OF FREEZING POINT BY $KClO_4$ IN AQUEOUS SOLUTIONS	400
A4-120	LOWERING OF FREEZING POINT BY $NaClO_4$ IN AQUEOUS SOLUTIONS	400

TABLE OF CONTENTS (Cont'd)

			Page
11.	OSMOTIC COEFFICIENTS		401
	A4-121	OSMOTIC COEFFICIENTS OF CHLORATE SOLUTIONS DETERMINED BY ISOPIESTIC VAPOR PRESSURE MEASUREMENT	403
	A4-122	OSMOTIC COEFFICIENTS OF PERCHLORATE SOLUTIONS DETERMINED BY ISOPIESTIC VAPOR PRESSURE MEASUREMENT	404
12.	MISCELLANEOUS		406
	A4-123	DIFFUSION COEFFICIENTS OF $LiClO_4$ SOLUTIONS	407
	A4-124	DIFFUSION COEFFICIENTS OF $KClO_4$ SOLUTIONS	408
	A4-125	SURFACE TENSION OF $KClO_3$ SOLUTIONS	409
	A4-126	SURFACE TENSION OF $NaClO_3$ SOLUTIONS	410
	A4-127	SURFACE TENSION OF $KClO_4$ SOLUTIONS	411
	A4-128	THE DEGREE OF DISSOCIATION OF $KClO_3$ IN AQUEOUS SOLUTIONS	412
	A4-129	THE DEGREE OF DISSOCIATION OF $NaClO_3$ IN AQUEOUS SOLUTIONS	413
	A4-130	THE DEGREE OF DISSOCIATION OF $KClO_4$ IN AQUEOUS SOLUTIONS	414
	A4-131	THE DEGREE OF DISSOCIATION OF $NaClO_4$ IN AQUEOUS SOLUTIONS	415
	A4-132	DISSOCIATION CONSTANTS OF CHLORATES AND PERCHLORATES	416
	A4-133	DIELECTRIC CONSTANTS OF AQUEOUS CHLORATE AND PERCHLORATE SOLUTIONS	417

TABLE OF CONTENTS (Cont'd)

		Page
A4-134	POLARIZABILITY AND IONIC RADIUS OF THE PERCHLORATE ION	418
A4-135	TRANSPORT NUMBER FOR THE CHLORATE ION	418
A4-136	OSMOTIC PRESSURE OF $KClO_3$ SOLUTION	418
A4-137	IONIC VELOCITY OF THE CHLORATE ION	419
A4-138	SOLUTION VELOCITY OF $NaClO_3$ IN WATER	419
A4-139	COMPRESSIBILITY OF AQUEOUS SOLUTIONS OF $KClO_3$	420
A4-140	COMPRESSIBILITY OF AQUEOUS SOLUTIONS OF $NaClO_3$	421
A4-141	COMPRESSIBILITY OF AQUEOUS SOLUTIONS OF NH_4ClO_4	422
A4-142	COMPRESSIBILITY OF AQUEOUS SOLUTIONS OF $Ca(ClO_4)_2$	423
A4-143	COMPRESSIBILITY OF AQUEOUS SOLUTIONS OF $LiClO_4$	424
A4-144	COMPRESSIBILITY OF AQUEOUS SOLUTIONS OF $NaClO_4$	424
A4-145	VARIATION OF pH OF SOLUTIONS OF CERTAIN PERCHLORATES WITH RESPECT TO CONCENTRATION	425
A4-146	MAGNETIC SUSCEPTIBILITY OF THE AQUEOUS SOLUTIONS OF SOME PERCHLORATES	426
A4-147	APPARENT VOLUMES OF AQUEOUS SOLUTIONS OF CHLORATES AND PERCHLORATES	427
A4-148	POTENTIAL OF $Ag\text{-}AgClO_4$ ELECTRODE	429

TABLE OF CONTENTS (Cont'd)

		Page
A4-149	REFERENCES FOR UNTABULATED MISCELLANEOUS SOLUTION PROPERTIES	430

1. SOLUBILITY AND SOLUBILITY PRODUCT

1. Solubility and Solubility Product

Seidell's compilation[261] has been used as the major source of solubility data since it is more recent than the International Critical Tables[310]. However, in some cases, where the data from the International Critical Tables are judged more reliable, they have been presented instead.

All solubilities are given in grams of anhydrous salt. The solid phase is also listed.

TABLE A4-1. SOLUBILITY OF $Ba(ClO_3)_2$ IN WATER(261, 310)

Temp., °C	g $Ba(ClO_3)_2$ per 100 g H_2O	Solid Phase
0	19.8	$Ba(ClO_3)_2 \cdot H_2O$
10	26.9	$Ba(ClO_3)_2 \cdot H_2O$
20	33.8	$Ba(ClO_3)_2 \cdot H_2O$
30	41.7	$Ba(ClO_3)_2 \cdot H_2O$
40	49.9	$Ba(ClO_3)_2 \cdot H_2O$
60	67.0	$Ba(ClO_3)_2 \cdot H_2O$
80	84.9	$Ba(ClO_3)_2 \cdot H_2O$
100	105.9	$Ba(ClO_3)_2 \cdot H_2O$
105	111.7	$Ba(ClO_3)_2 \cdot H_2O$

TABLE A4-2. SOLUBILITY OF $Ca(ClO_3)_2$ IN WATER[261]

Temp., °C	g $Ca(ClO_3)_2$ per 100 g H_2O	Solid Phase
- 1.0	4.90	Ice
- 4.2	16.1	Ice
- 9.1	30.2	Ice
- 17.1	48.1	Ice
- 32.9	72.4	Ice
- 39.6	81.8	Ice
- 41.0 (Eutec.)	83.5	Ice + $Ca(ClO_3)_2 \cdot 6H_2O$
- 37.5	85.2	$Ca(ClO_3)_2 \cdot 6H_2O$
- 30.2	92.3	$Ca(ClO_3)_2 \cdot 6H_2O$
- 28.0	105	$Ca(ClO_3)_2 \cdot 6H_2O$
- 26.8 (tr.pt.)	122	$Ca(ClO_3)_2 \cdot 6H_2O + Ca(ClO_3)_2 \cdot 4H_2O$
- 26.3	122	$Ca(ClO_3)_2 \cdot 4H_2O$
- 16.2	138	$Ca(ClO_3)_2 \cdot 4H_2O$
- 12.3	150	$Ca(ClO_3)_2 \cdot 4H_2O$
- 7.8 (tr.pt.)	168	$Ca(ClO_3)_2 \cdot 4H_2O + Ca(ClO_3)_2 \cdot 2H_2O$
- 5.0	170	$Ca(ClO_3)_2 \cdot 2H_2O$
+ 18 (7)	178	$Ca(ClO_3)_2 \cdot 2H_2O$
19.5	196	$Ca(ClO_3)_2 \cdot 2H_2O$
25.0	195	$Ca(ClO_3)_2 \cdot 2H_2O$

TABLE A4-2. SOLUBILITY OF $Ca(ClO_3)_2$ IN WATER[261] (Cont'd)

Temp., °C	g $Ca(ClO_3)_2$ per 100 g H_2O	Solid Phase
73.5	322	$Ca(ClO_3)_2 \cdot 2H_2O$
76.0 (tr. pt.)	335	$Ca(ClO_3)_2 \cdot 2H_2O + Ca(ClO_3)_2$
93.0	355	$Ca(ClO_3)_2$
127.0	403	$Ca(ClO_3)_2$
203.0	567	$Ca(ClO_3)_2$

TABLE A4-3. SOLUBILITY OF $LiClO_3$ IN WATER[261, 310**]

Temp., °C	g $LiClO_3$ per 100 g H_2O	Solid Phase
- 8.7	18.70	Ice
- 13.2	26.15	Ice
- 17.4	32.35	Ice
- 23.3	40.21	Ice
- 30.5	48.61	Ice
- 36.6	54.75	Ice
- 40.0(Eutec.)	58.73	Ice + $LiClO_3 \cdot 3H_2O$
- 37.1	61.55	$LiClO_3 \cdot 3H_2O$
- 33.9	64.07	$LiClO_3 \cdot 3H_2O$
- 15.7	82.98	$LiClO_3 \cdot 3H_2O$
- 8.8	92.09	$LiClO_3 \cdot 3H_2O$
- 4.8	102.0	$LiClO_3 \cdot 3H_2O$
- 1.8	108.1	$LiClO_3 \cdot 3H_2O$
+ 2.2	120.1	$LiClO_3 \cdot 3H_2O$
4.8	130.7	$LiClO_3 \cdot 3H_2O$
6.1	139.0	$LiClO_3 \cdot 3H_2O$
7.3	150.9	$LiClO_3 \cdot 3H_2O$
8.0(m.p.)	167.4	$LiClO_3 \cdot 3H_2O$
7.9	173.5	$LiClO_3 \cdot 3H_2O$
7.4	184.7	$LiClO_3 \cdot 3H_2O$
6.0	204.7	$LiClO_3 \cdot 3H_2O$

TABLE A4-3. SOLUBILITY OF $LiClO_3$ IN WATER[261, 310**] (Cont'd)

Temp., °C	g $LiClO_3$ per 100 g H_2O	Solid Phase
3.4	230.5	$LiClO_3 \cdot 3H_2O$
+ 1.5(Eutec.)	246.0	$LiClO_3 \cdot 3H_2O + LiClO_3 \cdot H_2O$
- 1.7	264.8*	$LiClO_3 \cdot 3H_2O$
- 3.6	280.8*	$LiClO_3 \cdot 3H_2O$
- 7.6	302.4*	$LiClO_3 \cdot 3H_2O$
- 9.0(Eutec.)	311.5*	$LiClO_3 \cdot 3H_2O + \gamma\ LiClO_3$
- 13.6	339.5*	$LiClO_3 \cdot 3H_2O$
- 25.0(Eutec.)	426.3	$LiClO_3 \cdot 3H_2O + \beta\ LiClO_3$
+ 3.8	255.7	$LiClO_3 \cdot H_2O$
6.0	265.0	$LiClO_3 \cdot H_2O$
9.1	280.8	$LiClO_3 \cdot H_2O$
14.0	318.1	$LiClO_3 \cdot H_2O$
18.9	366.0	$LiClO_3 \cdot H_2O$
+ 21.0(tr.pt.)	431.9	$LiClO_3 \cdot H_2O + \gamma\ LiClO_3$
- 3.2	327.2*	$\gamma\ LiClO_3$
+ 2.9	346.2*	$\gamma\ LiClO_3$
8.4	361.5*	$\gamma\ LiClO_3$
12.8	382.2*	$\gamma\ LiClO_3$
16.4	392.1*	$\gamma\ LiClO_3$
22.1	445.9	$\gamma\ LiClO_3$
27.4	460.9	$\gamma\ LiClO_3$

TABLE A4-3. SOLUBILITY OF $LiClO_3$ IN WATER[261, 310**] (Cont'd)

Temp., °C	g $LiClO_3$ per 100 g H_2O	Solid Phase
32.3	503.5	γ $LiClO_3$
36.5	564.0	γ $LiClO_3$
41.5(tr. pt)	646.3	γ $LiClO_3$ + β $LiClO_3$
36.9	628.3*	β $LiClO_3$
43.9	679.4*	γ $LiClO_3$
48.7	669.2	β $LiClO_3$
64.4	793.7	β $LiClO_3$
71.9	936.3	β $LiClO_3$
86.3	1225	β $LiClO_3$
95.7	1581	β $LiClO_3$
99.0(tr. pt)	1861	β $LiClO_3$ + α $LiClO_3$
103.0	1933	α $LiClO_3$
107.5	2406	α $LiClO_3$
115.2	3791	α $LiClO_3$
123.0	8672	α $LiClO_3$
127.3(m. p.)	anhyd salt	α $LiClO_3$

* metastable

** Other data in reference 291

TABLE A4-4. SOLUBILITY OF $Mg(ClO_3)_2$ IN WATER[261, 310, 198]

Temp., °C	gm $Mg(ClO_3)_2$ per 100 g H_2O	Solid Phase
- 20	106.0	$Mg(ClO_3)_2 \cdot 6H_2O$
- 10	109.2	$Mg(ClO_3)_2 \cdot 6H_2O$
0	114.0	$Mg(ClO_3)_2 \cdot 6H_2O$
+ 10	120.5	$Mg(ClO_3)_2 \cdot 6H_2O$
20	131.4	$Mg(ClO_3)_2 \cdot 6H_2O$
30	153.6	$Mg(ClO_3)_2 \cdot 6H_2O$
35	175.0*	$Mg(ClO_3)_2 \cdot 6H_2O$
35.1	177.0*	$Mg(ClO_3)_2 \cdot 6H_2O$
35(Eutec.)	180.8*	$Mg(ClO_3)_2 \cdot 6H_2O$ + $Mg(ClO_3)_2$ $2H_2O$
42	176.2	$Mg(ClO_3)_2 \cdot 4H_2O$
65.5	223.8	$Mg(ClO_3)_2 \cdot 4H_2O$
40	189.4*	$Mg(ClO_3)_2 \cdot 2H_2O$
50	206.8*	$Mg(ClO_3)_2 \cdot 2H_2O$
60	225.4*	$Mg(ClO_3)_2 \cdot 2H_2O$
70	244.9*	$Mg(ClO_3)_2 \cdot 2H_2O$

* metastable

TABLE A4-5. SOLUBILITY OF $KClO_3$ IN WATER

a. Reference 261, 310*

Temp., °C	gm $KClO_3$ per 100 g H_2O	Solid Phase
0	3.31	$KClO_3$
10	5.15	$KClO_3$
15	6.04	$KClO_3$
20	7.30	$KClO_3$
25	8.58	$KClO_3$
30	10.0	$KClO_3$
40	13.9	$KClO_3$
50	18.5	$KClO_3$
60	23.8	$KClO_3$
70	30.2	$KClO_3$
80	37.6	$KClO_3$
90	46.0	$KClO_3$
100	56.3	$KClO_3$
104(b.p.)	60.0	$KClO_3$
120	77.0	$KClO_3$
140	108	$KClO_3$
160	144	$KClO_3$

* Other data in Reference 291

TABLE A4-5. SOLUBILITY OF $KClO_3$ IN WATER (Cont'd)

Temp., °C	gm $KClO_3$ per 100 g H_2O	Solid Phase
180	190	$KClO_3$
200	257	$KClO_3$
220	355	$KClO_3$
240	488	$KClO_3$
260	669	$KClO_3$
280	1011	$KClO_3$
300	1718	$KClO_3$
330	2930	$KClO_3$

b. Reference 198

$S = 2.6 + 0.2000t$ between $t = 0°$ and 42° C

$S = 11.0 + 0.3706t$ between $t = 42°$ and 171° C

$S = 59.0 + 0.2186t$ between $t = 171°$ and 359° C

$S = 3.2 + 0.1090t + 0.00430t^2$ between $t = 0°$ and 30° C

$\log S = 0.5224 + 0.017834t - 0.0000555t^2$ between $t = 0°$ and 105° C

TABLE A4-6. SOLUBILITY OF $AgClO_3$ IN WATER(261, 310)

Temp., °C	gm $AgClO_3$ per 100 g H_2O	Solid Phase
0	0.17	$AgClO_3$
18	0.44	$AgClO_3$
35	0.60	$AgClO_3$
50	0.89	$AgClO_3$
75	1.42	$AgClO_3$
100	2.16	$AgClO_3$

TABLE A4-7. SOLUBILITY OF $NaClO_3$ IN WATER(310*)

Temp., °C	gm $NaClO_3$ per 100 g H_2O	Solid Phase
0	80	$NaClO_3$
20	98	$NaClO_3$
40	118	$NaClO_3$
60	143	$NaClO_3$
80	171	$NaClO_3$
100	207	$NaClO_3$

* The data presented is an average of many individual investigators. Other data are presented in References 261, 310, 213, 291.

TABLE A4-8. SOLUBILITY OF $Al(ClO_4)_3$ IN WATER

Temp., °C	gm $Al(ClO_4)_3$ per 100 g H_2O	Solid Phase	Reference
18.5	3.88	$Al(ClO_4)_3 \cdot 15H_2O$	67
90	30.1	$Al(ClO_4)_3 \cdot 15H_2O$	67
0	121.5	$Al(ClO_4)_3 \cdot 9H_2O$	261
14.3	130.8	$Al(ClO_4)_3 \cdot 9H_2O$	261
91.5	182.6	$Al(ClO_4)_3 \cdot 9H_2O$	261

TABLE A4-9. SOLUBILITY OF NH_4ClO_4 IN WATER(261*)

Temp., °C	gm NH_4ClO_4 per 100 g H_2O	Solid Phase
0	13.07	NH_4ClO_4
20	26.34	NH_4ClO_4
40	44.05	NH_4ClO_4
60	64.07	NH_4ClO_4
80	93.01	NH_4ClO_4
100	132.6	NH_4ClO_4
107(b.p.)	144.6	NH_4ClO_4

* Other data presented in References 261, 310, 189, Section 2.

TABLE A4-10. SOLUBILITY OF $Ba(ClO_4)_2$ IN WATER[261*]

Temp., °C	gm $Ba(ClO_4)_2$ per 100 g H_2O	Solid Phase
0	206	$Ba(ClO_4)_2 \cdot 3H_2O$
20	289	$Ba(ClO_4)_2 \cdot 3H_2O$
40	359	$Ba(ClO_4)_2 \cdot 3H_2O$
60	426	$Ba(ClO_4)_2 \cdot 3H_2O$
80	495	$Ba(ClO_4)_2 \cdot 3H_2O$
100	562	$Ba(ClO_4)_2 \cdot 3H_2O$
120	646	$Ba(ClO_4)_2 \cdot 3H_2O$
140	755	$Ba(ClO_4)_2 \cdot 3H_2O$

* Other data presented in Reference 175.

TABLE A4-11. SOLUBILITY OF $Ca(ClO_4)_2$ IN WATER[175]

Temp., °C	g $Ca(ClO_2)_2$ per 100 g H_2O	Solid Phase
0	170	?
5	174	?
10	179	?
15	183	?
20	189	?
25	196	?
25[261]	188.6	$Ca(ClO_4)_2$
30	202	?
35	209	?
40	212	?
45	222	?
50	227	?

TABLE A4-12. SOLUBILITY OF $LiClO_4$ IN WATER(261)

Temp., °C	gm $LiClO_4$ per 100 g H_2O	Solid Phase
0	42.65	$LiClO_4 \cdot 3H_2O$
10	48.99	$LiClO_4 \cdot 3H_2O$
20	56.13	$LiClO_4 \cdot 3H_2O$
25	59.95	$LiClO_4 \cdot 3H_2O$
30	63.59	$LiClO_4 \cdot 3H_2O$
40	72.32	$LiClO_4 \cdot 3H_2O$
64.6	100.0	$LiClO_4 \cdot 3H_2O$
77.9	122.2	$LiClO_4 \cdot 3H_2O$
89.2	150.0	$LiClO_4 \cdot 3H_2O$
92.3	166.7	$LiClO_4 \cdot 3H_2O$
94.3	185.7	$LiClO_4 \cdot 3H_2O$
95.1(m.p.)	196.9	$LiClO_4 \cdot 3H_2O$
94.8	200.0	$LiClO_4 \cdot 3H_2O$
93.2	233.3	$LiClO_4 \cdot 3H_2O$
92.7	236.7	$LiClO_4 \cdot 3H_2O$
92.5	237.0	$LiClO_4 \cdot 3H_2O + LiClO_4 \cdot H_2O$
93.2	239.0	$LiClO_4 \cdot H_2O$
97.3	244.8	$LiClO_4 \cdot H_2O$
108.9	267.6	$LiClO_4 \cdot H_2O$
120.7	300.0	$LiClO_4 \cdot H_2O$

TABLE A4-12. SOLUBILITY OF $LiClO_4$ IN WATER[261] (Cont'd)

Temp., °C	gm $LiClO_4$ per 100 g H_2O	Solid Phase
136.9	400.0	$LiClO_4 \cdot H_2O$
144.0	476.4	$LiClO_4 \cdot H_2O$
148.5	566 7	$LiClO_4 \cdot H_2O$
149.0(m.p.)	640.1	$LiClO_4 \cdot H_2O$
149.3	700.0	$LiClO_4 \cdot H_2O$
144.2	900.0	$LiClO_4 \cdot H_2O$
145.75(tr.pt.)	-----	$LiClO_4 \cdot H_2O + LiClO_4$
167.5	1016	$LiClO_4$
172.0	1025	$LiClO_4$

TABLE A4-13. SOLUBILITY OF $Mg(ClO_4)_2$ IN WATER[175]

Temp., °C	gm $Mg(ClO_4)_2$ per 100 g H_2O	Solid Phase
0	91.6	?
5	93.8	?
10	95.1	?
15	96.9	?
20	99.1	?
25	100	?
25[261]	99.6	?
30	102	?
35	105	?
40	105	?
45	107	?
50	109	?

TABLE A4-14. SOLUBILITY OF $KClO_4$ IN WATER[261a]

Temp., °C	gm $KClO_4$ per 100 g H_2O	Solid Phase
0	0.76	$KClO_4$
10	1.06	$KClO_4$
15	1.35	$KClO_4$
20	1.68	$KClO_4$
25	2.07	$KClO_4$
30	2.56	$KClO_4$
40	3.73	$KClO_4$
50	5.15	$KClO_4$
60	7.30	$KClO_4$
70	10.1	$KClO_4$
75	11.56	$KClO_4$
80	13.4	$KClO_4$
90	17.6	$KClO_4$
100	22.2	$KClO_4$
120	33.3	$KClO_4$
140	48.1	$KClO_4$
180	85.2	$KClO_4$
200	111	$KClO_4$
225	150	$KClO_4$
250	203	$KClO_4$
265	233	$KClO_4$

[a] Other data presented in References 310, 157, and 291.

TABLE A4-15. SOLUBILITY OF $AgClO_4$ IN WATER[261**]

Temp., °C	gm $AgClO_4$ per 100 g H_2O	Solid Phase
- 0.16	0.97	Ice
- 3.0	36.15	Ice
-10.0	82.48	Ice
-24.0	151.9	Ice
-40.0	237.8	Ice
-58.2(Eutec.)	283.1	Ice + $AgClO_4 \cdot H_2O$
0	434.8	$AgClO_4 \cdot H_2O$
25	545.2	$AgClO_4 \cdot H_2O$
43	640.7	$AgClO_4 \cdot H_2O + AgClO_4$
50*	681.3	$AgClO_4 \cdot H_2O$
75	740.3	$AgClO_4$
99	792.9	$AgClO_4$

* Unstable

** Other data presented in Reference 310

TABLE A4-16. SOLUBILITY OF $NaClO_4$ IN WATER(261**)

Temp., °C	gm $NaClO_4$ per 100 g H_2O	Solid Phase
- 3.0	11.1	Ice
- 6.8	25.0	Ice
-11.1	42.9	Ice
-17.8	66.7	Ice
-22.0	81.8	Ice
-32.0	127.0	Ice + $NaClO_4 \cdot H_2O$
0	169.3	$NaClO_4 \cdot H_2O$
15	191.0	$NaClO_4 \cdot H_2O$
25	210.8	$NaClO_4 \cdot H_2O$
38	237.6	$NaClO_4 \cdot H_2O$
50	274.0	$NaClO_4 \cdot H_2O$
15*	253.1	$NaClO_4$
25*	273.3	$NaClO_4$
38*	268.1	$NaClO_4$
55	283.7	$NaClO_4$
75	300.2	$NaClO_4$
100	330.1	$NaClO_4$

* Metastable

** Other data given in References 261, 310, 58, and 291

TABLE A4-17. SOLUBILITY PRODUCT OF SOME CHLORATES AND PERCHLORATES[291]

Temperature = 25 °C

Salt	L^a
$LiClO_3$	3.36×10^{2}
$NaClO_3$	8.46×10^{1}
$KClO_3$	3.36×10^{-1}
$NaClO_4 \cdot H_2O$	2.22×10^{2}
$KClO_4$	1.44×10^{-2}
	1.07×10^{-2}[329]

[a] L = Solubility Product

2. DENSITY OF SATURATED AQUEOUS SOLUTIONS

2. Density of Saturated Aqueous Solutions

Absolute density, d^t, gm/cc.

Relative density, d^t_4, gm/ml.

Specific gravity was converted to density using the value for the density of water at the particular temperature obtained from Handbook of Chemistry and Physics, 39th Edition, 1958.[115]

TABLE A4-18. DENSITY OF SATURATED SOLUTIONS OF $Ba(ClO_3)_2$ IN WATER[309]

Temp., °C	Wt % $Ba(ClO_3)_2$	d^t_4
0	19.2	1.195
10	23.0	1.234
20	26.6	1.274
30	30.3	1.315
40	33.9	1.355
50	37.2	1.395
60	40.2	1.433
70	42.8	1.470
80	45.3	1.508
90	47.8	1.545
100	50.1	1.580
105.6	51.5	1.600

TABLE A4-19. DENSITY OF SATURATED SOLUTIONS OF $Ca(ClO_3)_2 \cdot 2H_2O$ IN WATER[309]

Temp., °C	Wt % $Ca(ClO_3)_2$	d^t_4
18	64	1.729

TABLE A4-20. DENSITY OF SATURATED SOLUTIONS OF $LiClO_3$ IN WATER[198]

Temp., °C	Wt % $LiClO_3$	d^t_4
18	75.8	1.812

TABLE A4-21. DENSITY OF SATURATED SOLUTIONS OF $Mg(ClO_3)_2$ IN WATER

Temp., °C	Wt % $Mg(ClO_3)_2$	d^t_4	Reference
18	56.50	1.562	261
18	56.3	1.594	309

TABLE A4-22. DENSITY OF SATURATED SOLUTIONS OF $KClO_3$ IN WATER

Temp., °C	Wt % $KClO_3$	d^t_4	Reference
0	3.21	1.021	261, 3
10	5.01	1.033	309
15	5.7	1.0363	261
20	6.8	1.0420	261
20	6.96	1.045	309
25	7.9	1.0484	261
25	8.0	1.051	309
30	9.3	1.058	309
40	12.1	1.073	261, 309
50	15.6	1.092	309
60	19.4	1.115	261, 309
70	23.4	1.139	309
80	27.4	1.165	261, 309
90	31.6	1.192	309
100	35.9	1.219	261, 309
104 (b. pt.)	37.6	1.230	261, 309

TABLE A4-23. DENSITY OF SATURATED SOLUTIONS OF $NaClO_3$ IN WATER[309]

Temp., °C	Wt % $NaClO_3$	d^t_4
-15	41.9	1.380
0	44.1	1.389
10	47.4	1.409
20	50.2	1.430
25	51.7	1.44
30	53.1	1.451
40	55.8	1.472
50	58.2	1.493
60	60.8	1.514
70	63.1	1.536
80	65.4	1.559
90	67.6	1.581
100	69.7	1.604
110	72.0	1.625
120	73.8	1.649
122 (b. pt.)	74.1	1.654

TABLE A4-24. DENSITY OF SATURATED SOLUTIONS OF NH_4ClO_4 IN WATER[309]

Temp., °C	Wt % NH_4ClO_4	d^t_4
0	11.0	1.061
10	15.1	1.080
20	19.1	1.098
30	23.0	1.115
40	26.8	1.131
50	30.4	1.146
60	33.8	1.160
70	37.1	1.174
80	40.3	1.188
90	43.5	1.202
100	46.6	1.215

TABLE A4-25. DENSITY OF SATURATED SOLUTIONS OF $Ba(ClO_4)_2$ IN WATER[309]

Temp., °C	Wt % $Ba(ClO_4)_2$	d^t_4
0	67.3	1.782
20	74.3	1.912
25	66.48	1.9403[261]
40	78.2	2.009
60	81.2	2.070
80	83.2	2.114
100	84.9	2.155
120	86.6	2.195
140	88.3	2.230

TABLE A4-26. DENSITY OF SATURATED SOLUTIONS OF $Ca(ClO_4)_2$ IN WATER[261]

Temp., °C	Wt % $Ca(ClO_4)_2$	d^t_4
25	65.35	1.7191

TABLE A4-27. DENSITY OF SATURATED SOLUTIONS OF $LiClO_4$ IN WATER[261]

Temp., °C	Wt % $LiClO_4$	d^t_4
25	37.385	1.2683

TABLE A4-28. DENSITY OF SATURATED SOLUTIONS OF $LiClO_4 \cdot 3H_2O$ IN WATER[261]

Temp., °C	Wt % $LiClO_4$	d^t_4
0	29.90	1.215
10	32.88	1.236
20	35.95	1.258
25	37.48	1.269
30	38.87	1.277
40	41.97	1.300

TABLE A4-29. DENSITY OF SATURATED SOLUTIONS OF $Mg(ClO_4)_2 \cdot 6H_2O$ IN WATER[261]

Temp., °C	Wt % $Mg(ClO_4)_2$	d^t_4
25	49.90	1.4720

TABLE A4-30. DENSITY OF SATURATED SOLUTIONS OF $KClO_4$ IN WATER

Temp., °C	Wt % $KClO_4$	d^t_4	Reference
0	0.75	1.005	261
0	0.80	1.007	309
10	1.35	1.009	309
15	1.33	1.0076	261
20	1.65	1.0085	261
20	2.15	1.012	309
25	2.03	1.0096	261
30	3.20	1.016	309
40	4.45	1.021	309
50	4.90	1.017	261
50	6.00	1.026	309
60	7.85	1.034	309
70	9.95	1.040	309
75	10.36	1.036	261
80	12.3	1.050	309
90	14.9	1.060	309
100	17.7	1.069	309
100	18.4	1.0681	261

TABLE A4-31. DENSITY OF SATURATED SOLUTIONS OF $AgClO_4 \cdot H_2O$ IN WATER[261]

Temp., °C	Wt % $AgClO_4$	d^t_4
0	82.07	2.7251
10	82.88	2.7594
20	84.04	2.8163
25	84.78	2.8487
30	85.59	2.8825
35	86.21	2.9173

TABLE A4-32. DENSITY OF SATURATED SOLUTIONS OF $NaClO_4$ IN WATER

Temp., °C	Wt % $NaClO_4$	d^t_4	Reference
15	64.6	1.666	309
25	67.70	1.6821	261, 309
50	71.3	1.731	309
55	73.94	1.756	261
75	75.01	1.757	261
100	76.75	1.758	261
143	79.1	1.789	261, 309

TABLE A4-33. DENSITY OF SATURATED SOLUTIONS OF $NaClO_4 \cdot H_2O$ IN WATER[261]

Temp., °C	Wt % $NaClO_4$	d^t_4
15	65.63	1.663
25	67.82	1.683
38	70.38	1.713
50	73.26	1.749

3. DENSITY OF UNSATURATED AQUEOUS SOLUTIONS

3. Density of Unsaturated Aqueous Solutions

t = temperature in degrees centigrade

d^t = absolute density, gm/cc

d^t_4 = relative density, gm/ml

d = density; whether absolute or relative is unknown

wt% = weight percent of solute, except when water of hydration is shown, in which case it refers to the anhydrous substance.

f = concentration in equivalents per 1000 gm H_2O

Densities and percent are based on weights in vacuo, unless otherwise indicated.

TABLE A4-34. DENSITY OF NH_4ClO_3 IN AQUEOUS SOLUTIONS[309]

Wt.% NH_4ClO_3	d_4^{25}
2.54	1.00831

TABLE A4-35. DENSITY OF $LiClO_3$ IN AQUEOUS SOLUTIONS[152][a]

Wt% $LiClO_3$	d_4^t 18°	25°	75°	128°
1	1.0048[309]			
1.49		1.0169	0.9966	
2	1.0111[309]			
4	1.0237[309]			
5.93		1.0363	1.014	
6	1.0365[309]			
8	1.0495[309]			
10	1.0628[309]			
11.50		1.0656	1.0411	
12	1.0764[309]			
14	1.0903[309]			
16	1.1045[309]			
17.55		1.1182	1.0923	
18	1.1190[309]			
29.79				1.1386
31.03		1.2220	1.1944	
34.80		1.2509	1.2246	
36.40		1.2661	1.2353	
37.18		1.2741	1.2461	
37.75		1.2793	1.2506	

TABLE A4-35. DENSITY OF $LiClO_3$ IN AQUEOUS SOLUTIONS(152)[a] (Cont'd)

Wt % $LiClO_3$	d_4^t 18°	25°	75°	128°
38.29		1.2826	1.2542	
41.25		1.3109	1.2757	
44.15				1.2462
46.36		1.3714	1.3322	
51.57				1.3187
54.70		1.4558	1.4150	
59.50		1.5069	1.4782	
62.02		1.5454	1.4927	1.4212
63.31		1.5559	1.5224	
65.52		1.5843	1.5471	
67.29		1.5978	1.5633	
69.17		1.6181	1.5821	
70.90		1.6663	1.6261	1.5382
85.42		1.8926	1.8388	
87.27				1.7911
89.64			1.9271	1.8397
96.55			2.0542	1.9263
98.90				1.9436
99.25				1.9605
100				1.9715

[a] Additional data in Reference 236

TABLE A4-36. DENSITY OF $LiClO_3 \cdot 3H_2O$ IN AQUEOUS SOLUTIONS[152]

Wt % $LiClO_3$	d_4^t 0°	10°	25°
51.53	1.4896	1.4794	1.4692
54.60	1.5136	1.5054	1.4887
60.10	1.5506	1.5479	1.5294
62.28	1.5665	1.5570	1.5459
65.70	1.5861	1.5768	1.5650
66.73	1.6086	1.5967	1.5812

TABLE A4-37. DENSITY OF $Mg(ClO_3)_2$ IN AQUEOUS SOLUTIONS[309]

Wt % $Mg(ClO_3)_2$	d_4^{18}
2	1.0135
4	1.0287
6	1.0441
8	1.0597
10	1.0758
12	1.0922
14	1.1091
16	1.1264
18	1.1442
20	1.1624
22	1.1810
24	1.2001
26	1.2196
28	1.2395
30	1.2598

TABLE A4-38. DENSITY OF $KClO_3$ IN AQUEOUS SOLUTIONS

a. Reference 309[a]

Wt % $KClO_3$	d_4^t						
	0° C	10° C	15° C	18° C	20° C	25° C	30° C
1	1.0061	1.0059	1.0056	1.0049	1.0045	1.0034	1.0020
2	1.0124	1.0122	1.0122	1.0113	1.0109	1.0099	1.0085
3	1.0189	1.0187	------	1.0178	1.0174	1.0165	1.0151
4	1.0256	1.0254	1.0253	1.0245	1.0241	1.0233	1.0218
6			1.0385	1.0380			
8			1.0518				
10			1.0651				
12			1.0786				
14			1.0923				
16			1.1063				
18			1.1206				
20			1.1352				
22			1.1502				
24			1.1657				

[a] Additional data in References 232, 315.

TABLE A4-38. DENSITY OF $KClO_3$ IN AQUEOUS SOLUTIONS (Cont'd)

Wt % $KClO_3$	d_4^t						
	40° C	50° C	60° C	70° C	80° C	90° C	100° C
1	0.9986	0.9944	0.9895	0.9841	0.9781	0.9716	0.9646
2	1.0051	1.0008	0.9959	0.9905	0.9845	0.9780	0.9709
3	1.0116	1.0073	1.0024	0.9970	0.9910	0.9845	0.9774
4	1.0183	1.0140	1.0091	1.0036	0.9977	0.9912	0.9840

b. Reference 137

18°C		35°C	
Wt % $KClO_3$	d_4^t	Wt % $KClO_3$	d_4^t
0.0152	1.00010	0.0292	1.00018
.0601	1.00038	.0542	1.00034
.1013	0.999268[108]	.1065	1.00065
.1225	1.00078	----	----
.245	1.00155	.245	1.00150
.489	1.00310	.489	1.00300
.6065	1.002474[108]	----	----
.763	1.00483	----	----
.8358	1.003978[108]	----	----
1.518	1.00966	1.217	1.00750
1.7940	1.010042[108]	1.938	1.01200
3.007	1.01932	3.009	1.01864
4.756	1.03104	4.762	1.02984

TABLE A4-39. DENSITY OF $AgClO_3$ IN AQUEOUS SOLUTIONS

a. Reference 309

Wt % Ag ClO_3	d_4^{15}
1	1.0074
2	1.0158
4	1.0327
6	1.0503
8	1.0683

b. Reference 133

Up to the concentration of about 16g/1000g of solution, the measurements are linear and conform within 0.01% to the equation

$$d = 0.99707 + 0.000807g/1000g \text{ of solution}$$

TABLE A4.40 DENSITY OF $NaClO_3$ IN AQUEOUS SOLUTIONS(309)[a]

Wt % $NaClO_3$	d_4^{18}
1	1.0053
2	1.0121
4	1.0258
6	1.0397
8	1.0538
10	1.0681
12	1.0827
14	1.0977
16	1.1131
18	1.1288
20	1.1449
22	1.1614
24	1.1782
26	1.1953
28	1.2128
30	1.2307
32	1.2491
34	1.2680

(a) Other data given in References 281, 47, 236.

TABLE A4-41. DENSITY OF $Al(ClO_4)_3$ IN AQUEOUS SOLUTIONS[86]

f	d_4^t
0.8650	1.06167
1.0134	1.07230
1.8248	1..12846
2.9776	1.20270
4.3870	1.28570
4.3996	1.28638
5.9770	1.37057
6.3018	1.38689
8.4344	1.48678

TABLE A4-42. DENSITY OF $Al(ClO_4)_3 \cdot 9H_2O$ IN AQUEOUS SOLUTIONS[66]

Wt % $Al(ClO_4)_3$	$d_{15}^{18.5}$
54.5	1.5746
56.7	1.7068

TABLE A4-43. DENSITY OF NH_4ClO_4 IN AQUEOUS SOLUTIONS

a. Reference 309

Wt. % NH_4ClO_4	d, g/cm^3 15° C	20° C	25° C
1	1.0039	1.0029	1.0018
2	1.0088	1.0077	1.0065
4	1.0186	1.0173	1.0160
6	1.0285	1.0271	1.0257
8	1.0386	1.0370	1.0355
10	1.0489	1.0470	1.0455
12	1.0594	1.0572	1.0557
14	1.0701	1.0676	1.0660

b. Reference 193

Wt, % NH_4ClO_4	d, g/cm^3 15° C	25° C
2.072	1.0094	1.0070
3.728	1.0174	1.0147
4.952	1.0236	1.0207
6.515	1.0310	1.0282
7.685	1.0373	1.0340
8.768	1.0436	1.0403
11.713	1.0578	1.0544
12.447	1.0616	1.0579
13.386	1.0668	1.0628
14.553	1.0740	1.0700
15.394	1.0773	1.0731

$$d_{15} = 0.99913 + 4.6826 \times 10^{-3}p + 1.425 \times 10^{-5}p^2 + 2 \times 10^{-7}p^3$$

$$d_{25} = 0.99707 + 4.7898 \times 10^{-3}p + 1.920 \times 10^{-5}p^2 + 1.33 \times 10^{-8}p^3$$

Where p = Wt. % NH_4ClO_4

TABLE A4-44. DENSITY OF $Ba(ClO_4)_2$ IN AQUEOUS SOLUTIONS(160)

f	d_4^{25}
1.00030	1.11970
1.83489	1.21343
3.99728	1.24481
5.99545	1.58745
7.99972	1.72585
9.10521	1.79367

TABLE A4-45. DENSITY OF $Ca(ClO_4)_2$ IN AQUEOUS SOLUTIONS(87)

Wt. % $Ca(ClO_4)_2$	d_4^{25}
55.074	1.55554
47.620	1.45345
38.218	1.34475
28.387	1.23343
15.728	1.11782

TABLE A4-46. DENSITY OF $LiClO_4$ IN AQUEOUS SOLUTIONS

a. Reference 195

Wt. % $LiClO_4$	d_4^{15}
4.90	1.02876
9.93	1.06056
14.91	1.09386
	d_4^{25}
4.90	1.02610
9.93	1.05708
14.91	1.08954

b. Reference 86

f	d_4^{25}
1.9984	1.10968
2.0625	1.11296
2.0933	1.11451
2.4877	1.13409
3.9660	1.20184
4.8787	1.23970

TABLE A4-48 DENSITY OF $AgClO_4$ IN AQUEOUS SOLUTIONS (d^t, g/cm^3)

a. Reference 153

Wt. %	0°	25°	50°	75°
0.00	0.9999	0.9971	0.9881	0.9749
.57	1.0046	1.0021	.9940	.9819
1.49	1.0128	1.0092	1.0006	.9885
3.88	1.0352	1.0300	1.0178	1.0076
9.12	1.0815	1.0761	1.0651	1.0525
13.41	1.1218	1.1158	1.1050	1.0904
18.67	1.1801	1.1709	1.1588	1.1433
29.11	1.3068	1.2940	1.2790	1.2608
37.10	1.4238	1.4088	1.3911	1.3712
41.39	1.4970	1.4805	1.4620	1.4410
47.60	1.6077	1.5889	1.5681	1.5456
50.30	1.6591	1.6389	1.6174	1.5955
55.61	1.7829	1.7616	1.7383	1.7142
58.29	1.8483	1.8274	1.8026	1.7778
60.52	1.9114	1.8879	1.8636	1.8372
62.23	1.9498	1.9261	1.9016	1.8766
65.27	2.0503	2.0250	1.9989	1.9722
66.91	2.0993	2.0742	2.0480	2.0215
71.67	2.2737	2.2474	2.2191	2.1909
72.93	2.3107	2.2836	2.2553	2.2263

TABLE A4-48. DENSITY OF $AgClO_4$ IN AQUEOUS SOLUTIONS (Cont'd)
(d^t, g/cm^3)

Wt. %	0°	25°	50°	75°
77.47	2.5018	2.4735	2.4438	2.4145
80.34	2.6418	2.6127	2.5830	2.5519
81.96	2.7230	2.6927	2.6635	2.6317

b. Reference 195

Wt. %	15°	25°
4.99	1.04067	1.03816
9.98	1.08635	1.08317
15.03	1.13612	1.13238

TABLE A4-49. DENSITY OF $NaClO_4$ IN AQUEOUS SOLUTIONS

a. Reference 309(a)

Wt. % $NaClO_4$	d_4^{18}
1	1.0051
2	1.0116
4	1.0247
6	1.0381
8	1.0517
10	1.0656
12	1.0798
14	1.0943
16	1.1090
18	1.1241
20	1.1396
22	1.1554
24	1.1717
26	1.1883
28	1.2053
30	1.2227
32	1.2407
34	1.2591
36	1.2779
38	1.2969

TABLE A-49. DENSITY OF $NaClO_4$ IN AQUEOUS SOLUTIONS (Cont'd)

b. Reference 117, 160

f	d_4^{25}
1.00020	1.07133(160)
2.00248	1.13820(160)
2.6309	1.17624
2.77662	1.18532(160)
4.00094	1.25270(160)
5.00370	1.30254(160)
5.9001	1.34369
6.00284	1.34810(160)
7.00352	1.39011(160)

f	d_4^{35}
2.6349	1.17022
5.9144	1.33566
11.077	1.52169

f	d_4^{45}
2.6262	1.16282
5.2379	1.29668
5.9205	1.32713
7.2341	1.38092
11.072	1.51170

TABLE A4-49. DENSITY OF $NaClO_4$ IN AQUEOUS SOLUTIONS (Cont'd)

c. Reference 202

The densities of $NaClO_4$ solutions are represented by the Masson equation for $NaClO_4$ through and including 60 percent solution,

at 0° C

$$d = 0.9999 + 0.08749N - 0.00422N^{3/2}$$

at 29.87° C

$$d = 0.9957 + 0.07919N - 0.00185N^{3/2}$$

at 49.3° C

$$d = 0.9884 + 0.07558N - 0.000883N^{3/2}$$

N = moles/l at temperature designated

(a) Other data in Reference 58, 194

4. VAPOR PRESSURE

4. Vapor Pressure

Concentration, m = molality = moles of solute per 1000 gm of solvent.

TABLE A4-50. VAPOR PRESSURE OF $Ba(ClO_3)_2$ SOLUTIONS[309]

Temperature = 100°C

m	v. p., mm
0.28	751.3[198]
.3	750.7
.7	737.3
1.1	723.1
1.5	708.4
2.5	669.4
2.7	661.3
2.8	658.1
2.84	656.8[198]

TABLE A4-51. VAPOR PRESSURE OF $KClO_3$ SOLUTIONS

a. Reference 309

T, °C	m	v.p., mm	T, °C	m	v.p., mm
0	0.27	4.54	85	0.8	418.9
10	.42	9.10		1.2	415.5
20	.60	17.23		3.47	393.5
30	.83	31.07	90	0.8	510.7
35	.97	41.03		1.2	505.5
40	1.14	53.57		3.83	472.4
45	1.33	69.23	95	0.8	618.3
50	1.54	88.59		1,2	614.3
55	1.76	112.4		4.19	563.5
60	2.00	141.3	100	.5	749.1
65	0.7	179.8		1.0	738.3
	1.3	176.7		1.5	727.9
	2.25	176.5		2.5	707.9
70	0.8	223.1		3.0	698.2
	1.2	222.2		4.0	679.8
	2.54	217.8		4.58	668.1
75	0.8	227.7		4.7	668.9
	1.2	276.4		satd.	668.3[28]
	2.82	267.3	103.9	4.89	760.0

TABLE A4-51. VAPOR PRESSURE OF $KClO_3$ SOLUTIONS (Cont'd)

a. Reference 309

T, °C	m	v.p., mm	T, °C	m	v.p., mm
80	0.8	343.1	290	81.57	1170.0 (max)
	1.2	341.1	366	244.7	sec. B.P.
	3.13	325.7			

b. Reference 28

$$\log p_2 = 2.88160 - 0.01367\, m + 0.00035\, m^2$$

from m = 4.706 to 1

TABLE A4-52. VAPOR PRESSURE OF $NaClO_3$ SOLUTIONS

a. Reference 309

T, °C	m	v.p., mm	T, °C	m	v.p., mm
0	0.47	4.51	80	0.47	350.5
	.94	4.45		.94	345.1
	1.88	4.30		1.88	334.2
	3.76	4.03		3.76	313.0
	5.63	3.78		5.63	293.5
	7.51	3.47		7.51	275.7
	7.92	3.51		9.39	259.7
20	0.47	17.3		11.27	245.1
	.94	17.0		13.15	232.0
	1.88	16.5		15.02	220.0
	3.76	15.4		16.81	209.4
	5.63	14.5	100	0.47	749.4
	7.51	13.6		.5	749.5[295]
	9.39	12.8		.85	740.3[198]
	9.48	12.8		.94	737.9
35	13.05	26.74[45]		1	737.0[295]
40	0.47	54.6		1.88	714.4
	.94	53.7		2	711.6[295]
	1.88	52.0		3	686.5[295]
	3.76	48.7		3.76	669.1

TABLE A4-52. VAPOR PRESSURE OF $NaClO_3$ SOLUTIONS (Cont'd)

a. Reference 309

T, °C	m	v.p., mm	T, °C	m	v.p., mm
	5.63	45.7		4	661.5[295]
	7.51	42.9		5	636.7[295]
	9.39	40.4		5.63	627.4
	11.27	38.2		6	612.5[295]
	11.45	38.0		7.51	589.5
	13.05	36.07[45]		8	563.5[295]
45	13.05	48.36[45]		9.39	555.1
55	13.05	83.29[45]		10	536.5[295]
60	0.47	147.4		11.27	524.1
	.94	145.1		13.15	495.9
	1.88	140.5		15.02	470.3
	3.76	131.6		15.04	470.0[198]
	5.63	123.4		16.90	447.0
	7.51	115.9		18.78	425.6
	9.39	109.2		20.09	411.3
	11.27	103.1		satd	410[28]
	13.15	97.5	110	21.88	557.7
	13.90	95.5	120	23.57	741.4
			130	25.45	968.0

TABLE A4-52. VAPOR PRESSURE OF $NaClO_3$ SOLUTIONS (Cont'd)

b. Reference 28

$$\log p_2 = 2.88227 - 0.0146\, m - 2.1\times10^{-4} m^2 \quad \text{(from m = 8.0 to 1)}$$

$$\log p_2 = 2.83617 - 0.01065\, m - 1.9\times10^{-11} m^7 \quad \text{(from m = 19.24 to 8.0)}$$

TABLE A4-53. VAPOR PRESSURE OF $Mg(ClO_4)_2$ HYDRATES[53]

Equilibrium Reaction	Vapor Pressure mm at 23°C x 10^3
$Mg(ClO_4)_2 \cdot 6H_2O_{(s)} \rightleftharpoons Mg(ClO_4)_2 \cdot 4H_2O_{(s)} + 2H_2O_{(g)}$	20.9
$Mg(ClO_4)_2 \cdot 4H_2O_{(s)} \rightleftharpoons Mg(ClO_4)_2 \cdot 2H_2O_{(s)} + 2H_2O_{(g)}$	8.15
$Mg(ClO_4)_2 \cdot 2H_2O_{(s)} \rightleftharpoons Mg(ClO_4)_{2(s)} + 2H_2O_{(g)}$	<0.56

TABLE A4-54. VAPOR PRESSURE OF $KClO_4$ SOLUTIONS
Temperature = 100°C

m	v. p., mm	Reference
0.37	752.2	198
.4	751.3	309
.77	742.6	198
.8	742.0	309
.98	738.3	198
1.0	738.0	309

5. VISCOSITY AND TEMPERATURE COEFFICIENT OF VISCOSITY

5. Viscosity and Temperature Coefficient of Viscosity

C = Concentration in gram equivalents per liter of solution.

m = Concentration in moles of salt per 1000 grams of water.

η/η_0 = Relative viscosity referred to that of water at the same temperature as unity.

η = Absolute viscosity in centipoises.

TABLE A4-55. VISCOSITY OF $LiClO_3$ SOLUTIONS

a. Reference 152

Wt % $LiClO_3$	η 25°	50°	75°	100°	128°	136°
1.49	0.941	0.578	0.407	0.292		
5.93	.963	.606	.426	.308		
11.50	1.043	.662	.469	.344		
17.55	1.182	.738	.525	.385		
29.79					0.444	
31.03	1.615	1.028	.735	.545		
34.80	1.759	1.130	.806	.590		
36.40	1.823	1.175	.840	.628		
37.18	1.928	1.241	.887	.656		
37.75	1.976	1.267	.905	.674		
38.29	2.05	1.305	.930	.692		
41.25	2.42	1.543	1.100	.815		
46.36	3.32	2.10	1.486	1.100		
51.57					.968	0.882
54.70	5.17	3.20	2.25	1.620		
59.50	5.97	3.68	2.54	1.829		
62.02	7.43	4.53	3.09	2.21	1.471	1.345
63.31	8.57	5.19	3.52	2.50		
65.52	9.19	5.52	3.68	2.58		
67.29	11.06	6.53	4.46	3.10		

TABLE A4-55. VISCOSITY OF $LiClO_3$ SOLUTIONS (Cont'd)

a. Reference 152

	η					
Wt % $LiClO_3$	25°	50°	75°	100°	128°	136°
69.17	13.04	7.47	4.87	3.35		
70.90	16.42	9.22	5.86	4.00	2.38	2.15
85.42	95.0	36.7	18.01	10.74	6.72	5.89
87.27				14.19	8.25	7.15
89.64			33.1	17.68	9.95	8.54
96.55			90.9	41.4	23.4	19.12
98.90				76.6	43.6	34.8
99.25					62.9	49.8
100					66.1	52.2

b. Reference 311

	η/η_0
m	25°
1	1.141
3	1.456
7	2.44
17	9.19
35	61

TABLE A4-56. VISCOSITY OF $LiClO_3 \cdot 3H_2O$ SOLUTIONS[152]

	η		
Wt % $LiClO_3$	0°	10°	25°
51.53	6.53	5.01	3.51
54.60	8.31	6.12	4.21
60.10	12.49	8.82	6.19
62.28	14.36	10.39	7.00
65.70	18.39	12.96	8.77
66.73	21.96	15.04	10.17

TABLE A4-57. VISCOSITY OF $KClO_3$ SOLUTIONS

Temp = 15°

m	η/η_o	Ref
0.1	0.994	311
.2	.990	311
.3	.987	311
.5	.981	311

Temp = 18°

m	η/η_o [a]	Ref
0.00124	1.00014	137
.00490	1.00005	137
.00999	0.99993	137
.01997	.99957	137
.03988	.99875	137
.06230	.99785	137
.1	.998	311
.12380	.99527	137
.2	.995	311
.24526	.99086	137
.3	.992	311
.38796	.98711	137
.5	.985	311

Temp = 25°

m	η/η_o [b]	Ref
0.002007	1.00017	136
.005013	1.00021	136
.010022	1.00017	136
.020029	1.00011	136
.049955	0.99957	136
.099533	.99850	136
.1	.999	311
.2	.998	311
.3	.996	311

Temp = 35°

m	η/η_o	Ref
0.00238	1.00018	137
.00442	1.00030	137
.00868	1.00045	137
.01997	1.00062	137
.03988	1.00082	137
.09926	1.00113	137
.1	0.999	311
.15810	1.00146	137
.2	0.999	311
.24543	1.00175	137
.3	1.000	311
.38841	1.00328	137

(a) Additional data in the concentration range 0.0005 to 0.5 molal are given in Reference 118. These results are slightly lower than those quoted here.

(b) Additional data in the concentration range of 0.01 to 0.5 molal are given in Reference 118. These results are slightly lower than those quoted here.

TABLE A4-57. VISCOSITY OF $KClO_3$ SOLUTIONS (Cont'd)

Temp = 45°		
m	η/η_0	Ref
0.1	1.002	311
.2	1.004	311
.3	1.006	311

TABLE A4-58. VISCOSITY OF $NaClO_3$ SOLUTIONS [311]

	η/η_0 [a]		
m	15°	25°	40°
0.25	1.012	1.021	
.5	1.028	1.041	
1	1.067	1.086	1.10
2.5	1.24	1.265	1.285
4.5	1.61	1.625	1.64

[a] Other values are given in Reference 285 for 53.4 and 54.4 % salt solutions from 20° to 60° C.

TABLE A4-59. VISCOSITY OF $AgClO_4$ SOLUTIONS [153]

	$\eta \times 10^2$, Centipoise			
Wt % $AgClO_4$	0°	25°	50°	75°
0.57	1.788	0.892	0.552	0.380
1.49			.553	.381
3.88	1.779	.897	.554	.378
9.12	1.765	.887	.560	.388
13.41	1.769	.903	.574	.397
18.67	1.814	.932	.600	.419
29.11	1.910	.997	.646	.456
37.10	2.007	1.081	.698	.501
41.39	2.147	1.166	.751	.540
47.60	2.395	1.299	.836	.598
50.30	2.534	1.377	.887	.635
55.61	3.000	1.610	1.026	.731
58.29	3.262	1.731	1.105	.782
60.52	3.613	1.910	1.209	.857
62.23	3.858	2.036	1.287	.899
65.27	4.776	2.368	1.470	1.036
66.91	5.387	2.596	1.599	1.106
71.67	7.888	3.710	2.199	1.489
72.93	8.550	4.030	2.361	1.576
77.47	1[illegible].050	6.425	3.536	2.261
80.34	25.120	9.451	4.906	2.965
81.96	33.460	12.101	6.053	3.605

TABLE A4-60. VISCOSITY OF $NaClO_4$ SOLUTIONS

a Reference 311

Temp = 25°

m	η/η_o
0.25	1.008
.5	1.018
1	1.044

b Reference 202

	η/η_o		
m	0° C	29.87° C	49.8° C
1.156	0.984	1.057	1.084
2.330	1.078	1.150	1.198
4.170	1.341	1.406	1.443
6.39	1.887	1.862	1.908
8.331	2.637	2.494	2.415
12.936	5.641	4.703	4.032
16.581			6.070
17.120	11.127	8.045	

6. INDEX OF REFRACTION AND MOLAR REFRACTION

6. Index of Refraction and Molar Refraction

R = Molar refraction

n_λ^t = The index of refraction at t°C for wave length λ

C = Gram equivalents per liter of solution

f = Equivalents per 1000g H_2O

CONVERSION OF WAVELENGTH TO WAVE NUMBER

Wavelength, Å		Wave Number/cm
A line	7621	13,123
	7594	13,167
D_1 line	5895.94	16,963
D_2 line	5889.98	16,977
D_3 line	5875.63	17,019
F line	4861.34	20,570
H line	3968.49	25,200

TABLE A4-61. INDEX OF REFRACTION OF $Al(ClO_3)_3$ SOLUTIONS [86]

C	$n_{D_3}^{25}$
0.9183	1.341434
1.0867	1.342883
2.0592	1.350440
3.5812	1.360346
5.6404	1.371324
5.6596	1.371422
8.1919	1.382510
8.7399	1.384671
12.5400	1.397881

TABLE A4-62. INDEX OF REFRACTION OF $Ba(ClO_3)_2$ SOLUTIONS [313]

C	n_D^{18}
0.5	1.34097
1.0	1.34831
2.0	1.36283

TABLE A4-63. INDEX OF REFRACTION OF $Ca(ClO_3)_2$ SOLUTIONS[313]

C	n_D^{18}
0.5	1.33997
1.0	1.34647
2.0	1.35900
4.0	1.38255

TABLE A4-64. INDEX OF REFRACTION OF $LiClO_3$ SOLUTIONS[313][a]

C	n_{4679}^{18}	n_{3612}^{18}	n_{3405}^{18}	n_{3256}^{18}	n_{2981}^{18}	n_{2749}^{18}	n_{2574}^{18}
0.5124	1.34307	1.35246	1.35561	1.35825	1.36460	1.37184	1.37906
1.023	1.34769	1.35726	1.36043	1.36313	1.36959	1.37699	1.38436
2.043	1.35644	1.36631	1.36962	1.37211	1.37910	1.38674	1.39439
4.090	1.37303	1.38352	1.38701	1.39000	1.39701	1.40531	1.41352

(a) Additional data in Reference 236.

TABLE A4-65. INDEX OF REFRACTION OF $Mg(ClO_3)_2$ SOLUTIONS[313]

C	n_D^{18}
0.1	1.33452
.2	1.33571
.5	1.33831
1.0	1.34518
2.0	1.35649
4.0	1.33770

TABLE A4-66. INDEX OF REFRACTION OF $KClO_3$ SOLUTIONS[157]

Wt %	n_D^t	t, °C
5.739	1.33831	15
6.793	1.33873	20
7.999	1.33911	25

TABLE A4-67. INDEX OF REFRACTION OF $NaClO_3$ SOLUTIONS

a. Reference 313[a]

C	n_D^{18}
0.1	1.33431
.2	1.33532
.5	1.33833
1.0	1.34313
2.0	1.35229
4.0	1.36916

b. Reference 198

Wt %	n_D^t	t, °C
51.035	1.387083	43.5
55.77	1.39125	53.5

[a]Additional data in Reference 236

TABLE A4-68. INDEX OF REFRACTION OF $BaClO_4)_2$ SOLUTIONS [160]

f	n_D^{25}
1.12004	1.34480
2.22651	1.35395
4.97585	1.37382
9.51748	1.38863
13.80632	1.40100
16.33174	1.40710

TABLE A4-69. INDEX OF REFRACTION OF $KClO_4$ SOLUTIONS[157]

Wt %	n_D^t	t, °C
1.333	1.33420	15
1.647	1.33401	20
2.029	1.33378	25

TABLE A4-70. INDEX OF REFRACTION OF $NaClO_4$ SOLUTIONS

a. Reference 160[a]

f	n_D^{25}
1.07154	1.33978
2.27922	1.34597
3.29118	1.35032
5.01198	1.35613
6.51712	1.36040
8.09243	1.36422
9.73566	1.36772

b. Reference 117

f	$n_{D_3}^{25}$	f	$n_{D_3}^{35}$	f	$n_{D_3}^{45}$
2.6309	1.34953	2.6349	1.34743	2.6262	1.34522
5.9001	1.36397	5.9144	1.36157	5.2379	1.35656
8.2311	1.37175	11.077	1.37702	5.9205	1.35917
11.086	1.37948			7.2341	1.36368
				11.072	1.37461

(a) Other data in Reference 78.

TABLE 4-71. MOLAR REFRACTION OF CHLORATE SOLUTIONS

Molar Refraction[198]

Compound	Weight %	R (Temp not given)
NH_4ClO_3	4.53	29.51 for F line; 33.14 for H line
NH_4ClO_3	21.75	28.75 for F line; 30.01 for H line
$Ba(ClO_3)_2$	23.75	105.44 for A line; 106.72 for D line; 109.90 for H line

Molar Refraction of $NaClO_3$[78]

Temperature = 25°C

Wave no/cm	R
16,950	13.2
20,000	13.3
22,500	13.4
25,000	13.5
27,500	13.6
30,000	13.8
32,500	14.0
35,000	14.2
37,500	14.5
40,000	14.8
42,500	15.2

TABLE A4-72. IONIC AND MOLAR REFRACTION OF PERCHLORATE SOLUTIONS

a. Reference 78

Temperature = 25°C

	R			
Wave no/cm	ClO_4^{-}[(a)]	$LiClO_4$	$AgClO_4$	$NaClO_4$
16,950	4.75	12.8	18.1	13.4
20,000	4.85	12.9	18.3	13.5
22,500	5.0	13.0	18.4	13.6
25,000	5.0	13.1	18.5	13.7
27,500	5.1	13.2	18.7	13.8
30,000	5.2	13.4	18.9	13.9
32,500	5.35	13.5	19.1	14.0
35,000	5.6	13.6	19.5	14.1
37,500	5.9	13.7	20.0	14.3
38,750	6.1		20.3	
40,000	6.4	13.9	20.7	14.5
41,250	6.8		21.2	
42,500		14.0		14.7
45,000		14.2		15.0

(a) Determined from $AgClC_4$

TABLE A4-72. IONIC AND MOLAR REFRACTION OF PERCHLORATE SOLUTIONS (Cont'd)

Temperature = 25°C

b. $Ba(ClO_4)_2$ (160)

f	R_D^{25}
1.00030	15.44
1.83489	15.458
3.99728	15.477
5.99545	15.496
7.99972	15.515
9.10521	15.531

c. $LiClO_4$ (86)

f	R_D^{25}
1.9984	12.917
2.0625	12.914
2.0933	12.928
2.4877	12.928
3.9660	12.941
4.8787	12.947

d. $NaClO_4$ (160)

f	R_D
1.00020	13.45
2.00248	13.454
2.77662	13.462
4.00094	13.478
5.00370	13.489
6.00284	13.495
7.00352	13.502

e. $NaClO_4$ (117)

Temperature = 25°C

f	R_{D_3}
2.6309	13.464
5.9001	13.493
8.2311	13.512
11.086	13.530

Temperature = 35°C

f	R_{D_3}
2.6349	13.496
5.9144	13.525
11.077	13.557

Temperature 45°C

f	R_{D_3}
2.6262	13.533
5.2379	13.551
5.9205	13,560
7.2341	13.570
11.072	13.586

7. CONDUCTIVITY

7. Conductivity

There has been some confusion in the literature as to the absolute basis of conductivity data. Investigators prior to 1924 based their measurements on the original work of Kohlrausch[159]. International Critical Tables have corrected all conductivity data on the basis of a redetermination of the absolute values of the conductance of the original Kohlrausch solutions given by Parker and Parker[220]. However, Jones[131, 133] disagreed slightly with the latter's work, stating that the equivalent conductance values given in ICT are somewhat high and the corrections are unreliable. In the following tables, only ICT values are given for work prior to 1924. However, in view of the discrepancy mentioned above, the reader is cautioned not to rely on these data for accurate work. Conductance data later than 1924 are given in the tables as presented by the author of the work.

m	=	Moles of solute per 1000 gm water.
K	=	Specific conductance in ohm^{-1} cm^{-1}
c	=	Milliequivalent weight of the solute per liter of the solution at the given temperature.
Λ	=	Equivalent conductance in $ohms^{-1}$ cm^2 (per equiv).
Λ_o	=	Equivalent conductance at infinite dilution in $ohms^{-1}$ cm^2 (per equiv).
t	=	Temperature, °C.

TABLE A4-73. IONIC CONDUCTANCE IN AQUEOUS SOLUTIONS

Chlorate, ClO_3^-, at 25°C[133]

$\Lambda_0 = 64.65$

Perchlorate, ClO_4^-, at 25°C

$\Lambda_0 = 67.32 \pm 0.06$[133]

$\Lambda_0 = 64.58$[206]

TABLE A4-74. EQUIVALENT CONDUCTANCE OF $Ba(ClO_3)_2$ IN WATER[312]

c	Λ 6°	18°	30°
100		79.5	
200	55.3	73.8	93.8
500	48.9	64.7	82.0
700	46.1	61.0	77.0
1000	42.5	56.4	70.9
1500	37.9		62.4
2000	34.4	44.7	55.7

TABLE A4-75. EQUIVALENT CONDUCTANCE OF $Ca(ClO_3)_2$ IN WATER[312]

$t = 18°C$

c	Λ
100	79.9
200	75.0
500	68.0
700	64.8
1000	60.6
2000	49.9
3000	41.0
4000	33.7

TABLE A4-76. SPECIFIC CONDUCTANCE OF $LiClO_3$ IN WATER

a. Reference 152

Wt. % $LiClO_3$	K					
	25°	50°	75°	100°	128°	136°
1.49	0.0602	0.0904	0.1217	0.1564		
5.93	.0702	.1041	.1402	.1801		
11.50	.0857	.1261	.1680	.213		
17.55	.1110	.1629	.215	.274		
29.79					0.419	
31.03	.1481	.217	.286	.362		
34.80	.1532	.223	.294	.371		
36.40	.1541	.223	.295	.371		
37.18	.1534	.223	.295	.372	.429	
37.75	.1532	.223	.296	.372		
38.29	.1521	.223	.295	.372		
41.25	.1502	.220	.201	.369		
44.15					.411	
46.36	.1401	.206	.275	.348		
51.57					.381	0.404
54.70	.1160	.1742	.234	.302		
59.50	.1042	.1572	.214	.277		
62.02	.0971	.1472	.203	.263	.335	.355
63.31	.0901	.1382	.1910	.249		
65.52	.0852	.1318	.1842	.244		

TABLE A4-76. SPECIFIC CONDUCTANCE OF $LiClO_3$ IN WATER (Cont'd)

a. Reference 152

	K					
Wt % $LiClO_3$	25°	50°	75°	100°	128°	136°
67.29	.0796	.1244	.1750	.233		
69.17	.0740	.1184	.1682	.225		
70.90	.0679	.1118	.1585	.213	.271	.290
85.42	.0223	.0511	.0922	.1378	.204	.222
87.27				.1302	.1962	.215
89.64				.1203	.1842	.203
96.55			.0498	.0940	.1469	.1681
98.90				.0761	.1378	.1583
99.25					.1177	.1371
100					.1068	.1252

b. Reference 256

Temperature = 10°C

$mx10^3$	$Kx10^4$	$mx10^3$	$Kx10^4$
0.845	0.6019	123.25	72.894
1.046	.7433	200.29	113.64
3.545	2.460	334.37	179.90
4.151	2.872	380.15	201.41
8.834	5.987	576.24	288.38
12.000	8.049	747.04	358.41
36.491	23.333	977.23	445.17
47.568	29.981	1145.1	503.69
86.817	52.699	1286.3	549.89

TABLE A4-77. EQUIVALENT CONDUCTANCE OF $LiClO_3$ IN WATER(312)

	Λ	
c	18°	25°
1		101.3
2		100.4
5		98.4
10		96.0
20		93.3
100	74.5	
200	70.0	
500	62.7	
700	59.5	
1000	55.7	
2000	46.9	

TABLE A4-78. SPECIFIC CONDUCTANCE OF $LiClO_3 \cdot 3H_2O$ IN WATER(152)

	K		
Wt % $LiClO_3$	0°	10°	25°
51.53	0.0798	0.0993	0.1203
54.60	0.0718	0.0935	0.1159
60.10	0.0593	0.0770	0.1026
62.28	0.0541	0.0693	0.0934
65.70	0.0483	0.0603	0.0868
66.73	0.0454	0.0587	0.0827

TABLE A4-79. EQUIVALENT CONDUCTANCE OF $Mg(ClO_3)_2$ IN WATER(312)

Temperature = 18° C

c	Λ
100	76.1
200	70.6
500	62.7
700	59.2
1000	54.8
2000	44.3
3000	35.6
4000	28 4

TABLE A4-80. SPECIFIC CONDUCTANCE OF $KClO_3$ IN WATER (256)

Temperature = 10°C

$mx10^3$	$Kx10^4$	$mx10^3$	$Kx10^4$
0.539	0.532	36.680	32.411
.678	.668	41.891	36.740
2.082	2.018	62.568	53.527
2.355	2.272	92.694	77.129
6.308	5.973	98.294	81.416
8.352	7.844	125.11	101.65
8.954	8.393	172.90	136.55
15.595	14.339	201.66	156.98
21.112	19.168	290.63	217.91
28.279	25.324		

TABLE A4-81. EQUIVALENT CONDUCTANCE OF $KClO_3$ IN WATER(312)

	Λ				
c	0°	18°	25°	35°	100°
0.1		118.45			
.2		118.17			
.5	73.8	117.50			360.0
1	74.3	116.74	135.7	162	359.0
2	73.4	115.67	134.4	161	356.0
5	72.2	113.67	132.0	158	
10	71.0	111.47	129.6	154	
20	68.8	108.65	125.7	150	
50	65.4	101.45	119.2	142	
70	64.0		116.4	135	
100	62.6	99.04	113.3		
200		93.59			

TABLE A4-82. EQUIVALENT CONDUCTANCE OF $AgClO_3$ IN WATER(133)

Λ_0 at 25°C = 126.57(312)

Temperature = 25° C

c	Λ
1	124.1 (312)
1.0256	123.43
1.3694	122.94
2	123.5 (312)
2.9782	121.14
3.2500	120.95
5	121.8 (312)
6.693	118.57
7.223	118.29
10	119.7 (312)
11.165	116.38
20	113.2 (312)
20.409	113.05
25.945	111.52
29.471	110.70
30.005	110.57
45.927	107.33
61.064	104.82
85.240	101.58
92.665	100.80
136.30	96.50
199.45	91.90
284.88	87.15

TABLE A4-83. SPECIFIC CONDUCTANCE OF $NaClO_3$ IN WATER(256)

Temperature = 10° C

$mx10^3$	$Kx10^4$	$mx10^3$	$Kx10^4$
0.666	0.532	59.483	41.351
.808	.642	64.643	44.696
1.248	.986	145.52	94.782
2.418	1.889	179.85	114.98
2.437	1.903	360.57	214.27
2.631	2.053	540.72	304.29
6.598	5.037	643.51	352.57
7.279	5.544	654.20	357.45
7.308	5.566	783.19	413.97
21.614	15.843	1108.2	546.11
22.018	16.116	1444.5	664.83
58.347	40.000		

TABLE A4-84. EQUIVALENT CONDUCTANCE OF $NaClO_3$ IN WATER[312]

	Λ			
c	0°	18°	25°	35°
0.1		97.4		
.2		97.0		
.5		96.3		
1	59.8	95.5	113.0	
2	59.6	94.6	111.4	134
5	58.9	92.8	108.8	132
10	57.6	91.0	106.4	129
20	56.1	88.7	103.4	125
50	53.7	84.65	98.5	119
70	52.6	92.85		
100	51.3	80.8	94.0	113
200	48.3	76.4	88.3	106
500	43.6	69.1	79.5	96
700		65.8		
1000		61.8		
2000		54.9		
3000		46		
4000		38.7		

TABLE A4-85 EQUIVALENT CONDUCTANCE OF NH_4ClO_4 IN WATER[312]

Temperature = 18° C

c	Λ
200	96.0
500	90.2
1000	83.8

TABLE A4-86. EQUIVALENT CONDUCTANCE OF $Ba(ClO_4)_2$ IN WATER[307]

Λ_o at 0° C 160.9
25° C 201.2
50° C 248.2

	Λ		
c x 10^5	0° C	25° C	50° C
1.000	156.7	196.6	240.7
2.000	155.0	194.0	237.6
5.000	151.5	189.9	231.5
10.00	147.6	185.2	224 6
20.00	142.1	178.6	214.8
50.00	131.6	165.4	196.3
100.0	121.2	152.3	178.5

TABLE A4-87. SPECIFIC CONDUCTANCE OF $LiClO_4$ IN WATER[256]

Temperature = 10° C

$mx10^3$	$Kx10^4$	$mx10^3$	$Kx10^4$
0.811	0.593	357.68	202.80
1.507	1.092	397.05	222.77
2.568	1.847	449.18	248.66
6.914	4.868	660.94	348.76
17.236	11.792	765.90	395.61
31.405	20.972	938.87	469.34
61.488	39.708	1026.4	504.92
95.886	60.328	1249.8	591.29
176.22	106.26	1503.8	681.93
285.31	165.22		

TABLE A4-88 EQUIVALENT CONDUCTANCE OF $LiClO_4$ IN WATER[312]

Λ_0 at 25° C = 105.98[131]

c	Λ 0° C	Λ 18° C	Λ 25° C	Λ 100° C
0.2	54.3	87.9		293.1
.5	54.1	87.4	104.18[131]	290.6
1			103.44[131]	
1	53.7	86.9	112.8	287.6
2			102.46[131]	
2	53.3	86.2	111.4	284.6
5			100.57[131]	
5	52.5	84.6	108.9	278.6
10			98.61[131]	
10	51.5	83.0	106.5	272.6
20			96.18[131]	
20	50.3	81.0	103.9	264.1
50			92.20[131]	
70			90.52[131]	
100			88.56[131]	

TABLE A4-89. EQUIVALENT CONDUCTANCE OF $Mg(ClO_4)_2$ IN WATER(298)

Λ_0 at 25° C = 128.5

Temperature = 25° C

c	Λ	c	Λ
1	120.8	500	79.4
2	118.2	700	75.7
5	112.6	1000	71.0
10	108.0	2000	59.1
20	103.9	3000	49.4
50	98.3	4000	40.5
70	95.7	5000	31.4
100	93.1	6000	22.6
200	87.4	6588	17.5

TABLE A4-90. SPECIFIC CONDUCTANCE OF $KClO_4$ IN WATER[256]

Temperature = 10° C

$mx10^3$	$Kx10^4$
0.665	0.660
2.069	2.026
4.191	4.051
9.189	8.693
17.094	15.794
35.755	31.782
70.501	59.777

TABLE A4-91. EQUIVALENT CONDUCTANCE OF $KClO_4$ IN WATER[312]

Λ_0 at 25° = 140.86[131]
= 140.83[206]

	Λ				
c	0°	18°	25°	35°	100°
0.2					371.5
.5	76.3	120.6	138.76[131]		369.0
1			139.1		
1	75.9	118.8	137.87[131]	166	366.5
2			137.3		
2	75.3	118.5	136.62[131]	164	362.0
5			134.4		
5	74.0	116.4	134.16[131]	161	355.0
10			131.7		
10	72.6	114.0	131.46[131]	158	347.0
20			127.5		
20	70.5	110.9	127.92[131]	153	336.0
50		105.5	121.62[131]		
70			118.79[131]		
100			115.20[131]		

TABLE A4-92. SPECIFIC CONDUCTANCE OF $AgClO_4$ IN WATER[153]

	K			
Wt %	0°	25°	50°	75°
0.57	0.00164	0.00300	0.00455	0.00619
1.49	.00442	.00799	.01211	.01651
3.88	.01164	.02079	.03105	.04183
9.12	.02684	.04631	.06937	.09472
13.41	.03796	.06722	.1004	.1346
18.67	.05339	.09407	.1392	.1859
29.11	.08265	.1436	.2118	.2829
37.10	.1041	.1811	.2656	.3500
41.39	.1140	.1979	.2941	.3899
47.60	.1253	.2183	.3212	.4244
50.30	.1298	.2250	.3316	4430
55.61	.1329	.2332	.3458	.4594
58.29	.1324	.2336	.3489	.4639
60.52	.1289	.2326	.3488	.4661
62.23	.1286	.2311	.3476	.4656
65.27	.1224	.2240	.3398	.4596
66.91	.1179	.2142	.3331	4518
71.67	.09860	.1911	.3011	.4177
72.93	.09490	.1851	.2951	.4102
77.47	.07027	.1482	.2468	.3551
80.34	.05441	.1196	.2073	.3062
81.96	.04508	.1043	.1874	.2849
86.43	.01579	.05604	.1159	.1939

TABLE A4-93. EQUIVALENT CONDUCTANCE OF $AgClO_4$ IN WATER[312]

Temperature = 25° C

c	Λ
1	128.0
2	127.1
5	124.7
10	122.6
20	119.8

TABLE A4-94. SPECIFIC CONDUCTANCE OF $NaClO_4$ IN WATER[256]

Temperature = 10° C

$m \times 10^3$	$K \times 10^4$	$m \times 10^3$	$K \times 10^4$
0.746	0.608	203.08	133.74
1.102	0.895	267.36	171.70
1.575	1.272	451.32	273.59
3.374	2.693	647.41	373.60
5.025	3.976	727.23	411.86
12.824	9.882	866.90	476.34
29.136	21.740	1109.1	579.68
46.884	34.167	1245.3	633.71
111.34	76.908	1805.5	826.43
123.85	84.899		

TABLE A4-95. EQUIVALENT CONDUCTANCE OF $NaClO_4$ IN WATER

Λ_0 at 25° C = 117.48[131]

	Λ					
c	0°	18°	25°	29.9°	50°	Ref
0.5			115.64			131
1			123.4			312
1			114.87			131
2			121.7			312
2			113.80			131
5			119.1			312
5			111.75			131
10			116.6			312
10			109.59			131
20			113.5			312
20			106.96			131
50			102.40			131
70			100.52			131
100			98.43			131
500		71.6				312
700		68.6				312
1000		65				312
2000	34.7	54.97[312]		69 3	97 7	202[a]
3000		46				312
4000	24.4	38.70[312]		48.8	68.8	202
6000	16.4			34.5	47.4	202
8000	7.65			20.0	27.2	202

(a) Data taken from graph.

8. ACTIVITY COEFFICIENTS

8. Activity Coefficients

The activity coefficients were determined by the freezing point method or by isopiestic vapor pressure measurements. The isopiestic vapor pressure values are for 25° C whereas the data obtained by the freezing point method was obtained near zero degrees.

In the following tables,

m = Concentration in moles per 1000 gm of water

γ = Activity coefficient

TABLE A4-96. ACTIVITY COEFFICIENTS FOR $LiClO_3$[256][a]

Temperature near 0° C

m	γ
0.001	0.967
.002	.955
.005	.933
.01	.910
.02	.884
.05	.842
.1	.810
.2	.782
.3	.775
.4	.768
.5	.769
.6	.773
.7	.780
.8	.788
.9	.798
1.0	.809
1.1	.820

a From freezing point data.

TABLE A4-97. ACTIVITY COEFFICIENTS FOR $KClO_3$

	γ		
m	Near 0° C(256)[a]	25° C(134)[b]	25° C(246)[b]
0.001	0.968		
.002	.956		
.005	.933		
.01	.908		
.02	.874		
.05	.810		
.1	.745		0.749
.2	.665	0.681	.681
.3		.634	.635
.4		.598	.599
.5		.568	.568
.6		.542	.541
.7		.519	.518

a From freezing point data.
b From isopiestic vapor pressure data.

TABLE A4-98. ACTIVITY COEFFICIENTS FOR $NaClO_3$

m	γ Near 0° C(256)[a]	γ 25° C(130)[b]	γ 25° C(246)[b]
0.001	0.967		
.002	.954		
.005	.930		
.01	.905		
.02	.873		
.05	.819		
.1	.769		0.772
.2	.711	0.720	.720
.3	.673	.687	.688
.4	.645	.663	.664
.5	.622	.644	.645
.6	.602	.630	.630
.7	.585	.616	.617
.8	.570	.605	.606
.9	.556	.595	.597
1.0	.544	.586	.589
1.1	.534		
1.2		.566	.575
1.4		.557	.563
1.6		.547	.553
1.8			.545
2.0		.529	.538
2.5		.516	.525
3.0		.506	.515
3.5			508

a From freezing point data.
b From isopiestic vapor pressure data.

TABLE A4-99. ACTIVITY COEFFICIENTS FOR $Ba(ClO_4)_2$

	γ	
m	Near 0°C(217)[a]	25°C(245)[b]
0.001	0.897	
.002	.864	
.005	.805	
.01	.751	
.02	.689	
.05	.602	
.1	.541	0.523
.2	.489	.480
.3	.463	.463
.4	.449	.458
.5	.441	.461
.6	.438	.468
.7	.437	.476
.8	.438	.486
.9	.442	.499
1.0	.449	.512
1.2		.544
1.4		.580
1.6		.621
1.8		.673
2.0		.717
2.5		.866
3.0		1.045
3.5		1.284
4.0		1.542
4.5		1.822
5.0		2.13
5.5		2.53

a From freezing point data.
b From isopiestic vapor pressure data.

TABLE A4-100. ACTIVITY COEFFICIENTS FOR $Ca(ClO_4)_2$

m	γ Near 0° C(217)[a]	γ 25° C(245)[b]
0.001	0.900	
.002	.869	
.005	.814	
.01	.763	
.02	.706	
.05	.633	
.1	.587	0.565
.2	.554	.540
.3	.551	.540
.4	.561	.552
.5	.579	.573
.6	.603	.598
.7	.633	.627
.8	.668	.664
.9	.710	.706
1.0	.763	.754
1.2		.866
1.4		1.007
1.6		1.179
1.8		1.393

TABLE A4-100. ACTIVITY COEFFICIENTS FOR $Ca(ClO_4)_2$ (Cont'd)

m	γ Near 0° C(217)[a]	γ 25° C(245)[b]
2.0		1.659
2.5		2.66
3.0		4.27
3.5		6.86
4.0		10.93
4.5		17.28
5.0		27.1
5.5		42.3
6.0		64.7
6.5		95.7
7.0		139.3

a From freezing point data.
b From isopiestic vapor data.

TABLE A4-101. ACTIVITY COEFFICIENTS FOR $LiClO_4$

	γ		
m	Near 0° C(256)[a]	25° C(132)[b]	25° C(246)[b]
0.001	0.968		
.002	.956		
.005	.935		
.01	.915		
.02	.890		
.05	.853		
.1	.825		0.812
.2	.805	0.792	.794
.3	.804	.792	.792
.4	.810	.799	.798
.5	.821	.808	.808
.6	.835	.821	.820
.7	.853	.836	.834
.8	.871	.851	.852
.9	.891	.869	.869
1.0	.913	.888	.887
1.1	.936		
1.2		.930	.931
1.4		.978	.979
1.6		1.031	1.034

TABLE A4-101. ACTIVITY COEFFICIENTS FOR $LiClO_4$ (Cont'd)

	γ		
m	Near 0° C(256)[a]	25° C(132)[b]	25° C(246)[b]
1.8		1.090	1.093
2.0		1.156	1.158
2.4		1.316	
2.5			1.350
2.7		1.440	
3.0		1.585	1.582
3.4		1.803	
3.5			1.866
3.7		1.984	
4.0		2.170	2.18
4.5		2.415	

a From freezing point data.
b From isopiestic vapor pressure data.

TABLE A4-102. ACTIVITY COEFFICIENTS FOR $Mg(ClO_4)_2$

m	γ Near 0° C (217)[a]	γ 25° C (279)[b]
0.001	0.910	
.002	.869	
.005	.814	
.01	.764	
.02	.707	
.05	.633	
.1	.587	0.590
.2	.567	.558
.3	.575	.567
.4	.598	.584
.5	.630	.614
.6	.668	.653
.7	.713	.698
.8	.767	.753
.9	.828	.817
1.0	.898	.892
1.2		1.069
1.4		1.291
1.6		1.705
1.8		2.13
2.0		2.65
2.5		4.89
3.0		9.19
3.5		17.65
4.0		34.1
4.4		56.6

a From freezing point data
b From isopiestic vapor pressure data

TABLE A4-103. ACTIVITY COEFFICIENTS FOR ClO_4

m	γ Near 0° C(256)[a]	γ 25° C(104)[b]
0.001	0.965	
.002	.951	
.005	.923	
.01	.893	
.02	.852	
.04834*	.777	
satd. soln		0.649

* Eutectic
a From freezing point data.
b From solubility data

TABLE A4-104. ACTIVITY COEFFICIENTS FOR $AgClO_4$(26)

Temperature = 25° C

M[a]	γ[b]
0.001	0.962
.003	.940
.01	.904
.03	.851
.1	.767

a M= Moles of the salt/liter of solution.
b From measurements of the e. m. f. of the $Ag/AgClO_4$ electrode.

TABLE A4-105. ACTIVITY COEFFICIENTS OF $NaClO_4$

	γ			
m	Near 0° C(256)[a]	25° C(246)[b]	25°C(132)[b]	25° C(202)[b]
0.001	0.966			
.002	.953			
.005	.929			
.01	.904			
.02	.873			
.05	.821			
.1	.773	0.775		
.2	.720	.729	0.728	
.3	.686	.701	.701	
.4	.661	.683	.681	
.5	.640	668	.667	
.6	.624	.656	.656	
.7	.609	.648	.647	
.8	.597	.641	.640	
.9	.586	.635	.634	
1.0	.576	.629	.629	
1.1	.568			
1.2		.622	.621	
1.4		.616	.616	
1.6		.631	.612	

TABLE A4-105. ACTIVITY COEFFICIENTS FOR $NaClO_4$ (Cont'd)

m	Near 0° C(256)[a]	25° C(246)[b]	25° C(132)[b]	25° C(204)[b]
1.8		.611	.610	
2.0		.609	.608	
2.4			.608	
2.5		.609		
2.7			.610	
3.0		.611	.612	
3.4			.617	
3.5		.617		
3.7			.622	
4.0		.626	.627	0.626
4.5		.637	.637	
5.0		.649	.649	.649
5.5		.662	.662	
6.0		.677	.675	.676
6.5			.691	
7.0				.706
8.0				.736
9.0				.77
10				.81
12				.89
14				.97
16				1.06

a From freezing point data.
b From isopiestic vapor pressure data.

9. BOILING POINT ELEVATION

9. Boiling Point Elevation

Δt_b = boiling point elevation in degrees centigrade corrected to standard atmospheric pressure

m = number of moles of solute per 1000 gm of water

TABLE A4-106. BOILING POINT ELEVATION BY CHLORATES IN SOLUTION(309)

Solute	m	Δt_b
$Ba(ClO_3)_2$	3.66	5.32
$KClO_3$	0.5	0.53
	1.0	.97
	2.0	1.79
	3.0	2.56
	4.0	4.15
	5.0	4.21
	satd.	5(198)
$NaClO_3$	10.0	8.9
	15.0	12.6
	20.0	16.4
	(satd.) 26.86	21.8

TABLE A4-107. BOILING POINT ELEVATION BY PERCHLORATES IN SOLUTION(198)

Solute	m	Δt_b
$KClO_4$	0.95	1
	2.01	2
	3.22	3
	4.49	4
	4.99	4.4

10. FREEZING POINT LOWERING

10. Freezing Point Lowering

Δt = freezing point lowering in °C

m - number of moles of solute per 1000 gm of water

TABLE A4-108. LOWERING OF FREEZING POINT BY $Al(ClO_3)_3$ IN AQUEOUS SOLUTIONS(310)

m	Δt
0.013	0.078
.02	.116
.05	.281
.10	.569
.20	1.19
.50	3.36
.70	5.33

TABLE A4-109. LOWERING OF FREEZING POINT BY $Ba(ClO_3)_2$ IN AQUEOUS SOLUTIONS(38)

m	Δt
0.01032	0.05206
.02815	.13638
.05808	.27495
.07678	.36094
.10128	.47297
.13514	.62800
.19152	.88846
.30040	1.4059
.44337	2.1286
.5927E* (310)	2.75

* Ice + $Ba(ClO_3)_2 \cdot H_2O$

TABLE A4-110. LOWERING OF FREEZING POINT BY $Ca(ClO_3)_2$ IN AQUEOUS SOLUTIONS (38)

m	Δt
0.01032	0.05261
.02815	.13939
.05808	.28017
.07678	.36785
.10128	.48331
.13514	.64381
.19152	.9191
.30040	1.4831
.44337	2.3046
.73760	4.1220

TABLE A4-111. LOWERING OF FREEZING POINT BY $LiClO_3$ IN AQUEOUS SOLUTIONS

m	Δt	Reference	m	Δt	Reference
0.000516	0.00190	37	.6	2.19	256
.001	.0037	256	.63021	2.3091	37
.001015	.00373	37	.7	2.58	256
.002	.0073	256	.76745	2.8536	37
.002100	.00769	37	.8	2.98	256
.004988	.01814	37	.86140	3.2358	37
.005	.0182	256	0.9	3.39	256
.01	.036	256	1.0	3.80	256
.010121	.03654	37	1.0311	3.9378	37
.02	.072	256	1.1	4.23	256
.020417	.07318	37	1.2241	4.803	37
.05	.177	256	1.5733	6.438	37
.069044	.24456	37	1.8781	7.782	37
.1	.352	256	2	8.84	310
.12276	.43316	37	2.1447	8.904	37
.19920	.70413	37	2.5	11.23	310
.2	.705	256	3	13.84	310
.28004	.9940	37	3.5	16.80	310
.3	1.06	256	4	21.20	310
.36550	1.3052	37	4.5	23.69	310
.4	1.43	256	5	27.54	310
.5	1.80	256	5.5	31.48	310
.50314	1.8204	37	6.0	36.64	310
			6.50*	40.04	310

* Ice + $LiClO_3 \cdot 3H_2O$

TABLE A4-112. LOWERING OF FREEZING POINT BY $Mg(ClO_3)_2$ IN AQUEOUS SOLUTIONS[38]

m	Δt
0.01032	0.05475
.02815	.14395
.05808	.28900
.07678	.37913
.10128	.49576
.13514	.65989
.19152	.94438
.30040	1.5311
.44337	2.3521
1.496(7)	8.00
1.871(7)	11.99

TABLE A4-113. LOWERING OF FREEZING POINT BY $KClO_3$ IN AQUEOUS SOLUTIONS

a.

m	Δt	Reference	m	Δt	Reference
0.001	0.0037	256	0.05	0.172	310
.002	.0073	256	.063280	.21714	40
.005	.018	256	.094279	.31777	40
.01	.036	256	.1	.336	256
.01	036	310	.1	.333	310
.019521	.06970	40	.11734	.39174	40
.02	.071	256	.18634	.60690	40
.02	.070	310	.2	.645	256
.040307	.14045	40	.24598	.79217	40
.05	.173	256			

b. Reference 198

The freezing point of a solution containing n moles of $KClO_3$ per 100 grams of water can be represented by:

$$3.5690\ n - 2.3067\ n^2$$

TABLE A4-114. LOWERING OF FREEZING POINT BY $NaClO_3$ IN AQUEOUS SOLUTIONS

a.

m	Δt	Reference	m	Δt	Reference
0.001	0.0037	310	0.1	0.343	256
.001	.0037	256	.2	.672	256
.002	.0073	310	.20119	.6767	40
.002	.0073	256	.3	.993	256
.004	.0145	310	.30302	1.0070	40
.005	.018	256	.4	1.31	256
.007	.025	310	.5	1.62	256
.01	.036	310	.50729	1.6809	40
.01	.036	256	.6	1.92	256
.02	.071	310	.7	2.23	256
.02	.071	256	.75792	2.5282	40
.04	.140	310	.8	2.52	256
.05	.172	256	.9	2.82	256
.05017	.17529	40	1.0	3.11	256
.07	.242	310	1.03488	3.4227	40
.09996	.34391	40	1.1	3.41	256
.1	.343	310	1.5753	5.505	40
			2.1558	7.814	40

b. Reference 198

The freezing point of a solution containing n moles of $NaClO_3$ per 100 grams of water can be represented by:

$$3.5812\,n - 1.3040n^2$$

TABLE A4-115. LOWERING OF FREEZING POINT BY $Ba(ClO_4)_2$ IN AQUEOUS SOLUTION[216]

m	Δt	m	Δt
0.001	0.0036	0.3	0.958
.002	.0071	.4	1.29
.005	.017	.5	1.63
.01	.034	.6	1.99
.02	.067	.7	2.35
.05	.162	.8	2.73
.1	.319	.9	3.12
.2	.635	1.0	3.53

TABLE A4-116. LOWERING OF FREEZING POINT BY $Ca(ClO_4)_2$ IN AQUEOUS SOLUTION[216]

m	Δt	m	Δt
0.001	0.0036	0.3	1.04
.002	.0071	.4	1.43
.005	.017	.5	1.86
.01	.034	.6	2.31
.02	.067	.7	2.79
.05	.165	.8	3.31
.1	.329	.9	3.87
.2	.672	1.0	4.49

TABLE A4-117. LOWERING OF FREEZING POINT BY $LiClO_4$ IN AQUEOUS SOLUTIONS(256)

m	Δt	m	Δt
0.001	0.0037	0.4	1.47
.002	.0073	.5	1.86
.005	.0182	.6	2.26
.01	.036	.7	2.68
.02	.072	.8	3.11
.05	.178	.9	3.56
.1	.355	1.0	4.01
.2	.714	1.1	4.48
.3	1.08		

TABLE A4-118. LOWERING OF FREEZING POINT BY $Mg(ClO_4)_2$ IN AQUEOUS SOLUTIONS (216)

m	Δt	m	Δt
0.001	0.0036	0.3	1.07
.002	.0071	.4	1.49
.005	.0175	.5	1.95
.01	.034	.6	2.44
.02	.067	.7	2.97
.05	.165	.8	3.54
.1	.330	.9	4.15
.2	.686	1.0	4.80

TABLE A4-119. LOWERING OF FREEZING POINT BY $KClO_4$ IN AQUEOUS SOLUTIONS(256)

m	Δt
0.001	0.0037
.002	.0073
.005	.0181
.01	.036
.02	.070

TABLE A4-120. LOWERING OF FREEZING POINT BY $NaClO_4$ IN AQUEOUS SOLUTIONS (256)

m	Δt	m	Δt
0.001	0.0037	0.4	1.33
.002	.0073	.5	1.65
.005	.0181	.6	1.96
.01	.036	.7	2.28
.02	.071	.8	2.56
.05	.175	.9	2.90
.1	.345	1.0	3.22
.2	.677	1.1	3.53
.3	1.00		

11. OSMOTIC COEFFICIENTS

11. Osmotic Coefficients

ϕ = osmotic coefficient

m = concentration in moles per 1000 gm of water

TABLE A4-121. OSMOTIC COEFFICIENTS OF CHLORATE SOLUTIONS DETERMINED BY ISOPIESTIC VAPOR PRESSURE MEASUREMENT(246)

Temperature = 25°C

m	$LiClO_3$	$KClO_3$	$NaClO_3$
0.1		0.913	0.927
.2		.887	.913
.3		.867	.904
.4		.849	.897
.5		.832	.892
.6		.816	.888
.7		.802	.885
.8			.883
.9			.882
1.0	1.02*		.880; .84*
1.2			.878
1.4			.876
1.6			.874
1.8			.875
2.0			.876
2.5			.879
3.0			.881
3.5			.886

* Reference 115, data from freezing point data.

TABLE A4-122. OSMOTIC COEFFICIENTS OF PERCHLORATE SOLUTIONS DETERMINED BY ISOPIESTIC VAPOR PRESSURE MEASUREMENT

Temperature = 25°C

m	$Ba(ClO_4)_2$ (245)	$Ca(ClO_4)_2$ (245)	$LiClO_4$ (246)	$Mg(ClO_4)_2$ (280)	$NaClO_4$ (246)	$NaClO_4$ (202)
0.1	0.857	0.883	0.951	0.898	0.930	
.2	.868	.911	.959	.935	.920	
.3	.884	.942	.971	.974	.915	
.4	.905	.976	.985	1.016	.912	
.5	.929	1.014	.999	1.062	.910	
.6	.954	1.051	1.013	1.108	.909	
.7	.977	1.089	1.027	1.158	.910	
.8	1.000	1.131	1.043	1.211	.911	
.9	1.024	1.175	1.058	1.267	.912	
1.0	1.046	1.219	1.072;1.08*	1.328	.913;.87*	
1.2	1.094	1.310	1.104	1.437	.916	
1.4	1.141	1.405	1.137	1.558	.920	
1.6	1.188	1.503	1.170	1.683	.925	
1.8	1.233	1.605	1.204	1.815	.930	
2.0	1.279	1.710	1.238	1.945	.934	
2.5	1.394	1.992	1.328	2.306	.947	

* Reference 115, from freezing point data.

TABLE A4-122. OSMOTIC COEFFICIENTS OF PERCHLORATE SOLUTIONS DETERMINED BY ISOPIESTIC VAPOR PRESSURE MEASUREMENT (Cont'd)

Temperature = 25°C

m	$Ba(ClO_4)_2$ [245]	$Ca(ClO_4)_2$ [245]	$LiClO_4$ [246]	$Mg(ClO_4)_2$ [280]	$NaClO_4$ [246]	$NaClO_4$ [202]
3.0	1.509	2.261	1.419	2.667	.960	
3.5	1.619	2.521	1.512	3.036	.975	
4.0	1.713	2.769	1.595	3.397	.991	.991
4.4				3.664		
4.5	1.791	3.005			1.008	
5.0	1.862	3.233			1.025	1.025
5.5	1.945	3.454			1.042	
6.0		3.655			1.060	1.056
6.5		3.828				
7.0		3.989				1.083
8.0						1.107
9.0						1.134
10.0						1.156
12.0						1.202
14.0						1.246
16.0						1.286

* Reference 115, from freezing point data.

12. MISCELLANEOUS

TABLE A4-123. DIFFUSION COEFFICIENTS OF $LiClO_4$ SOLUTIONS[107]

Temperature = 25°C

M	D x 10^5
0.0033	1.277
0.0043	1.278
0.00455	1.275
0.0053	1.273
0.0064	1.271

where:

D = diffusion coefficient in $cm^2 sec^{-1}$

M = concentration in moles salt per liter of solution

TABLE A4-124. DIFFUSION COEFFICIENTS OF $KClO_4$ SOLUTIONS[107]

Temperature = 25°C

M	D x 10^5
0.0012	1.843
0.0018	1.842
0.0023	1.839
0.0034	1.832
0.0049	1.829
0.0063	1.825
0.0075	1.813
0.0084	1.814
0.0097	1.792

where:

D = diffusion coefficient in $cm^2 sec^{-1}$

M = concentration in moles salt per liter of solution

TABLE A4-125. SURFACE TENSION OF $KClO_3$ SOLUTIONS

a. Reference 281

Wt % $KClO_3$	γ_{18}
3.26	72.63
5.02	72.90

b. Reference 135*

M	γ_{25}
0.00010	71.964
0.00020	71.961
0.00050	71.958
0.00100	71.958
0.00200	71.960
0.00500	71.969
0.01000	71.978
0.02000	71.986
0.05000	72.018
0.10000	72.065
0.20000	72.153
0.50000	72.372

where:

M = concentration in moles salt per liter of solution

γ_t = surface tension (at temperature t°, C) in dynes per centimeter

* data calculated from relative surface tension, using the value for water at 25°C from Handbook for Chemistry and Physics, 39th Edition, 1957-1958.(115)

TABLE A4-126. SURFACE TENSION OF $NaClO_3$ SOLUTIONS

a. Reference 281

Wt % $NaClO_3$	γ_{18}
5.99	72.65
10.52	73.02

b. Reference 310

m	γ_{15}
0.5	73.79
1.7	74.45

m = concentration in gram moles per 1000 gm of water

TABLE A4-127. SURFACE TENSION OF $KClO_4$ SOLUTIONS

a. Reference 281

Wt % $KClO_4$	γ_{18}
0.987	72.61
1.417	72.63

b. Reference 257

M	γ_{20}*
0.02	72.714
.04	72.740
.06	72.772
.08	72.798
.10	72.828

M = concentration in moles per liter of solution

* Data taken from graph

TABLE A4-128. THE DEGREE OF DISSOCIATION OF $KClO_3$ IN AQUEOUS SOLUTIONS[129][a]

C	α 0°	12.5°	25°	35°	50°	65°
0.00025	1.000	1.000	1.000	1.000	1.000	1.000
.00049	0.983	0.977	0.977	0.977	0.982	0.980
.00098	.975	.972	.972	.971	.966	.967
.00195	.968	.960	.959	.957	.946	.957
.00781	.946	.935	.932	.929	.906	.916
.03125	.888	.876	.875	.871	.849	.848
.1250	.813	.802	.797	.792	.776	.768

where:

α = degree of dissociation (from conductance measurements)

C = concentration in gram equivalents per liter of solution

a Other data given in Reference 9.

TABLE A4-129. THE DEGREE OF DISSOCIATION OF $NaClO_3$ IN AQUEOUS SOLUTIONS (129)[a]

C	α 0°	12.5°	25°	35°	50°	65°	100°
0.00049	0.997	0.997	-----	-----	1.000	0.990	
0.0098	1.000	1.000	-----	-----	0.996	1.000	
0.00195	0.998	1.000	1.000	1.000	0.981	0.967	
0.00781	0.973	0.973	0.966	0.964	0.941	0.940	
0.03125	0.919	0.916	0.908	0.907	0.900	0.881	
0.1250	0.843	0.836	0.829	0.814	0.795	0.777	
0.5000	0.740	0.728	0.714	0.708			0.56(295)
1							.73(295)
2							.89(295)
3							.98(295)
4							1.07(295)
5							1.15(295)
6							1.23(295)
8							1.42(295)
10							1.31(295)

where:

α = degree of dissociation[b]

C = concentration in gram equivalents per liter of solution

a Other data given in References 76 and 9.

b Reference 129, from conductance measurements. Reference 295, from vapor pressure lowering.

TABLE A4-130. THE DEGREE OF DISSOCIATION OF $KClO_4$ IN AQUEOUS SOLUTIONS[129]

C	α					
	0°	12.5°	25°	35°	50°	65°
0.00025	1.000	1.000	1.000	1.000	1.000	1.000
.00049	0.986	0.985	0.985	0.986	0.969	0.972
.00098	.970	.969	.971	.966	.949	.957
.00195	.965	.957	.959	.953	.941	.942
.00781	.927	.925	.930	.930	.921	.924
.03125	.876	.876	.869	.869	.862	.864

where:

α = degree of dissociation (from conductance measurements)

C = concentration in gram equivalents per liter of solution

TABLE A4-131. THE DEGREE OF DISSOCIATION OF $NaClO_3$ IN AQUEOUS SOLUTIONS[129]

C	α			
	0°	12.5°	25°	35°
0.00098	0.996	0.996	0.997	1.000
.00195	1.000	1.000	1.000	0.999
.00781	0.993	0.990	0.985	.987
.03125	.993	.931	.930	.924
.1250	.884	.862	.845	.845

where:

α = degree of dissociation (from conductance measurements)

C = concentration in gram equivalents per liter of solution

TABLE A4-132. DISSOCIATION CONSTANTS OF CHLORATES AND PERCHLORATES

Salt	M	Temp.	K	Reference
$KClO_3$	0.02	18	1.05	9
$KClO_3$	0.05	18	1.04	9
$KClO_3$	0.1	18	1.18	9
$KClO_3$	---	18	1.4	60
$KClO_3$	---	25	1.4	61
$NaClO_3$	0.05	18	3.0	9
$NaClO_3$	0.1	18	4.0	9
$KClO_4$	---	25	3.0(avg)	206

where:

M = concentration in moles per liter of solution

K = dissociation constant

TABLE A4-133. DIELECTRIC CONSTANTS OF AQUEOUS CHLORATE AND PERCHLORATE SOLUTIONS

a. Reference 13

Temperature = 18°C

Salt	$M \times 10^3$	D
$NaClO_3$	0.5	79.1
$NaClO_3$	1	77.6
$NaClO_3$	1.5	75.9
$KClO_3$	0.5	78.4
$KClO_3$	1	76.3
$KClO_3$	1.5	74.0

b. Reference 312

$NaClO_4$

Temp.	Wt % $NaClO_4$	D
-90	10	98.5
-110	10	44.7
-130	10	14.2
-150	10	8.7
-170	10	7.2
-180	10	6.9

where:

M = concentration in moles per liter of solution

D = Dielectric constant

TABLE A4-134. POLARIZABILITY AND IONIC RADIUS OF THE PERCHLORATE ION[24]

Temperature = 25°C

From $LiClO_4$ solutions:

Polarizability of ClO_4^-, α_D = 4.158 $Å^3$

Radius of ClO_4^- = 1.82 Å

TABLE A4-135. TRANSPORT NUMBER FOR THE CHLORATE ION

C	Transport Number
0.02	0.505
.07	.465
.3	.445

TABLE A4-136. OSMOTIC PRESSURE OF $KClO_3$ SOLUTION[310]

The osmotic pressure of a 0.50 molal solution of $KClO_3$, at 15°C, with a copper ferrocyanide membrane, is 1.73 atm.

TABLE A4-137. IONIC VELOCITY OF THE CHLORATE ION[48]

Temperature = 18°

	Chlorate Ionic Velocity (from NH_4ClO_3)		
C	2×10^{-9}	10^{-9}	5×10^{-10}
ν	59×10^{-5}	58×10^{-5}	59×10^{-5}

where:

C = gm equivalents per liter of solution

ν = ion velocity

TABLE A4-138. SOLUTION VELOCITY OF $NaClO_3$ IN WATER[311]

Temp., °C	Wt % $NaClO_3$	K
4.8	45.47	0.043
30.1	51.22	0.083

K, the velocity constant, is defined by the equation

$$K = \frac{v}{S(t_2 - t_1)} \ln \frac{C_s - C_1}{C_s - C_2}$$

where:

v = volume in cm^3

S = surface of contact in cm^2

C = concentration at time t

TABLE A4-139. COMPRESSIBILITY OF AQUEOUS SOLUTIONS OF $KClO_3$

a. Reference 57

M	β *
0.1694	43.861×10^{-12}

b. Reference 88

Temperature = 25°C

Wt %	β (up to 1000 bars)
3.10	0.03851
7.06	.03730

c. Reference 198

Temperature = 17°C

Sp. Gr.	β
1.009	0.0000454
1.019	0.0000429
1.024	0.0000409

d. Reference 182

M	$\beta \times 10^{10}$ **
0.5000	31.37
.2500	33.1
.1250	33.9
.0625	25.2

β = compressibility coefficient

M = concentration in moles per liter of solution

* Determined from sound velocity measurements in aqueous solution at 25°C at a supersonic frequency of 1015.24 kc/sec.

** From sound velocity measurements.

TABLE A4-140. COMPRESSIBILITY OF AQUEOUS SOLUTIONS OF $NaClO_3$[182]

Temperature = 20°C

M	$\beta \times 10^{10}$ *
1.0000	37.27
0.5001	40.0
.2500	41.4
.1249	41.9
.0624	43.2

β = compressibility coefficient

M = concentration in moles per liter of solution

* From sound velocity measurements

TABLE A4-141. COMPRESSIBILITY OF AQUEOUS SOLUTIONS OF NH_4ClO_4 (182)

Temperature = 20°C

M	$\beta \times 10^{10}$ *
1.0001	5.04
0.5001	4.5
.2500	4.0
.1250	4.1
.0625	3.7

where:

β = compressibility coefficient

M = concentration in moles per liter of solution

* From sound velocity measurements

TABLE A4-142. COMPRESSIBILITY OF AQUEOUS SOLUTIONS OF $Ca(ClO_4)_2$[87]

Wt %	$\beta \times 10^{12}$ *	s**
55.074	22.34	5.2
47.620	24.88	6.2
38.218	28.35	7.5
28.387	32.77	8.6
15.728	38.26	9.8

where:

β = compressibility coefficient

M = concentration in moles per liter of solution

* Determined by ultrasonic velocity measurements.

** s = solvation in moles solvent/mole of electrolyte The solvation increases with dilution. The degree of hydration was calculated as $Ca(ClO_4)_2 \cdot 11\,H_2O$.

TABLE A4-143. COMPRESSIBILITY OF AQUEOUS SOLUTIONS OF $LiClO_4$[182]

M	$\beta \times 10^{10}$ *
0.9880	21.74
.4941	22.8
.2471	23.1
.1235	23.7
.0617	28.8

β = compressibility coefficient

M = concentration in moles per liter of solution

* From sound velocity measurements

TABLE A4-144. COMPRESSIBILITY OF AQUEOUS SOLUTIONS OF $NaClO_4$[182]

Temperature = 20°C

M	$\beta \times 10^{10}$ *
1.0090	32.01
0.5047	33.5
.2523	34.3
.1261	34.8
.0630	35.1

β = compressibility coefficient

M = concentration in moles per liter of solution

* From sound velocity measurements

TABLE A4-145. VARIATION OF pH OF SOLUTIONS OF CERTAIN PERCHLORATES WITH RESPECT TO CONCENTRATION(176)

$Ba(ClO_4)_2$	
M	pH
0.0558	6.15
0.478	5.85
1.255	5.61
1.915	5.17
4.581	4.85

$Ca(ClO_4)_2$	
M	pH
0.232	5.82
0.326	5.70
0.731	5.49
1.523	4.90
5.380	3.53

$Mg(ClO_4)_2$	
M	pH
0.0430	5.90
0.392	5.33
0.667	5.08
1.30	4.64
2.51	3.78
4.00	2.51

where:

M = concentration in moles per liter of solution

TABLE A4-146 MAGNETIC SUSCEPTIBILITY OF THE AQUEOUS SOLUTIONS OF SOME PERCHLORATES[82]

Temperature = 20°C

$\psi_{H_2O} = -0.7199 \times 10^{-6}$

$Ba(ClO_4)$

Wt %	$-\psi \times 10^6$
4.26	0.6999
5.70	.6949
6.96	.6882
9.82	.6756
12.68	.6626
17.25	.6439

$NaClO_4$

Wt %	$-\psi \times 10^6$
6.24	0.6949
8.25	0.6869
13.19	0.6674
15.01	0.6593
16.96	0.6514
19.80	0.6399

ψ = magnetic susceptibility in c g.s.e.m.u.

TABLE A4-147 APPARENT VOLUMES OF AQUEOUS SOLUTIONS OF CHLORATES AND PERCHLORATES

a. Reference 241

$KClO_3$

Temperature = 24.81°C

m	ϕ
0.008710	45.861
0.010400	45.874
0.012735	45.920
0.029083	46.018
0.037754	46.004
0.039931	46.079
0.054768	46.132
0.064056	46.160
0.091097	46.276
0.14088	46.417
0.14572	46.460
0.17587	46.541
0.20796	46.600
0.27062	46.778
0.36786	46.963
0.46054	47.106
0.56917	47.330
0.66033	47.471

where:

ϕ = apparent molal volume in ml/mole

m = concentration in gram moles per kilogram of water

TABLE A4-147. APPARENT VOLUMES OF AQUEOUS SOLUTIONS OF CHLORATES AND PERCHLORATES (Cont'd)

b. Reference 74

In infinitely dilute solutions at 25°C, the apparent molar volume for ClO_3^- is 35.1 cc/equivalent.

c. Reference 74

In infinitely dilute solutions at 25° and 35°C, the apparent molar volume for ClO_4^- is 44.5 and 45.6 cc/equivalent, respectively.

d. Reference 255

The apparent molal volume of $NaClO_3$ = 37.2 ml/mole

The apparent molal volume of $NaClO_4$ = 45.7 ml/mole

e. Reference 51

The partial molar volume for $NaClO_3$ changes from 3 to 43 cc/mole at 0.25 and 16 moles per 100 moles H_2O, respectively.

The partial molar volume for $NaClO_4$ changes from 4 to 52 cc/mole at 0.25 and 30 moles per 100 moles H_2O, respectively.

TABLE A4-148. POTENTIAL OF $Ag-AgClO_4$ ELECTRODE[26]

Temperature = 25°C

M	E
0.271	0.4221
.0813	.3943
.0271	.3683
.00813	.3388
.00271	.3114

$E_o(Ag-AgClO_4)$ = 0.7993

where:

E = measured EMF referred to the calomel electrode in volts (E_{cal} = 0.3551)

M = concentration in moles per liter of solution

TABLE A4-149 REFERENCES FOR UNTABULATED MISCELLANEOUS SOLUTION PROPERTIES

Infrared, Raman, and X-ray Spectra: 210, 149, 150, 8, 266, 65, 239, 184, 218, 322, 231, 85, 84

Absorption Coefficients: 253

Specific Cohesion: 281

Solution Affinities: 28

Certain Optical and Magneto-optic Constants of Some Chlorates: 236

Anisotropy Coefficient for Chlorate Ion: 178

Supersaturation of $KClO_3$ in Solutions: 290

A5. PROPERTIES OF NONAQUEOUS SOLUTIONS

TABLE OF CONTENTS

			Page
1.		SOLUBILITY IN NONAQUEOUS SOLVENTS	439
	A5-1	SOLUBILITY OF $KClO_3$ IN NONAQUEOUS SOLVENTS	440
	A5-2	SOLUBILITY OF $NaClO_3$ IN NONAQUEOUS SOLVENTS	441
	A5-3	SOLUBILITIES OF SEVERAL CHLORATES IN NONAQUEOUS SOLVENTS	441
	A5-4	SOLUBILITY OF $Al(ClO_4)_3$ IN NONAQUEOUS SOLVENTS	442
	A5-5	SOLUBILITY OF NH_4ClO_4 IN NONAQUEOUS SOLVENTS	443
	A5-6	SOLUBILITY OF $Ba(ClO_4)_2$ IN NONAQUEOUS SOLVENTS	444
	A5-7	SOLUBILITY OF $Ca(ClO_4)_2$ IN NONAQUEOUS SOLVENTS	445
	A5-8	SOLUBILITY OF $LiClO_4$ IN NONAQUEOUS SOLVENTS	446
	A5-9	SOLUBILITY OF $LiClO_4 \cdot 3H_2O$ IN NONAQUEOUS SOLVENTS	447
	A5-10	SOLUBILITY OF $Mg(ClO_4)_2$ IN NONAQUEOUS SOLVENTS	448
	A5-11	SOLUBILITY OF $KClO_4$ IN NONAQUEOUS SOLVENTS	449
	A5-12	SOLUBILITY OF $AgClO_4$ IN NONAQUEOUS SOLVENTS	450
	A5-13	SOLUBILITY OF $NaClO_4$ IN NONAQUEOUS SOLVENTS	455

TABLE OF CONTENTS (Cont'd)

		Page
2.	DENSITY OF SATURATED NONAQUEOUS SOLUTIONS	456
A5-14	DENSITY OF SATURATED SOLUTIONS OF NH_4ClO_4 IN NONAQUEOUS SOLVENTS	458
A5-15	DENSITY OF SATURATED SOLUTIONS OF $Ba(ClO_4)_2$ IN NONAQUEOUS SOLVENTS	459
A5-16	DENSITY OF SATURATED SOLUTIONS OF $Ca(ClO_4)_2$ IN NONAQUEOUS SOLVENTS	460
A5-17	DENSITY OF SATURATED SOLUTIONS OF $LiClO_4$ IN NONAQUEOUS SOLVENTS	461
A5-18	DENSITY OF SATURATED SOLUTIONS OF $LiClO_4 \cdot 3H_2O$ IN NONAQUEOUS SOLVENTS	462
A5-19	DENSITY OF SATURATED SOLUTIONS OF $Mg(ClO_4)_2$ IN NONAQUEOUS SOLVENTS	463
A5-20	DENSITY OF SATURATED SOLUTIONS OF $KClO_4$ IN NONAQUEOUS SOLVENTS	464
A5-21	DENSITY OF SATURATED SOLUTIONS OF $AgClO_4$ IN NONAQUEOUS SOLVENTS	465
A5-22	DENSITY OF SATURATED SOLUTIONS OF $NaClO_4$ IN NONAQUEOUS SOLVENTS	466
3.	DENSITY OF UNSATURATED NONAQUEOUS SOLUTIONS	467
A5-23	DENSITY OF SOLUTIONS OF $LiClO_4$ IN NONAQUEOUS SOLVENTS	469
A5-24	DENSITY OF SOLUTIONS OF $AgClO_4$ IN NONAQUEOUS SOLVENTS	470
4.	VISCOSITY	474
A5-25	VISCOSITY OF SOLUTIONS OF $LiClO_4$ IN ETHER	476

TABLE OF CONTENTS (Cont'd)

			Page
	A5-26	VISCOSITY OF SOLUTIONS OF $AgClO_4$ IN NONAQUEOUS SOLVENTS	477
5.		CONDUCTANCE IN NONAQUEOUS SOLUTIONS	480
	A5-27	LIMITING PERCHLORATE IONIC CONDUCTANCE IN NONAQUEOUS SOLVENTS	482
	A5-28	CONDUCTANCE OF THE PERCHLORATE ION IN NONAQUEOUS SOLVENTS	482
	A5-29	SPECIFIC AND MOLAR CONDUCTIVITY OF $Al(ClO_4)_3$ IN NONAQUEOUS SOLVENTS	483
	A5-30	EQUIVALENT CONDUCTANCE OF NH_4ClO_4 IN NITROMETHANE	484
	A5-31	EQUIVALENT CONDUCTANCE OF $Ba(ClO_4)_2$ IN ACETONE	485
	A5-32	EQUIVALENT CONDUCTANCE OF $Ba(ClO_4)_2$ IN 2-ETHOXYETHANOL	486
	A5-33	EQUIVALENT CONDUCTANCE OF $Ba(ClO_4)_2$ IN FURFURAL	486
	A5-34	EQUIVALENT CONDUCTANCE OF $Ba(ClO_4)_2$ IN GLYCOL	487
	A5-35	EQUIVALENT CONDUCTANCE OF $Ba(ClO_4)_2$ IN N-METHYLACETAMIDE	487
	A5-36	EQUIVALENT CONDUCTANCE OF $Ca(ClO_4)_2$ IN N-METHYLACETAMIDE	487
	A5-37	EQUIVALENT CONDUCTANCE OF $Ca(ClO_4)_2$ IN ACETONE	488
	A5-38	SPECIFIC AND EQUIVALENT CONDUCTANCE OF $LiClO_4$ IN TOLUENE	488

TABLE OF CONTENTS (Cont'd)

		Page
A5-39	SPECIFIC AND EQUIVALENT CONDUCTANCE OF $LiClO_4$ IN ETHER	489
A5-40	EQUIVALENT CONDUCTANCE OF $LiClO_4$ IN NITROMETHANE	491
A5-41	EQUIVALENT CONDUCTANCE OF $LiClO_4$ IN ACETONE	492
A5-42	EQUIVALENT CONDUCTANCE OF $LiClO_4$ IN ACETIC ACID	492
A5-43	EQUIVALENT CONDUCTANCE OF $LiClO_4$ IN CYCLOHEXANOL	493
A5-44	EQUIVALENT CONDUCTANCE OF $LiClO_4$ IN ETHYL ALCOHOL	494
A5-45	EQUIVALENT CONDUCTANCE OF $LiClO_4$ IN METHYL ALCOHOL	495
A5-46	EQUIVALENT CONDUCTANCE OF $Mg(ClO_4)_2$ IN ISOPROPYL ALCOHOL	496
A5-47	EQUIVALENT CONDUCTANCE OF $Mg(ClO_4)_2$ IN ACETONE	497
A5-48	EQUIVALENT CONDUCTANCE OF $Mg(ClO_4)_2$	499
A5-49	EQUIVALENT CONDUCTANCE OF $Mg(ClO_4)_2$ IN NITROMETHANE	500
A5-50	EQUIVALENT CONDUCTANCE OF $Mg(ClO_4)_2$ IN n-PROPYL ALCOHOL	501
A5-51	EQUIVALENT CONDUCTANCE OF $KClO_4$ IN DIMETHYLFORMAMIDE	502
A5-52	EQUIVALENT CONDUCTANCE OF $KClO_4$ IN N, N-DIMETHYLACETAMIDE	503

TABLE OF CONTENTS (Cont'd)

		Page
A5-53	EQUIVALENT CONDUCTANCE OF $KClO_4$ IN ACETONE	503
A5-54	EQUIVALENT CONDUCTANCE OF $KClO_4$ IN DIMETHYL SULFOXIDE	504
A5-55	SPECIFIC CONDUCTANCE OF $AgClO_4$ IN NITROBENZENE	504
A5-56	SPECIFIC AND EQUIVALENT CONDUCTANCE OF $AgClO_4$ IN PYRIDINE	505
A5-57	SPECIFIC AND EQUIVALENT CONDUCTANCE OF $AgClO_4$ IN ACETONE	506
A5-58	SPECIFIC AND EQUIVALENT CONDUCTANCE OF $AgClO_4$ IN ANILINE	507
A5-59	EQUIVALENT CONDUCTANCE OF $AgClO_4$ IN PYRIDINE	508
A5-60	EQUIVALENT CONDUCTANCE OF $AgClO_4$ IN NITROBENZENE	509
A5-61	EQUIVALENT CONDUCTANCE OF $AgClO_4$ IN METHYL ALCOHOL	510
A5-62	EQUIVALENT CONDUCTANCE OF $AgClO_4$ IN NITROMETHANE	511
A5-63	EQUIVALENT CONDUCTANCE OF $AgClO_4$ IN ACETONE	512
A5-64	EQUIVALENT CONDUCTANCE OF $AgClO_4$ IN ETHYL ALCOHOL	513
A5-65	EQUIVALENT CONDUCTANCE OF $AgClO_4$ IN BENZENE	514
A5-66	EQUIVALENT CONDUCTANCE OF $AgClO_4$ IN 2-ETHOXYETHANOL	515

TABLE OF CONTENTS (Cont'd)

		Page
A5-67	EQUIVALENT CONDUCTANCE OF $AgClO_4$ IN PYRIDINE	515
A5-68	EQUIVALENT CONDUCTANCE OF $AgClO_4$ IN FURFURAL	516
A5-69	EQUIVALENT CONDUCTANCE OF $AgClO_4$ IN CYCLOHEXANONE	516
A5-70	EQUIVALENT CONDUCTANCE OF $AgClO_4$ IN ISOBUTYL ALCOHOL	517
A5-71	EQUIVALENT CONDUCTANCE OF $NaClO_4$ IN DIMETHYL SULFOXIDE	517
A5-72	EQUIVALENT CONDUCTANCE OF $NaClO_4$ IN ETHYL ALCOHOL	518
A5-73	EQUIVALENT CONDUCTANCE OF $NaClO_4$ IN METHYL ALCOHOL	519
A5-74	EQUIVALENT CONDUCTANCE OF $NaClO_4$ IN NITROMETHANE	520
A5-75	EQUIVALENT CONDUCTANCE OF $NaClO_4$ IN ACETONE	521
A5-76	EQUIVALENT CONDUCTANCE OF $NaClO_4$ IN N, N-DIMETHYLACETAMIDE	521
A5-77	EQUIVALENT CONDUCTANCE OF $NaClO_4$ IN DIMETHYLFORMAMIDE	522
6.	MISCELLANEOUS	523
A5-78	LOWERING OF THE FREEZING POINT OF CYCLOHEXANOL BY $LiClO_4$	524
A5-79	LOWERING OF THE FREEZING POINT OF BENZENE BY $AgClO_4$	525

TABLE OF CONTENTS (Cont'd)

		Page
A5-80	DIELECTRIC CONSTANTS, MOLAR POLARIZATION, AND ELECTRIC MOMENTS FOR $AgClO_4$ IN BENZENE	526
A5-81	MOBILITIES OF CHLORATE AND PERCHLORATE IONS IN VARIOUS NONAQUEOUS SOLVENTS	528
A5-82	DISSOCIATION CONSTANTS OF SOME PERCHLORATES IN NONAQUEOUS SOLVENTS	529
A5-83	RADIUS OF THE CHLORATE AND PERCHLORATE IONS IN NONAQUEOUS SOLVENTS	529
A5-84	MAGNETIC SUSCEPTIBILITY OF THE NONAQUEOUS SOLUTIONS OF SOME PERCHLORATES	530
A5-85	COMPRESSIBILITY OF SOLUTIONS OF $LiClO_4$ IN ACETONE	531
A5-86	PARTIAL MOLAR VOLUMES OF $LiClO_4$ AND ETHER SOLUTIONS	532

1. NONAQUEOUS SOLUBILITY

TABLE A5-1. SOLUBILITY OF $KClO_3$ IN NONAQUEOUS SOLVENTS

Solvent	Temp., °C	gm $KClO_3$ per 100 g Solvent	Reference
Liquid Ammonia	0	2.59	261
Ethyl Alcohol	25	0.81	310
Glycerol	15-16	3.54	261
	20	1.32	261
	20	1.03	261
	25	1.05	261
Ethylene Glycol	?	0.91	261
Methyl Alcohol	0	0.055	310
	20	0.095	310
Liquid Sulfur Dioxide		Appreciably Soluble	31
		Less than 0.01%	263
Phosphorus Oxychloride		Appreciably Soluble	30
Ethylenediamine	25	0.145	123
Monoethanolamine	25	0.30	123
Ethylene Glycol	25	1.21	123
Acetone		Insoluble	200
Hydrofluoric Acid		Dissolves readily and reacts	79

TABLE A5-2. SOLUBILITY OF $NaClO_3$ IN NONAQUEOUS SOLVENTS

Solvent	Temp., °C	gm $NaClO_3$ per 100 g Solvent	Reference
Ethylenediamine	25	52.8	123
Monoethanolamine	25	19.7	123
Ethylene Glycol	25	16.0	123
Ethyl Alcohol	25	1.	198
	b.p	2.5	198
Liquid Ammonia		Very Soluble	198
Glycerol	15.5	20.	198
Hydrazine	25	65.8	198
Acetone		Insoluble	200

TABLE A5-3. SOLUBILITIES OF SEVERAL CHLORATES IN NONAQUEOUS SOLVENTS

Salt	Temp., °C	Solubility and Solvent	Reference
NH_4ClO_3		Insoluble in Acetone	200
$Ba(ClO_3)_2$		Moderately Soluble in HF	79
$Ca(ClO_3)_2$		Appreciably Soluble in Liquid SO_2	31
$LiClO_3$		Limited Solubility in Acetone	200

TABLE A5-4. SOLUBILITY OF $Al(ClO_4)_3$ IN NONAQUEOUS SOLVENTS[103]

Solvent	Solubility	Reaction	Remarks
Acetonitrile	Miscible	Moderate	Turned Yellow
Acetone	Miscible	Vigorous	Resinified
Methyl Alcohol	Miscible	Vigorous	
Hexane	Not Miscible		Resinified
Dioxane		Explosion	
Aniline		Explosion	
Pyridine		Explosion	

TABLE A5-5. SOLUBILITY OF NH_4ClO_4 IN NONAQUEOUS SOLVENTS

Solvent	Temp., °C	gm NH_4ClO_4 per 100 g Solvent	Reference
Acetone	25	2.26	261
n-Butyl Alcohol	25	0.017	261
Ethyl Acetate	25	0.032	261
Ethyl Alcohol	25	1.908	261
Ethyl Ether	25	0.000	310
Isobutyl Alcohol	25	0.127	261
Methyl Alcohol	25	6.85	261
n-Propyl Alcohol	25	0.386	261
Sulfur Dioxide	0	0.025	261
Liquid Ammonia	25	137.93	261

TABLE A5-6. SOLUBILITY OF $Ba(ClO_4)_2$ IN NONAQUEOUS SOLVENTS

Solvent	Temp., °C	gm $Ba(ClO_4)_2$ per 100 g Solvent	Reference
Acetone	25	124.7	261
n-Butyl Alcohol	25	58.18	261
2-Ethoxyethanol	20	107.	261
	?	107.	43
Ethyl Acetate	25	112.9	261
Ethyl Alcohol	25	124.6	261
Furfural	20	43.	261
	?	43.	43
Isobutyl Alcohol	25	56.23	261
Methyl Alcohol	25	217.1	261
n-Propyl Alcohol	25	75.65	261

TABLE A5-7. SOLUBILITY OF $Ca(ClO_4)_2$ IN NONAQUEOUS SOLVENTS[261]

Solvent	Temp., °C	gm $Ca(ClO_4)_2$ per 100 g Solvent
Acetone	25	61.76
n-Butyl Alcohol	25	113.5
Ethyl Acetate	25	75.62
Ethyl Alcohol	25	166.2
Ethyl Ether	25	0.26
Isobutyl Alcohol	25	56.96
Methyl Alcohol	25	237.4
n-Propyl Alcohol	25	144.9

TABLE A5-8. SOLUBILITY OF $LiClO_4$ IN NONAQUEOUS SOLVENTS

Solvent	Temp., °C	gm $LiClO_4$ per 100 g Solvent	Reference
Acetone	25	136.5	261
	25	136.5	231
n-Butyl Alcohol	25	79.31	261
	25	79.69	231
Ethyl Acetate	25	95.12	261
	25	95.27	231
Ethyl Alcohol	25	151.8	261
	25	226.4	231
Ethyl Ether	25	113.7	261
	25	137.1	231
Isobutyl Alcohol	25	58.05	261
	25	58.06	231
Methyl Alcohol	25	182.2	261
	25	182.0	231
n-Propyl Alcohol	25	105.0	261
	25	104.9	231

TABLE A5-9. SOLUBILITY OF $LiClO_4 \cdot 3H_2O$ IN NONAQUEOUS SOLVENTS[261]

Solvent	Temp., °C	gm $LiClO_4 \cdot 3H_2O$ per 100 g Solvent
Acetone	25	96.23
n-Butyl Alcohol	25	27.23
Ethyl Acetate	25	35.78
Ethyl Alcohol	25	72.89
Ethyl Ether	25	0.196
Isobutyl Alcohol	25	23.23
Methyl Alcohol	25	156.1
n-Propyl Alcohol	25	36.65

TABLE A5-10. SOLUBILITY OF $Mg(ClO_4)_2$ IN NONAQUEOUS SOLVENTS

Solvent	Temp., °C	gm $Mg(ClO_4)_2$ per 100 g Solvent	Solid Phase	Reference
Acetone	25	42.887		261
n-Butyl Alcohol	25	64.37		261
Ethyl Acetate	25	70.91		261
Ethyl Alcohol	25	23.96		261
Ethyl Ether	0	0.0437	$Mg(ClO_4)_2 \cdot 3C_2H_5OC_2H_5$ (Unstable)	252, 249
	0		$Mg(ClO_4)_2 \cdot 2C_2H_5OC_2H_5$ (Fairly stable at 25° C)	249
	15	0.0588		252
	25	0.0643		252
	?		$Mg(ClO_4)_2 \cdot C_2H_5OC_2H_5$	249
Isobutyl Alcohol	25	49.50		261
Methyl Alcohol	25	51.84		261
n-Propyl Alcohol	25	73.40		261

NAVORD REPORT 7147 (VOLUME 1)

TABLE A5-11. SOLUBILITY OF $KClO_4$ IN NONAQUEOUS SOLVENTS

Solvent	Temp., °C	gm $KClO_4$ per 100 g Solvent	Reference
Acetone	25	0.155	261
n-Butyl Alcohol	25	0.0045	261
Ethyl Acetate	25	0.0015	261
Ethyl Alcohol	25	0.012	261
Ethyl Ether	25	0.000	310
Isobutyl Alcohol	25	0.005	261
Methyl Alcohol	25	0.105	261
n-Propyl Alcohol	25	0.010	261
Liquid Sulfur Dioxide		Insoluble	31
Phosphorus Oxychloride		Slightly Soluble	30
2-Methoxyethanol	30	0.868	293
	35	0.875	293
	40	0.883	293
	45	0.898	293
Ethylenediamine	25	2.81	123
Monoethanolamine	25	1.36	123
Ethylene Glycol	25	1.03	123
Hydrofluoric Acid		Slightly Soluble	79

TABLE A5-12. SOLUBILITY OF $AgClO_4$ IN NONAQUEOUS SOLVENTS

Solvent	Temp., °C	gm $AgClO_4$ per 100 g Solvent	Solid Phase	Reference
Acetone	0	166.7		154
	25	178.6		154
	50	189.4		154
Aniline	- 6.15m. pt.	0.00	$C_6H_5NH_2$	261
	- 6.6	0.75	$C_6H_5NH_2$ + $AgClO_4 \cdot 6C_6H_5NH_2$	261
	+ 25.0	5.3	$AgClO_4 \cdot 6C_6H_5NH_2$	261
	40.0	12.9	$AgClO_4 \cdot 6C_6H_5NH_2$	261
	50.1	20.5	$AgClO_4 \cdot 6C_6H_5NH_2$	261
	60.52*	37.10	$AgClO_4 \cdot 6C_6H_5NH_2$	261
	55.0	44.7	$AgClO_4 \cdot 6C_6H_5NH_2$	261
	48.3 tr. pt.	49.3	$AgClO_4 \cdot 6C_6H_5NH_2$ + $AgClO_4 \cdot 3C_6H_5NH_2$	261
	58.1	53.8	$AgClO_4 \cdot 3C_6H_5NH_2$	261
	66.6 tr. pt.	62.3	$AgClO_4 \cdot 3C_6H_5NH_2$ + $AgClO_4 \cdot 2C_6H_5NH_2$	261

* Congruent m. pt. (3)

TABLE A5-12. SOLUBILITY OF $AgClO_4$ IN NONAQUEOUS SOLVENTS (Cont'd)

Solvent	Temp., °C	gm $AgClO_4$ per 100 g Solvent	Solid Phase	Reference
Aniline	88.0	66.7	$AgClO_4 \cdot 2C_6H_5NH_2$	261
	48.0 m.pt.	100.0	$AgClO_4$	261
Benzene	5.48	0.00	C_6H_6	261
	5.12	3.56	$C_6H_6 + AgClO_4 \cdot C_6H_6$	261
	25.00	5.26	$AgClO_4 \cdot C_6H_6$	261
	50.00	11.30	$AgClO_4 \cdot C_6H_6$	261
	80.3	47.5	$AgClO_4 \cdot C_6H_6$	261
	92.0	66.9	$AgClO_4 \cdot C_6H_6$	261
	115.5	102.	$AgClO_4 \cdot C_6H_6$	261
	138.5	150.	$AgClO_4 \cdot C_6H_6$	261
	140.0	167.	$AgClO_4$ (Unstable)	261
	145.0	170.	$AgClO_4 +$ $AgClO_4 \cdot C_6H_6$	261
	159.0	182.	$AgClO_4$	261
	160.0	190.	$AgClO_4$	261

TABLE A5-12. SOLUBILITY OF $AgClO_4$ IN NONAQUEOUS SOLVENTS (Cont'd)

Solvent	Temp., °C	gm $AgClO_4$ per 100 g Solvent	Solid Phase	Reference
Pyridine	- 40.3 f. pt.	0.0	C_5H_5N	261
	- 41.5	4.2	C_5H_5N	261
	- 43.0	7.8	C_5H_5N + $AgClO_4 \cdot 4C_5H_5N$	261
	- 35.0	9.1	$AgClO_4 \cdot 4C_5H_5N$	261
	- 11.5	13.93	$AgClO_4 \cdot 4C_5H_5N$	261
	- 1.3	17.00	$AgClO_4 \cdot 4C_5H_5N$	261
	+ 25.0	26.42	$AgClO_4 \cdot 4C_5H_5N$	261
	36.1	32.49	$AgClO_4 \cdot 4C_5H_5N$	261
	49.2	41.6	$AgClO_4 \cdot 4C_5H_5N$	261
	60.4	52.7	$AgClO_4 \cdot 4C_5H_5N$	261
	66.8	69.8	$AgClO_4 \cdot 4C_5H_5N$	261
	68.0	71.5	$AgClO_4 \cdot 4C_5H_5N$ + $AgClO_4 \cdot 9C_5H_5N$	261
	71.0	73.6	$AgClO_4 \cdot 9C_5H_5N$	261

NAVORD REPORT 7147 (VOLUME 1)

TABLE A5-12. SOLUBILITY OF $AgClO_4$ IN NONAQUEOUS SOLVENTS (Cont'd)

Solvent	Temp., °C	gm $AgClO_4$ per 100 g Solvent	Solid Phase	Reference
Pyridine	75.0	75.4	$AgClO_4 \cdot 9C_5H_5N$	261
	86.3	84.5	$AgClO_4 \cdot 9C_5H_5N$	261
	95.6	91.6	$AgClO_4 \cdot 9C_5H_5N$ + $AgClO_4 \cdot 2C_5H_5N$	261
	110.	100.0	$AgClO_4 \cdot 2C_5H_5N$	261
	144-147	-----	$AgClO_4 \cdot 2C_5H_5N$ + $AgClO_4$	261
Toluene	- 75.3	0.0	$AgClO_4 \cdot C_7H_8$	261
	- 24.1	6.39	$AgClO_4 \cdot C_7H_8$	261
	0	35.89	$AgClO_4 \cdot C_7H_8$	261
	16.	72.4	$AgClO_4 \cdot C_7H_8$	261
	16.5	75.10	$AgClO_4 \cdot C_7H_8$	261
	18.	78.92	$AgClO_4 \cdot C_7H_8$	261
	22.6 tr. pt.	-------	$AgClO_4 \cdot C_7H_8$ + $AgClO_4$	261
	25.	101.2	$AgClO_4$	261

TABLE A5-12. SOLUBILITY OF $AgClO_4$ IN NONAQUEOUS SOLVENTS (Cont'd)

Solvent	Temp., °C	gm $AgClO_4$ per 100 g Solvent	Solid Phase	Reference
Toluene	50.	111.3	$AgClO_4$	261
	75.	120.3	$AgClO_4$	261
Furfural	?	35.		43
2-Ethoxyethanol	?	134.		43
Chlorobenzene		Soluble		114
Glycerol		Soluble		114
Acetic Acid		Soluble		114
Nitrobenzene		Soluble		114

NAVORD REPORT 7147 (VOLUME 1)

TABLE A5-13. SOLUBILITY OF $NaClO_4$ IN NONAQUEOUS SOLVENTS

Solvent	Temp., °C	gm $NaClO_4$ per 100 g Solvent	Reference
Acetone	25	51.75	261
	25	51.72	231
n-Butyl Alcohol	25	1.86	261
	116	8.20	310
	25	1.84	231
Ethyl Acetate	25	9.65	261
	25	9.66	231
Ethyl Alcohol	25	14.71	261
	25	14.59	231
Isobutyl Alcohol	25	0.77	261
	25	0.83	231
Methyl Alcohol	25	51.35	261
	25	51.13	231
n-Propyl Alcohol	25	4.88	261
	25	4.80	231
Ethylenediamine	25	30.1	123
Monoethanolamine	25	90.8	123
Ethylene Glycol	25	75.5	123

2. DENSITY OF SATURATED NONAQUEOUS SOLUTIONS

2. Density of Saturated Nonaqueous Solutions

Absolute Density, d^t = gm/cc

Relative Density, d_4^t = gm/ml

Density, d = unknown whether or not value is absolute or relative quantity.

TABLE A5-14. DENSITY OF SATURATED SOLUTIONS OF NH_4ClO_4 IN NONAQUEOUS SOLVENTS(261)

Temperature = 25°C

Solvent	Wt % Na_4ClO_4	d_4^t
Ethyl Acetate	0.032	0.8947
Acetone	2.21	0.7997
Isobutyl Alcohol	0.127	0.7988
n-Butyl Alcohol	0.017	0.8069
n-Propyl Alcohol	0.385	0.8016
Ethyl Alcohol	1.872	0.79505
Methyl Alcohol	6.41	0.8218

TABLE A5-15. DENSITY OF SATURATED SOLUTIONS OF $Ba(ClO_4)_2$ IN NONAQUEOUS SOLVENTS[261]

Temperature = 25°C

Solvent	Wt % $Ba(ClO_4)_2$	d_4^t
Ethyl Acetate	53.04	1.5236
Acetone	55.49	1.4607
Isobutyl Alcohol	35.99	1.1171
n-Butyl Alcohol	36.78	1.1342
n-Propyl Alcohol	43.07	1.2145
Ethyl Alcohol	55.48	1.4157
Methyl Alcohol	68.46	1.7507

TABLE A5-16. DENSITY OF SATURATED SOLUTIONS OF $Ca(ClO_4)_2$ IN NONAQUEOUS SOLVENTS[261]

Temperature = 25°C

Solvent	Wt % $Ca(ClO_4)_2$	d_4^t
Ethyl Ether	0.26	0.7098
Ethyl Acetate	43.06	1.3325
Acetone	38.18	1.1475
Isobutyl Alcohol	36.29	1.0903
n-Butyl Alcohol	53.17	1.2868
n-Propyl Alcohol	59.17	1.3806
Ethyl Alcohol	62.44	1.4342
Methyl Alcohol	70.36	1.6155

TABLE A5-17. DENSITY OF SATURATED SOLUTIONS OF $LiClO_4$ IN NONAQUEOUS SOLVENTS[261]

Temperature = 25°C

Solvent	Wt % $LiClO_4$	d
Ethyl Ether	53.21	1.2116
Ethyl Acetate	48.75	1.3005
Acetone	57.72	1.3233
Isobutyl Alcohol	36.73	1.0602
n-Butyl Alcohol	44.23	1.1326
n-Propyl Alcohol	51.22	1.2006
Ethyl Alcohol	60.28	1.3173
Methyl Alcohol	64.57	1.3849

TABLE A5-18. DENSITY OF SATURATED SOLUTIONS OF $LiClO_4$ $3H_2O$ IN NONAQUEOUS SOLVENTS[261]

Temperature = 25°C

Solvent	Wt % $LiClO_4 \cdot 3H_2O$	d
Ethyl Ether	0.196	0.7091
Ethyl Acetate	26.35	1.0402
Acetone	49.04	1.0965
Isobutyl Alcohol	18.85	0.8887
n-Butyl Alcohol	21.40	0.9082
n-Propyl Alcohol	26.82	0.9349
Ethyl Alcohol	42.16	1.0241
Methyl Alcohol	60.95	1.1420

TABLE A5-19. DENSITY OF SATURATED SOLUTIONS OF $Mg(ClO_4)_2$ IN NONAQUEOUS SOLVENTS[261]

Temperature = 25°C

Solvent	Wt % $Mg(ClO_4)_2$	d
Ethyl Ether	0.29	0.7101
Ethyl Acetate	41.49	1.3057
Isobutyl Alcohol	31.27	1.0609
n-Butyl Alcohol	39.16	1.1399
n-Propyl Alcohol	42.33	1.1926
Ethyl Alcohol	19.33	0.9518
Methyl Alcohol	34.14	1.1057
Acetone	30.015	1.0798

TABLE A5-20. DENSITY OF SATURATED SOLUTIONS OF $KClO_4$ IN NONAQUEOUS SOLVENTS[261]

Temperature = 25°C

Solvent	Wt % $KClO_4$	d_4^t
Ethyl Acetate	0.0015	0.8945
Acetone	0.155	0.7868
Isobutyl Alcohol	0.005	0.7981
n-Butyl Alcohol	0.0045	0.8060
n-Propyl Alcohol	0.010	0.8011
Methyl Alcohol	0.105	0.7878
Ethyl Alcohol	0.012	0.7852

TABLE A5-21. DENSITY OF SATURATED SOLUTIONS OF $AgClO_4$ IN NONAQUEOUS SOLVENTS[261]

Solvent	Temp, °C	Wt % $AgClO_4$	d	Solid Phase	Reference
Toluene	-75.3	0.0	0.854	$AgClO_4 \cdot C_7H_8$	261
	-24.1	6.01	0.920	$AgClO_4 \cdot C_7H_8$	261
	0.0	26.41	1.129	$AgClO_4 \cdot C_7H_8$	261
	16.	42.0	1.375	$AgClO_4 \cdot C_7H_8$	261
	16.5	42.89	1.388	$AgClO_4 \cdot C_7H_8$	261
	18.	44.11	1.417	$AgClO_4 \cdot C_7H_8$	261
	22.6 tr. pt.	-	-	$AgClO_4 \cdot C_7H_8 + AgClO_4$	261
	25.	50.30	1.523	$AgClO_4$	261
	50.	52.68	1.576	$AgClO_4$	261
	75.	54.60	1.665	$AgClO_4$	261
Pyridine	-11.5	12.23	1.118	$AgClO_4 \cdot 4C_5H_5N$	261
	- 1.3	14.53	1.139	$AgClO_4 \cdot 4C_5H_5N$	261
	+25.0	20.90	1.201	$AgClO_4 \cdot 4C_5H_5N$	261
	36.1	24.52	1.221	$AgClO_4 \cdot 4C_5H_5N$	261
	49.2	29.4	1.278	$AgClO_4 \cdot 4C_5H_5N$	261
Benzene	5.12	3.44	0.909	$C_6H_6 + AgClO_4 \cdot C_6H_6$	261
	25.0	5.00	0.906	$AgClO_4 \cdot C_6H_6$	261
	50.0	10.07	0.896	$AgClO_4 \cdot C_6H_6$	261
	80.3	32.2	1.164	$AgClO_4 \cdot C_6H_6$	261
Aniline	- 6.6	0.74	1.030	$C_6H_5NH_2 + AgClO_4 \cdot 6C_6H_5NH_2$	261
	+25.0	5.0	1.063	$AgClO_4 \cdot 6C_6H_5NH_2$	261
	55.0	30.9	1.281	$AgClO_4 \cdot 6C_6H_5NH_2$	261
	58.1	35.0	1.101	$AgClO_4 \cdot 3C_6H_5NH_2$	261

TABLE A5-22. DENSITY OF SATURATED SOLUTIONS OF $NaClO_4$ IN NONAQUEOUS SOLUTIONS[261]

Temperature = 25°C

Solvent	Wt % $NaClO_4$	d_4^t
Ethyl Acetate	8.80	0.9574
Acetone	34.10	1.0732
Isobutyl Alcohol	0.78	0.8031
n-Butyl Alcohol	1.83	0.8167
n-Propyl Alcohol	4.66	0.8308
Ethyl Alcohol	12.82	0.8685
Methyl Alcohol	33.93	1.0561

3. DENSITY OF UNSATURATED NONAQUEOUS SOLUTIONS

3 Density of Unsaturated Nonaqueous Solutions

Absolute density, d^t = gm/cc

Relative density, d_4^t = gm/ml

Density, d = unknown whether or not value is absolute or relative quantity

TABLE A5-23. DENSITY OF SOLUTIONS OF $LiClO_4$ IN NONAQUEOUS SOLVENTS

a. Reference 77

Acetone	
Temperature = 17° C ± 0.1°	
Wt. % $LiClO_4$	Density, g/cm^3
0.186	0.8140
.428	.8364
.754	.8742
1.307	.9518
1.905	1.0314
2.142	1.0836
2.921	1.2196

b. Reference 71

Ether	
Temperature = 23.5° C	
Wt. % $LiClO_4$	Density
8.50	0.76595
12.06	.79265
17.09	.83301
20.84	.86661
30.756	.95999
36.942	1.02559
41.025	1.07330
53.018	1.20807

TABLE A5-24. DENSITY OF SOLUTIONS OF $AgClO_4$ IN NONAQUEOUS SOLVENTS

a. Reference 156

	Aniline			
	Density, g/cm^3			
Wt. % $AgClO_4$	25° C	55° C	65° C	75° C
0.00	1.0189	0.9943	0.9858	0.9774
0.68	1.0254	0.9999	0.9973	0.9831
2.20	1.0374	1.0112	0.9987	0.9941
3.87	1.0406	1.0295	1.0158	-
5.00	-	1.0372	1.0290	1.0210
7.51	-	1.0603	1.0507	-
9.93	-	1.0839	1.0757	1.0676
12.99	-	1.1079	1.1002	1.0914
16.55	-	1.1524	1.1443	1.1361
19.47	-	-	1.1765	1.1657
23.15	-	-	1.2195	
25.67	-	-	1.2533	1.2424
27.15	-	-	1.2686	1.2619
28.23	-	1.2947	1.2868	1.2801

TABLE A5-24. DENSITY OF SOLUTIONS OF $AgClO_4$ IN NONAQUEOUS SOLVENTS (Cont'd)

Toluene

Wt. % $AgClO_4$	Density, gm/cm^3	
	25° C	50° C
1.57	0.8173	0.8489
4.96	0.9067	0.8838

Nitrobenzene

Wt. % $AgClO_4$	Density, gm/cm^3		
	25° C	50° C	75° C
0.059	1.2002	1.1770	1.1036

b. Reference 321

Benzene

Wt. % $AgClO_4$	Temp., °C	Density, gm/ml
0.34	25	0.8770
0.73	25	0.8790
1.42	25	0.8832
2.06	25	0.8901[119]
2.36	25	0.8940

TABLE A5-24. DENSITY OF SOLUTIONS OF $AgClO_4$ IN NONAQUEOUS SOLVENTS (Cont'd)

c. Reference 154

Acetone

Wt. % $AgClO_4$	Density, gm/cm^3		
	0° C	25° C	50° C
0.00	0.8168	0.7892	0.7618
.63	.8193	.7925	.7642
1.38	.8252	.7992	.7675
10.51	.9042	.8725	.8415
11.47	.9144	.8825	.8515
22.24	1.0269	.9992	.9672
27.67	1.0880	1.0640	1.0375
30.54	1.1240	1.1015	1.0775
37.30	1.2329	1.2059	1.1786
38.41	1.2465	1.2213	1.1970
41.12	1.3002	1.2685	1.2465
41.24	1.3035	1.2690	1.2475
42.53	1.3230	1.2872	1.2745
43.45	1.3475	1.3094	1.2965
45.15	1.3874	1.3566	1.3251
52.10	1.5403	1.5110	1.4799
56.75	1.6592	1.6279	1.5975
64.10	------	1.8194	1.7877

TABLE A5-24. DENSITY OF SOLUTIONS OF $AgClO_4$ IN NONAQUEOUS SOLVENTS (Cont'd)

d. Reference 155

Pyridine

Wt. % $AgClO_4$	Density, gm/cm^3		
	0° C	25° C	50° C
0.00	1.0034	0.9794	0.9545
.72	1.0098	.9861	.9614
1.04	1.0130	1.0014	.9638
3.15	1.0323	1.0084	.9843
4.85	1.0469	1.0236	.9992
7.16	1.0571	1.0456	1.0232
8.34	1.0811	1.0584	1.0343
10.92	1.1068	1.0836	1.0602
15.07	1.1525	1.1283	1.1059
19.48	------	1.1791	1.1560

4. VISCOSITY

4. Viscosity

η_t = viscosity in centipoises at temperature indicated

M = concentration in moles per liter of solution

TABLE A5-25. VISCOSITY OF SOLUTIONS OF $LiClO_4$ IN ETHER[71]

Conc. $LiClO_4$, M	η_{20}	Conc. $LiClO_4$, M	η_{25}
0.12	0.230	0.25	0.220
.15	.234	.56	.257
.25	.242	1.09	.345
.35	.272	2.09	.815
.66	.288	2.74	1.33
.76	.330	2.95	2.16
1.09	.394	3.20	2.51
1.42	.475	3.34	3.25
1.98	.70	3.49	4.44
2.43	1.13	3.56	4.87
2.74	1.49	4.18	11.7
2.91	1.95	4.46	18.2
3.34	3.54	4.92	50.1
3.49	4.74	5.07	63.5
3.75	7.02	5.65	180.
4.12	16.3		
4.53	24.8		
5.20	91.		
5.65	236.		

where

η_t = viscosity in centipoises at temperature indicated

TABLE A5-26. VISCOSITY OF SOLUTIONS OF $AgClO_4$ IN NONAQUEOUS SOLVENTS

a. Reference 156

Wt % $AgClO_4$	Aniline Viscosity x 10^2 centipoises			
	25°C	55°C	65°C	75°C
0.00	3.705	1.718	1.407	1.167
0.68	3.891	1.743	1.425	1.175
2.20	4.186	1.851	1.472	1.211
3.87	-	1.945	1.561	-
5.00	-	2.074	1.623	1.301
7.51	-	2.428	1.909	-
9.93	-	2.965	2.269	1.797
12.99	-	3.513	2.660	2.052
16.55	-	4.586	3.435	2.602
19.47	-	-	4.401	3.294
21.69	-	7.782	5.664	4.284
23.15	-	-	6.393	4.720
25.67	-	-	-	6.387
27.15	-	-	9.931	7.202
28.23	-	-	-	8.117

Wt % $AgClO_4$	Nitrobenzene Viscosity x 10^2 centipoises			
	0°C	25°C	50°C	75°C
0.059	-	1.8277	1.2611	0.9200

Wt % $AgClO_4$	Toluene Viscosity x 10^2 centipoises		
	0°C	25°C	50°C
1.57	-	0.568	0.419
4.96	-	0.625	0.470

TABLE A5-26. VISCOSITY OF SOLUTIONS OF $AgClO_4$ IN NONAQUEOUS SOLVENTS (Cont'd)

b. Reference 155

Wt % $AgClO_4$	Pyridine Viscosity x 10^2 centipoises 0°C	25°C	50°C
0.00	1.345	0.892	0.636
.72	1.390	.922	.656
1.04	1.408	.934	.663
3.15	1.590	1.037	.726
4.85	1.777	1.145	.793
7.16	2.038	1.271	.886
8.34	2.229	1.341	.944
10.92	2.644	1.554	1.064
15.07	3.498	2.042	1.332
19.48		2.689	1.675

c. Reference 154

Wt % $AgClO_4$	Acetone Viscosity x 10^2 centipoises 0°C	25°C	50°C
0.00	0.416	0.322	0.251
0.63	0.427	0.328	0.254
1.38	0.436	0.337	.266
10.51	.550	.417	.328
11.47	.620	.459	.353
22.24	.964	.674	.512
27.67	1.259	.895	.613

TABLE A5-26. VISCOSITY OF SOLUTIONS OF $LiClO_4$ IN NONAQUEOUS SOLVENTS (Cont'd)

c. Reference 154 (Cont'd)

	Acetone		
	Viscosity x 10^2 centipoises		
Wt % $AgClO_4$	0°C	25°C	50°C
30.54	1.472	1.025	.731
37.30	2.456	1.500	1.048
38.41	2.623	1.622	1.121
41.12	3.330	1.917	1.271
41.24	3.390	1.975	1.318
42.53	3.706	2.197	1.420
43.45	4.057	2.297	1.495
45.15	4.994	2.691	1.704
52.10	12.118	5.360	3.026
56.75	26.242	8.986	4.568
64.10		21.903	9.342

5. CONDUCTANCE IN NONAQUEOUS SOLUTIONS

5. Conductance in Nonaqueous Solutions

Wt % = weight percent salt

M = moles solute per liter of solution

m = moles solute per 1000 gm solvent

C = gram-equivalents salt per liter solution

c = milliequivalent weight of the salt per liter of solution

K = specific conductance, $ohm^{-1}\ cm^{-1}$

Λ = equivalent conductance, $ohm^{-1}\ cm^{-2}$ (per equiv.)

Λ_o = equivalent conductance at infinite dilution, $ohm^{-1}\ cm^{-2}$

λ = ion conductance of anion at infinite dilution

μ = molar conductance, $ohm^{-1}\ cm^{-2}$ (per mole)

TABLE A5-27. LIMITING PERCHLORATE IONIC CONDUCTANCE IN NONAQUEOUS SOLVENTS (260)

Temperature = 25°C

λ_-	Solvent
24.6	Dimethyl Sulfoxide

TABLE A5-28. CONDUCTANCE OF THE PERCHLORATE ION IN NONAQUEOUS SOLVENT

Temperature = 25°C

λ_-	Solvent	Reference
115.3	Acetone	1
42.8	N, N dimethylacetamide	174
47.6	Pyridine	180

TABLE A5-29. SPECIFIC AND MOLAR CONDUCTIVITY OF $Al(ClO_4)_3$ IN NONAQUEOUS SOLVENTS

a. Reference 103

Temperature = 25°C

Nitrobenzene

m	K x 10^3	μ
0.0145	0.10	6.98
.0340	.22	6.47
.0487	.30	6.16
.0682	.40	5.87
.0876	.50	5.71
.105	.60	5.70
.180	1.0	5.56

Acetonitrile

m	K x 10^3	μ
0.0095	1.2	126.
.0236	2.0	84.7
.0568	4.0	70.4
.114	6.0	52.6

2-Ethoxyethanol

m	K x 10^3	μ
0.0129	1.0	77.5
.0309	2.0	64.7
.0517	3.0	58.0
.0567	3.2	56.4
.124	5.3	46.1

TABLE A5-29. SPECIFIC AND MOLAR CONDUCTIVITY OF $Al(ClO_4)_3$ IN NONAQUEOUS SOLVENTS (Cont'd)

b. Reference 125

Temperature = 20°C

Lithium Ethoxide

Moles of $LiOC_2H_5$ per 1 mol $Al(ClO_4)_3$*	$K \cdot 10^{-10}$
1	180
2	270
3	560
4	570
5	570

* Data taken from graph

TABLE A5-30. EQUIVALENT CONDUCTANCE OF NH_4ClO_4 IN NITROMETHANE[211]

Temperature = 25°C

Λ_o = 128.3

$c \times 10^4$	Λ
1.065	125.3
2.025	123.7
3.415	121.8
5.435	119.5
7.719	117.0
10.54	114.6

TABLE A5-31. EQUIVALENT CONDUCTANCE OF $Ba(ClO_4)_2$ IN ACETONE[307]

Temperature = 25°C

$M \times 10^5$	Λ
0.7880	196.1
1.504	194.4
2.158	193.9
7.831	187.3
10.75	185.1
14.11	182.4
14.95	181.1
20.53	178.4
21.46	177.9
26.56	176.1
27.43	175.1
29.46	173.9
32.92	172.2
37.64	170.2
41.32	168.7
45.17	167.3
56.69	163.3
66.09	160.5
90.74	154.4

TABLE A5-32. EQUIVALENT CONDUCTANCE OF $Ba(ClO_4)_2$ IN 2-ETHOXYETHANOL[43]

Temperature = 25°C[a]

C	Λ^b
.0025	8.2
.01	5.5
.0225	4.4
.04	4.2
.0625	3.7

a Temperature was not found in article, assumed to be 25°C
b Data taken from graph

TABLE A5-33. EQUIVALENT CONDUCTANCE OF $Ba(ClO_4)_2$ IN FURFURAL[43]

Temperature = 25°C[a]

C	Λ^b
.0025	48
.01	39
.0225	31
.04	27
.0625	23

a Temperature was not found in article, assumed to be 25°C
b Data taken from graph

TABLE A5-34. EQUIVALENT CONDUCTANCE OF $Ba(ClO_4)_2$ IN GLYCOL[43]

Temperature = 25°C[a]

C	Λ[b]
.0025	1.8
.01	3.6
.0225	5.1
.04	5.5
.0625	5.6
.09	5.5

a Temperature was not found in article, assumed to be 25°C
b Data taken from graph

TABLE A5-35. EQUIVALENT CONDUCTANCE OF $Ba(ClO_4)_2$ IN N-METHYLACETAMIDE[63]

Temperature = 40°C

Salt	Λ_o
$Ba(ClO_4)_2$	27.05
$Ba(ClO_4)_2 \cdot 3H_2O$	27.05

TABLE A5-36. EQUIVALENT CONDUCTANCE OF $Ca(ClO_4)_2$ IN N-METHYLACETAMIDE[63]

Temperature = 40°C

Salt	Λ_o
$Ca(ClO_4)_2 \cdot 4H_2O$	27.00

TABLE A5-37. EQUIVALENT CONDUCTANCE OF $Ca(ClO_4)_2$ IN ACETONE[296]

Temperature = 25°C

Λ_o = 198.9

C	Λ
0.0004798	137.0
0.0006296	129.4
0.0009158	123.9
0.001993	111.5
0.002492	105.5
0.003322	99.31
0.004984	91.52
0.04068	41.25
0.1221	31.78
0.1831	28.69
0.3662	24.37
0.7324	20.33

TABLE A5-38. SPECIFIC AND EQUIVALENT CONDUCTANCE OF $LiClO_4$ IN TOLUENE[156]

Temperature = 50°C

Wt %	K	Λ
4.96	7.4×10^{-8}	3.5×10^{-4}

TABLE A5-39. SPECIFIC AND EQUIVALENT CONDUCTANCE OF $LiClO_4$ IN ETHER[71]

Temperature = 23.5°C

C	K	Λ
0.060	2.33×10^{-8}	3.88×10^{-4}
0.084	3.67×10^{-8}	4.37×10^{-4}
0.132	6.35×10^{-8}	4.81×10^{-4}
0.165	8.74×10^{-8}	5.30×10^{-4}
0.27	2.05×10^{-7}	7.59×10^{-4}
0.34	3.27×10^{-7}	9.62×10^{-4}
0.49	8.93×10^{-7}	1.82×10^{-3}
0.58	1.55×10^{-6}	2.67×10^{-3}
0.71	2.62×10^{-6}	3.69×10^{-3}
0.86	6.16×10^{-6}	7.16×10^{-3}
1.02	1.08×10^{-5}	1.06×10^{-2}
1.19	1.87×10^{-5}	1.57×10^{-2}
1.33	3.10×10^{-5}	2.33×10^{-2}
1.55	4.99×10^{-5}	3.22×10^{-2}
1.72	7.59×10^{-5}	4.41×10^{-2}
1.94	1.13×10^{-4}	5.83×10^{-2}
2.35	2.10×10^{-4}	8.94×10^{-2}
2.64	2.56×10^{-4}	9.70×10^{-2}
2.96	3.23×10^{-4}	1.09×10^{-1}
3.34	3.75×10^{-4}	1.12×10^{-1}
3.50	3.96×10^{-4}	1.13×10^{-1}
3.84	4.11×10^{-4}	1.07×10^{-1}
	Temperature = 25°C	
0.6120	9.86×10^{-7}	1.611×10^{-3}
0.8983	4.659×10^{-6}	5.186×10^{-3}
1.3381	2.144×10^{-5}	1.602×10^{-2}

TABLE A5-3° SPECIFIC AND EQUIVALENT CONDUCTANCE OF $LiClO_4$ IN ETHER (Cont'd)

Temperature = 25°C

C	K	Λ
1.7101	5.913×10^{-5}	3.458×10^{-2}
2.7750	2.552×10^{-4}	9.196×10^{-2}
3.5606	3.969×10^{-4}	1.115×10^{-1}
4.1383	4.339×10^{-4}	1.049×10^{-1}
6.0109	3.111×10^{-4}	5.169×10^{-2}

TABLE A5-40. EQUIVALENT CONDUCTANCE OF $LiClO_4$ IN NITROMETHANE[211]

Temperature = 25°C

$C \times 10^4$	Λ
1.153	118.0
1.253	117.8
2.240	113.1
2.443	112.3
3.741	108.1
4.737	104.9
6.031	102.2
8.223	97.6
8.639	95.9
13.03	89.9
14.341	86.7
20.89	79.1
26.77	74.0

TABLE A5-41. EQUIVALENT CONDUCTANCE OF $LiClO_4$ IN ACETONE[1]

Temperature = 25.00°C

Λ_o = 187.3

$C \times 10^4$	Λ
2.9980	168.7
6.5019	156.9
8.4100	151.4
9.7393	148.9
16.9412	139.5

TABLE A5-42. EQUIVALENT CONDUCTANCE OF $LiClO_4$ IN ACETIC ACID[244]

Temperature = 20°C

M	Λ
0.05	0.81

TABLE A5-43. EQUIVALENT CONDUCTANCE OF $LiClO_4$ IN CYCLOHEXANOL

a. Reference 81

Temperature = 25°C

Λ_o = 1.42

C x 10^4	Λ
0.1381	1.251
.2647	1.284
.3540	1.276
.7944	1.192
1.328	1.146
2.593	1.013
3.395	.997
7.737	.785
10.45	.775
35.25	.291

b. Reference 158

Temperature = 25°C

Λ_o = 1.29

C x 10^4	K x 10^9	Λ
0.1146	14.67	1.280
.2571	31.68	1.232
1.567	168.04	1.072
5.105	427.05	0.837

TABLE A5-44. EQUIVALENT CONDUCTANCE OF $LiClO_4$ IN ETHYL ALCOHOL[55]

Temperature = 25°C

$\Lambda_o = 48.50$

$C \times 10^4$	Λ
2.0027	46.29
2.0202	46.07
3.6493	45.48
3.806	45.34
5.826	44.61
6.614	44.31
10.001	43.32
10.075	43.34
13.296	42.58
13.655	42.49
18.695	41.56
18.809	41.55

TABLE A5-45. EQUIVALENT CONDUCTANCE OF $LiClO_4$ IN METHYL ALCOHOL[54]

Temperature = 25°C

Λ_o = 110.50

$C \times 10^4$	Λ
1.2863	107.55
2.1939	106.67
3.3276	105.76
4.9352	104.71
7.8521	103.22
1.1676	107.80
2.1926	106.73
3.7707	105.52
5.6449	104.36
9.7881	102.40

TABLE A5-46. EQUIVALENT CONDUCTANCE OF $Mg(ClO_4)_2$ IN ISOPROPYL ALCOHOL[297]

Temperature = 25°C

Λ_o = 13.50

C	Λ
0.0002910	10.258
0.0008490	7.988
0.002359	4.905
0.005520	3.574
0.01447	2.122
0.02512	1.976
0.06496	1.176
0.1559	0.7261
0.3877	0.5174
0.5272	0.5076
1.2041	0.4593

TABLE A5-47. EQUIVALENT CONDUCTANCE OF $Mg(ClO_4)_2$ IN ACETONE[296]

Temperature = 25°C

Λ_o = 185.5

C	Λ
0.0004520	135.6
0.0004958	133.0
0.0005498	130.3
0.0006168	127.2
0.0007024	123.9
0.0008156	120.2
0.0009728	116.4
0.001205	110.8
0.001581	105.0
0.002088	97.90
0.002278	95.85
0.002500	94.05
0.002778	91.65
0.003124	89.50
0.003572	87.05
0.004164	84.26
0.004222	83.44
0.004998	81.15
0.006248	77.32
0.008332	72.68
0.01250	66.12
0.02542	52.24
0.05798	35.94

TABLE A5-47. EQUIVALENT CONDUCTANCE OF $Mg(ClO_4)_2$ IN ACETONE[296] (Cont'd)

C	Λ
0.1407	26.30
0.3732	22.52
0.6538	17.93
1.553	12.57

TABLE A5-48. EQUIVALENT CONDUCTANCE OF $Mg(ClO_4)_2$ IN METHYL ALCOHOL[296]

Temperature = 25°C

Λ_o = 83.2

C	Λ
0.0001145	81.03
0.002186	74.34
0.004002	71.39
0.007926	61.88
0.01189	59.43
0.01439	56.49
0.02378	54.63
0.04762	47.29
0.2196	36.18
0.5854	29.26

TABLE A5-49. EQUIVALENT CONDUCTANCE OF $Mg(ClO_4)_2$ IN NITROMETHANE[296]

Temperature = 25°C

Λ_0 = 115.7

C	Λ
0.0005858	94.30
0.0006982	93.33
0.0008644	91.03
0.001134	86.57
0.001649	80.09
0.003590	53.70
0.004488	49.96
0.005981	44.93
0.008976	37.71
0.01795	22.27
0.05702	14.38
0.08556	12.20
0.1222	9.671
0.1711	7.347
0.2140	6.916
0.2852	4.941
0.3914	3.728
0.8556	2.299

TABLE A5-50. EQUIVALENT CONDUCTANCE OF $Mg(ClO_4)_2$ IN n-PROPYL ALCOHOL[297]

Temperature = 25°C

Λ_o = 25.75

C	Λ
0.0001814	20.105
0.0004950	16.562
0.001727	10.753
0.003748	7.723
0.005804	6.239
0.009888	5.971
0.01240	5.292
0.01510	4.616
0.02562	4.419
0.03245	3.994
0.04318	3.748
0.05117	3.357
0.05200	3.310
0.08833	3.044
0.1195	2.859
0.1351	2.762
0.1766	2.566
0.2408	2.322
0.2696	2.295
0.4952	1.923
0.5372	1.914
0.8567	1.794
1.0703	1.684
1.139	1.659

TABLE A5-51. EQUIVALENT CONDUCTANCE OF $KClO_4$ IN DIMETHYLFORMAMIDE[3]

Temperature = 25°C

Λ_o = 82.7

$C \times 10^4$	Λ
0.374	81.9
1.112	81.4
2.757	80.6
6.745	79.2
12.49	78.0
22.85	76.2
35.15	74.8

TABLE A5-52. EQUIVALENT CONDUCTANCE OF $KClO_4$ IN N, N-DIMETHYLACETAMIDE[174]

Temperature = 25°C

Λ_o = 68.11

$C \times 10^4$	Λ
0.9743	66.86
3.617	65.74
10.38	64.12
23.26	62.42
37.96	61.07
55.44	59.82

TABLE A5-53. EQUIVALENT CONDUCTANCE OF $KClO_4$ IN ACETONE[1]

Temperature = 25°C

Λ_o = 188.7

$C \times 10^4$	Λ
1.1432	177.2
1.6645	173.1
2.3255	168.8
3.1430	164.5

TABLE A5-54. EQUIVALENT CONDUCTANCE OF $KClO_4$ IN DIMETHYL SULFOXIDE[260]

Temperature = 25°C

Λ_o = 39.1

$C \times 10^4$	Λ
1.867	38.44
3.641	38.15
9.470	37.58
19.13	36.96
27.39	36.52
37.66	36.13

TABLE A5-55. SPECIFIC CONDUCTANCE OF $AgClO_4$ IN NITROBENZENE[156]

0.059 Wt % $AgClO_4$

t, °C	K
25	8.72×10^{-5}
50	11.7×10^{-5}
75	14.2×10^{-5}

TABLE A5-56. SPECIFIC AND EQUIVALENT CONDUCTANCE OF $AgClO_4$ IN PYRIDINE[155]

Wt %	K x 10^3 0°C	K x 10^3 25°C	K x 10^3 50°C	Λ 25°C
0.72	0.990	1.329	1.639	38.8
1.04	1.399	1.895	2.320	37.7
3.15	3.792	5.250	6.602	
4.85	5.500	7.688	9.775	
7.16	7.506	10.72	13.91	
8.34	8.333	12.05	15.74	
10.92	9.645	14.29	18.99	
15.07	10.92	16.90	23.47	
19.48		17.36	25.14	
20.20		17.36	25.16	
23.56			24.75	
27.50			22.98	

TABLE A5-57. SPECIFIC AND EQUIVALENT CONDUCTANCE OF $AgClO_4$ IN ACETONE(154)

Wt %	K x 10^2 0°C	K x 10^2 25°C	K x 10^2 50°C	Λ 25°C
0.63	0.194	0.219	0.233	90.95
1.38	.418	.481	.509	90.42
10.51	1.787	1.969	2.071	
11.47	1.929	2.127	2.233	
22.24	2.912	3.471	3.785	
27.67	3.188	3.895	4.396	
30.54	3.260	4.098	4.721	
34.34	3.275	4.275	5.038	
37.30	3.228	4.337	5.276	
38.41	3.169	4.343	5.366	
41.12	3.025	4.282	5.405	
41.24	2.989	4.255	5.412	
42.53	2.910	4.163	5.379	
43.45	2.819	4.115	5.339	
45.15	2.643	3.985	5.214	
52.10	1.839	3.275	4.525	
56.75	1.106	2.684	3.959	
64.10	-----	1.557	3.021	

TABLE A5-58. SPECIFIC AND EQUIVALENT CONDUCTANCE OF $AgClO_4$ IN ANILINE(156)

	K x 10^3				Λ
Wt %	25°C	55°C	65°C	75°C	25°C
0.68	0.0198	0.0339	0.0387	0.0420	0.59
2.20	.114	.236	.270	.301	1.02
3.87	.224	.668	.747		1.155
4.44	.249				
5.00		1.107	1.280	1.453	
7.51		2.446	2.512		
9.93		3.025	3.782	4.393	
12.99		4.220	5.256	6.212	
16.55		5.264	6.379	7.711	
18.22		5.355	6.722	8.173	
19.47			7.093	8.747	
19.51		5.564	7.201	8.838	
23.15			7.054	8.869	
25.67			6.781	8.688	
27.15		5.081	6.616	8.423	
28.23		4.545	6.195	8.147	
30 03		3.934	5.633	7.673	
33.33		3.280	4.699	6.613	
35.15		2.504	4.089	5.842	
37.07			3.702	5.365	

TABLE A5-59. EQUIVALENT CONDUCTANCE OF $AgClO_4$ IN PYRIDINE(180)

Temperature = 25°C

Λ_o = 81.9

C x 10^4	Λ
0.2157	78.92
.4406	77.41
.9235	75.09
1.762	72.29
4.008	67.58

TABLE A5-60. EQUIVALENT CONDUCTANCE OF $AgClO_4$ IN NITROBENZENE[212]

Temperature = 25°C

Λ_o = 38.4 (approx.)

$C \times 10^4$	Λ
0.596	37.58
.851	37.19
.986	37.04
1.184	36.19
1.292	36.75
1.627	36.34
2.390	35.38
3.016	34.90
3.108	34.70
3.152	34.58
5.593	32.71
7.109	31.62
7.683	31.32
9.777	30.12
10.27	29.91

TABLE A5-61. EQUIVALENT CONDUCTANCE OF $AgClO_4$ IN METHYL ALCOHOL(54)

Temperature = 25°C

$\Lambda_0 = 121.5$

$C \times 10^4$	Λ
1.3204	117.73
1.3590	117.46
1.3968	117.85
1.5627	117.03
2.3941	116.89
2.5405	116.55
2.7317	116.35
2.7815	116.58
3.6300	115.94
4.2188	115.42
4.2863	115.36
5.0585	115.03
5.1613	114.82
6.1936	114.28
6.7881	113.79
7.3469	113.73
9.0148	112.82
9.5848	112.62
9.5985	112.63
13.8284	110.84
13.8941	110.85
14.1630	110.84

TABLE A5-62. EQUIVALENT CONDUCTANCE OF $AgClO_4$ IN NITROMETHANE[211]

Temperature = 25°C

Λ_o = 116.5

$C \times 10^4$	Λ
1.336	114.5
1.463	114.4
2.573	113.0
2.652	113.7
2.997	113.3
4.756	112.4
4.993	111.6
6.055	112.3
7.452	110.4
7.660	110.7
10.51	110.1
10.90	108.8
10.90	109.2
14.82	108.2
15.40	107.2
16.19	106.6
19.96	106.1

TABLE A5-63. EQUIVALENT CONDUCTANCE OF $AgClO_4$ IN ACETONE[101]

Temperature = 25°C

Λ_o = 181.5

$C \times 10^4$	Λ*
0.25	175
0.56	172
1.00	169
1.56	166
2.25	163
3.06	159

* Data taken from graph

TABLE A5-64. EQUIVALENT CONDUCTANCE OF $AgClO_4$ IN ETHYL ALCOHOL(55)

Temperature = 25°C

$\Lambda_o = 51.2$

$C \times 10^4$	Λ
1.791	49.22
1.894	48.78
1.952	48.45
3.705	47.63
3.755	47.67
3.993	47.51
5.492	46.90
6.981	46.35
7.492	46.02
8.446	45.78
10.149	45.20
11.352	45.02
12.550	44.57
14.042	44.17
15.760	43.96
18.823	43.20
21.191	42.91

TABLE A5-65. EQUIVALENT CONDUCTANCE OF $AgClO_4$ IN BENZENE (181)

Temperature = 25°C

Λ_o = 150

$C \times 10^4$	$\Lambda \times 10^6$
0.230	2.20
0.953	1.47
2.10	1.12
4.04	0.87
7.53	.71
12.6	.63
15.3	.64
23.0	.63
33.0	.66
$C \times 10^2$	
0.473	0.72
0.703	.83
1.030	.99
1.33	1.17
1.62	1.35
3.49	2.41
5.77	4.93
9.05	11.70
14.10	36.3

TABLE A5-66. EQUIVALENT CONDUCTANCE OF $AgClO_4$ IN 2-ETHOXYETHANOL[43]

Temperature = 25°C[a]

C	Λ[b]
.0025	20
.01	16
.0225	13
.04	11
.0625	11

a Temperature was not found in article, assumed to be 25°C
b Data taken from graph

TABLE A5-67. EQUIVALENT CONDUCTANCE OF $AgClO_4$ IN PYRIDINE[43]

Temperature = 25°C[a]

C	Λ[b]
.0025	52
.01	44
.0225	38
.04	36
.0625	34

a Temperature was not found in article, assumed to be 25°C
b Data taken from graph

TABLE A5-68. EQUIVALENT CONDUCTANCE OF $AgClO_4$ IN FURFURAL[43]

Temperature = 25°C[a]

C	Λ[b]
0.0025	45
.01	42
.0225	39
.04	35
.0625	32

a Temperature was not found in article, assumed to be 25°C
b Data taken from graph

TABLE A5-69. EQUIVALENT CONDUCTANCE OF $AgClO_4$ IN CYCLOHEXANONE[100]

Temperature (not given in article)

Λ_o = 27.5

C x 10^4	Λ*
.25	26.75
1.0	25.5
1.25	24.14
2.25	23.29

* Data taken from graph

TABLE A5-70. EQUIVALENT CONDUCTANCE OF $AgClO_4$ IN ISOBUTYL ALCOHOL(100)

Temperature (not given in article)

$\Lambda_o = 12.2$

$C \times 10^4$	Λ*
.25	12.0
1.0	11.54
1.25	11.12
2.25	10.80

* Data taken from graph

TABLE A5-71. EQUIVALENT CONDUCTANCE OF $NaClO_4$ IN DIMETHYL SULFOXIDE(260)

Temperature = 25°C

$\Lambda_o = 38.3$

$C \times 10^4$	Λ
0.7860	37.86
4.644	37.24
8.771	36.88
14.25	36.49
22.19	36.06
44.51	35.25

TABLE A5-72. EQUIVALENT CONDUCTANCE OF $NaClO_4$ IN ETHYL ALCOHOL[55]

Temperature = 25°C

Λ_o = 52.45

$C \times 10^4$	Λ
1.6622	49.52
1.797	49.27
3.261	48.31
3.581	48.00
5.500	47.00
7.593	45.97
8.791	45.56
11.483	44.54
11.812	44.48
17.517	42.70
17.802	42.94

TABLE A5-73. EQUIVALENT CONDUCTANCE OF $NaClO_4$ IN METHYL ALCOHOL[54]

Temperature = 25°C

Λ_o = 116.50

$C \times 10^4$	Λ
1.4627	112.97
2.4318	112.02
3.7478	111.83
5.7517	109.54
9.3164	107.71
1.1266	113.40
2.2003	112.16
3.5368	111.01
5.7591	109.49
9.1420	107.78

TABLE A5-74. EQUIVALENT CONDUCTANCE OF $NaClO_4$ IN NITROMETHANE[211]

Temperature = 25°C

C x 10^4	A
0.770	118.7
.863	119.2
1.310	117.8
1.507	117.2
1.710	117.7
2.458	115.7
3.061	114.7
3.172	115.3
3.864	113.2
5.522	111.2
5.648	111.6
5.954	110.4
7.369	109.5
7.613	108.2
8.131	108.2
10.519	105.1
10.56	105.9
11.75	104.5

TABLE A5-75. EQUIVALENT CONDUCTANCE OF $NaClO_4$ IN ACETONE[1]

Temperature = 25°C

Λ_o = 191.2

$C \times 10^4$	Λ
0.8467	185.4
2.5905	177.4
4.2955	170.2
6.026	165.9
16.798	149.6

TABLE A5-76. EQUIVALENT CONDUCTANCE OF $NaClO_4$ IN N,N-DIMETHYLACETAMIDE[174]

Temperature = 25°C

Λ_o = 68.56

$C \times 10^4$	Λ
1.082	67.19
5.577	65.66
12.77	64.20
26.90	62.55
43.66	61.17
64.55	59.90

TABLE A5-77. EQUIVALENT CONDUCTANCE OF $NaClO_4$ IN DIMETHYLFORMAMIDE[3]

Temperature = 25°C

Λ_o = 82.1

$C \times 10^4$	Λ
0.969	80.7
2.919	79.5
6.124	78.5
11.69	77.1
20.33	75.6
26.73	74.8
32.08	74.2

6. MISCELLANEOUS

TABLE A5-78. LOWERING OF THE FREEZING POINT OF CYCLOHEXANOL BY $LiClO_4$[259]

M	Δt
First Series	
0.000849	0.057
.001548	.097
.002751	.162
.005231	.285
.010447	.542
.011766	.597
.016810	.820
.021707	1.032
.025597	1.203
.031701	1.474
Second Series	
0.001410	0.096
.003338	.207
.005521	.323
.007176	.405
.008273	.461
.010393	.564
.011899	.635
Third Series	
0.000432	0.028
.001203	.077
.002287	.139
.004287	.235
.006522	.340
.010273	.517
.01346	.671
.01436	.703

M = Concentration in moles per liter of solution

Δt = Freezing point lowering in °C

TABLE A5-79. LOWERING OF THE FREEZING POINT OF BENZENE BY $AgClO_4$[243]

$\frac{\text{gm } AgClO_4}{100 \text{ g Benzene}}$	Δt
0.106	0.008
.767	.061
.877	.070
1.842	.138
2.162	.169
2.432	.189
2.681	.208
3.032	.236
3.294	.251

Δt = Freezing point lowering in °C

TABLE A5-80 DIELECTRIC CONSTANTS, MOLAR POLARIZATION, AND ELECTRIC MOMENTS FOR $AgClO_4$ IN BENZENE

Temperature = 25° C

Concentration $AgClO_4$	Dielectric Constant of Solution	Molar Polarization of Solution, cc	Electric Moment, Debyes	Reference
C x 10^4				
0.0	2.267			
2.04	2.26978	2220	10.7×10^{-18}	119
3.18	2.27071	1900		
4.83	2.27273	1930		
9.47	2.2761	1560		
11.45	2.2774	1470		
30.4	2.2860	1000		
54.5	2.2939	783		
64.9	2.2979	756		
80.7	2.3035	715		
99.1	2.3089	664		
199.7	2.3371	546		

Limited value for solution = 2400

TABLE A5-80. DIELECTRIC CONSTANT, MOLAR POLARIZATION, AND ELECTRIC MOMENTS FOR $AgClO_4$ IN BENZENE (Cont'd)

Temperature = 25° C

Concentration $AgClO_4$	Dielectric Constant of Solution	Molar Polarization of Solution, cc	Electric Moment, Debyes	Reference
Wt. %				
0.0	2.280	26.68	4.7×10^{-18}	321, 320
0.34	2.336	27.44		321
0.73	2.384	28.12		321
1.42	2.454	29.13		321
2.36	2.597	30.85		321
		Limited value for $AgClO_4$ = 477.0		
$M \times 10^4$				
10.	2.2835*	3020.	11.97×10^{-18}	163
20.	2.289			
30.	2.293			
40.	2.296			
50.	2.299			

C = Concentration in gram equivalents per liter of solution

M = Concentration in gram moles per liter of solution

* Data taken from graph. Values based on International Critical Tables value of 2.274 for dielectric constant for benzene at 25° C.

TABLE A5-81. MOBILITIES OF CHLORATE AND PERCHLORATE IONS IN VARIOUS NONAQUEOUS SOLVENTS

Ion	Solvent	Temp., °C	$l_o \times 10^5$	Reference
ClO_3^-	Methyl Alcohol	25	61.4	283
ClO_3^-	Ethyl Alcohol	25	29.3	283
ClO_4^-	Methyl Alcohol	25	70.9	283
ClO_4^-	Methyl Alcohol	25	69.	307
ClO_4^- (Li salt)	Methyl Alcohol	25	70.90	54
ClO_4^- (Na salt)	Methyl Alcohol	25	70.80	54
ClO_4^- (Ag salt)	Methyl Alcohol	25	68.95*	54
ClO_4^-	Ethyl Alcohol	25	33.8	283
ClO_4^-	Acetone	25	117.	283
ClO_4^-	Acetone	25	115.6	307
ClO_4^-	Acetonitrile	25	105.	283
ClO_4^-	Dichloroethylene	25	89.85	91
ClO_4^-	Tetrachloroethane	25	24.0	91
ClO_4^-	Nitromethane	25	64.	211
ClO_4^-	Nitrobenzene	25	19.9	212

* This value suspected of being too low(54)

l_o = ionic mobility at infinite dilution, cm/sec

TABLE A5-82. DISSOCIATION CONSTANTS OF SOME PERCHLORATES IN NONAQUEOUS SOLVENTS

Salt	Solvent	Temp., °C	K x 10^4	Reference
$AgClO_4$	Pyridine	25.	19.1	180
$LiClO_4$	Acetone	25.00	1.9	1
$KClO_4$	Acetone	25.00	1.4	1
$NaClO_4$	Acetone	25.00	2.3	1

K = Dissociation Constant

TABLE A5-83. RADIUS OF THE CHLORATE AND PERCHLORATE IONS IN NONAQUEOUS SOLVENTS(283)

Temperature = 25° C

Ion	Solvent	r_s	r_c
ClO_3^-	Methyl Alcohol	2.40	2.53
ClO_3^-	Ethyl Alcohol	2.56	2.53
ClO_4^-	Methyl Alcohol	2.08	2.55
ClO_4^-	Ethyl Alcohol	2.22	2.55
ClO_4^-	Acetone	1.97	2.55
ClO_4^-	Acetonitrile	2.24	2.55

r_s = Solute radius, Å
r_c = Crystalline radius, Å

TABLE A5-84. MAGNETIC SUSCEPTIBILITY OF THE NONAQUEOUS SOLUTIONS OF SOME PERCHLORATES[109]

Temperature = 20° C

$NaClO_4$ in Acetone

$\psi_s = -0.5858 \times 10^{-6}$		$\psi_s = -0.5861 \times 10^{-6}$	
Wt. % $NaClO_4$	$-\psi_g \times 10^6$	Wt. % $NaClO_4$	$-\psi_g \times 10^6$
6.63	0.5666	8.87	0.5601
16.2	0.5384	16.0	0.5408
23.8	0.5187	19.1	0.5346
		22.4	0.5220

$NaClO_4$ in Ethyl Alcohol

$\psi_s = -0.7333 \times 10^{-6}$		$\psi_s = -0.7349 \times 10^{-6}$	
Wt. % $NaClO_4$	$-\psi_g \times 10^6$	Wt. % $NaClO_4$	$-\psi_g \times 10^6$
3.11	0.7190	5.16	0.7122
7.89	0.6980	9.82	0.6919

$Ba(ClO_4)_2$ in Acetone

$\psi_s = -0.5859 \times 10^{-6}$		$\psi_s = -0.5858 \times 10^{-6}$	
Wt. % $Ba(ClO_4)_2$	$-\psi_g \times 10^6$	Wt. % $Ba(ClO_4)_2$	$-\psi_g \times 10^6$
6.14	0.5665	7.48	0.5639
11.1	0.5508	14.42	0.5397
14.8	0.5390	19.21	0.5253

ψ_g = Magnetic susceptibility of the solution, c.g.s.e.m.u.
ψ_s = Magnetic susceptibility of the solvent, c.g.s.e.m.u.

TABLE A5-85. COMPRESSIBILITY OF SOLUTIONS OF $LiClO_4$ IN ACETONE[77]

Temperature = 17 ± 0.1° C

M	β[a]	s[b]
∞	-	4
0.0142	0.951	3.40
.0336	.900	2.87
.0619	.814	2.83
.1169	.738	2.44
.1847	.558	1.95
.2181	.504	1.78
.3348	.416	1.16

a Determined by sound velocity measurements.
b s = solvation number, moles solvent/mole of salt.
M = Concentration in moles per liter of solution
β = Compressibility coefficient

TABLE A5-86. PARTIAL MOLAR VOLUMES OF $LiClO_4$ AND ETHER SOLUTIONS[71]

Temperature = 23.5° C

M	Method 1		Method 2		Method 3	
	v_1	v_2	v_1	v_2	v_1	v_2
0	104.7	15.2	104.7	14.2	104.7	13.0
0.612	104.6	17.5	104.4	19.0	104.3	19.0
0.8983	104.6	19.5	104.3	19.9	104.2	19.9
1.3381	104.0	22.6	104.1	21.6	104.0	21.7
1.6970	103.9	23.5	103.8	23.1	103.2	26.0
2.7750	102.7	28.2	102.3	29.2	101.4	31.6
3.5608	101.3	31.8	100.7	33.7	99.8	35.2
4.1383	99.4	36.2	98.9	37.9	98.0	39.2
6.0196	89.7	52.4	92.0	48.9	94.7	45.6

v_1 = Partial molar volume of ether
v_2 = Partial molar volume of $LiClO_4$
M = Concentration in moles per liter of solution
Method 1 - Values obtained by plotting the "shrinkage" d vs x_2
Method 2 - Values obtained by plotting the apparent molar volume, ϕ_2, vs log η_2
Method 3 - Values obtained by plotting volume 1 mole solution, v, vs x_2

A6. THERMODYNAMIC PROPERTIES

TABLE OF CONTENTS

Table		Page
A6-1	HEAT FORMATION OF CHLORATES ΔH_f°, kg cal/mole	537
A6-2	HEAT OF FORMATION OF PERCHLORATES ΔH_f°, kg cal/mole	541
A6-3	FREE ENERGY OF FORMATION OF CHLORATES F_f°, kg cal/mole	545
A6-4	FREE ENERGY OF FORMATION OF PERCHLORATES F_f°, kg cal/mole	545
A6-5	EQUILIBRIUM CONSTANT OF FORMATION FOR CHLORATES. $\text{Log}_{10} K_f$	546
A6-6	EQUILIBRIUM CONSTANT OF FORMATION FOR PERCHLORATES. $\text{Log}_{10} K_f$	546
A6-7	ENTROPY OF CHLORATES, S., cal/degree mole	547
A6-8	ENTROPY OF PERCHLORATES, S, cal/degree mole	547
A6-9	HEAT CAPACITY OF CHLORATES C_p, cal/degree mole	548
A6-10	HEAT CAPACITY OF PERCHLORATES C_p°, cal/degree mole	550
A6-11	HEAT OF SOLUTION OF CHLORATES, kg cal/mole	553
A6-12	HEAT OF SOLUTION OF PERCHLORATES, kg cal/mole	554
A6-13	HEAT OF DILUTION OF CHLORATES IN WATER, cal/mole	556
A6-14	HEAT OF DILUTION OF PERCHLORATES IN WATER cal/mole	558
A6-15	HEAT OF DILUTION OF PERCHLORATES IN NONAQUEOUS SOLVENTS, kg cal/mole	559

TABLE OF CONTENTS (Cont'd)

		Page
A6-16	HEAT OF FUSION OF CHLORATES H, kg cal/mole	559
A6-17	ENTROPY OF FUSION OF CHLORATES S, cal/degree mole	560
A6-18	HEAT CAPACITY OF FUSION OF CHLORATES Cp, cal/degree mole	560
A6-19	HEAT OF HYDRATION OF CHLORATE ION kg cal/mole	560
A6-20	HEAT OF HYDRATION OF PERCHLORATES kg cal/mole	560
A6-21	HEAT OF DECOMPOSITION OF CHLORATES kg cal/mole	561
A6-22	HEAT OF DECOMPOSITION OF PERCHLORATES kg cal/mole	561
A6-23	HEAT OF TRANSITION OF $KClO_4$ H, kg cal/mole	561
A6-24	ENTROPY OF TRANSITION OF $KClO_4$ S, cal/degree mole	562
A6-25	HEAT OF NEUTRALIZATION OF $NaClO_3$	562
A6-26	FREE ENERGY OF SOLUTION OF $KClO_3$ kg cal/mole	562
A6-27	HEAT OF COMBUSTION OF CHLORATE MIXTURES kg cal/kg	562
A6-28	HEAT OF COMBUSTION OF PERCHLORATE MIXTURES kg cal/kg	563
A6-29	LATTICE ENERGY OF CHLORATES kg cal/mole	563

TABLE OF CONTENTS (Cont'd)

Table		Page
A6-30	LATTICE ENERGY OF PERCHLORATES kg cal/mole	563
A6-31	HEAT OF ACTIVATION OF VISCOUS FLOW OF $NaClO_4$ kg cal/mole	564
A6-32	FREE ENERGY OF ACTIVATION OF VISCOUS FLOW OF $NaClO_4$, kg cal/mole	565
A6-33	ENTROPY OF ACTIVATION OF VISCOUS FLOW OF $NaClO_4$, cal/degree mole	566
A6-34	MISCELLANEOUS PARTIAL MOLAR QUANTITIES FOR CHLORATES	566
A6-35	MISCELLANEOUS PARTIAL MOLAR QUANTITIES FOR PERCHLORATES	567
A6-36	THERMOCHEMICAL RADII OF THE CHLORATE AND PERCHLORATE IONS	567

TABLE A6-1. HEAT FORMATION OF CHLORATES
ΔH_f°, kg cal/mole

Formula	Conditions	State	Value	Reference
ClO_3^-	Std. state hyp. m = 1, at 25° C	aq	-23.50	250
	at 18° C	aq	-19.1	311
	at -33° C in liq. NH_3	-	-48	127
		g	-37.0	250
		g	-57.4 ± 1.1	325
$Ba(ClO_3)_2$	at 25° C		-181.7	250
			-181.2	198
	at 18° C		-174.0	31
	at 25° C	aq	-175.6	250
	at 18° C in 200 H_2O	aq	-167.0	311
$Ba(ClO_3)_2 \cdot H_2O$	at 25° C		-254.9	250
	at 18° C		-247.0	311
$LiClO_3$	in soln at 25° C	aq	- 87.5	169
$KClO_3$	at 25° C		- 93.50	250
			- 95.86	198
	at 18° C		- 89.9	311
	at 25° C, std. state, hyp. m = 1	aq	- 83.540	250
	At 25° C in 100 H_2O	aq	- 84.090	250

TABLE A6-1. HEAT OF FORMATION OF CHLORATES

ΔH_f°, kg cal/mole (Cont'd)

Formula	Conditions	State	Value	Reference
$KClO_3$	at 25° C in 200 H_2O	aq	- 83.720	250
	at 25° C in 300 H_2O	aq	- 83.670	250
	at 25° C in 400 H_2O	aq	- 83.610	250
	at 25° C in 500 H_2O	aq	- 83.580	250
	at 25° C in 600 H_2O	aq	- 83.555	250
	at 25° C in 800 H_2O	aq	- 83.543	250
	at 25° C in 900 H_2O	aq	- 83.535	250
	at 25° C in 1000 H_2O	aq	- 83.531	250
	at 25° C in 2000 H_2O	aq	- 83.514	250
	at 25° C in 3000 H_2O	aq	- 83.511	250
	at 25° C in 4000 H_2O	aq	- 83.511	250
	at 25° C in 5000 H_2O	aq	- 83.512	250
	at 25° C in 10,000 H_2O	aq	- 83.515	250
	at 25° C in 20,000 H_2O	aq	- 83.520	250
	at 25° C in 50,000 H_2O	aq	- 83.526	250
	at 25° C in 100,000 H_2O	aq	- 83.530	250
	at 25° C in 200,000 H_2O	aq	- 83.532	250
	at 25° C in 500,000 H_2O	aq	- 83.535	250
	at 25° C ∞ H_2O	aq	- 83.540	250
	at 18° C, in 125 moles H_2O	aq	- 80.5	311

TABLE A6-1. HEAT OF FORMATION CHLORATES

$\Delta H_f°$, kg cal/mole (Cont'd)

Formula	Conditions	State	Value	Reference
$KClO_3$	at 18° C, in 250 moles H_2O	aq	- 79.8	311
	at 18° C, in 400 moles H_2O	aq	- 79.6	311
	at 18° C, in 500 moles H_2O	aq	- 79.6	311
	at 18° C, in ∞ moles H_2O	aq	- 79.5	311
$AgClO_3$	at 25° C		- 5.73	250
	at 18° C		- 1.7	311
	at 25° C	aq	- 1.81	250
	at 18° C	aq	- 5.7	311
$NaClO_3$	at 25° C		- 85.73	250
			- 84.40	198
	at 18° C		- 82.5	311
	at 18° C	aq	- 77.1	311
	at 25° C in 400 H_2O	aq	- 80.744	250
	at 25° C in 600 H_2O	aq	- 80.739	250
	at 25° C in 800 H_2O	aq	- 80.734	250
	at 25° C in 1000 H_2O	aq	- 80.733	250
	at 25° C in 2000 H_2O	aq	- 80.735	250
	at 25° C in 5000 H_2O	aq	- 80.744	250
	at 25° C in 10,000 H_2O	aq	- 80.752	250
	at 25° C in 20,000 H_2O	aq	- 80.760	250
	at 25° C in 50,000 H_2O	aq	- 80.766	250

TABLE A6-1. HEAT OF FORMATION CHLORATES
ΔH_f°, kg cal/mole (Cont'd)

Formula	Conditions	State	Value	Reference
$NaClO_3$	at 25° C in 100,000 H_2O	aq	- 80.770	250
	at 25° C in ∞ H_2O	aq	- 80.780	250
	at -33° C in liq NH_3	-	- 83.6	127

TABLE A6-2. HEAT OF FORMATION OF PERCHLORATES
H_f°, kg cal/mole

Formula	Conditions	State	Value	Reference
ClO_4^-	Std. state, hyp. m. = 1	aq	- 40.0	311
	Std. state, hyp. m. = 1 at 25°C	aq	- 31.41	250
		g	- 89.0	56
		g	- 80. ± 1	325
NH_4ClO_4			- 79.7	198
	at 18°C		- 78.3	311
	at 25°C	II	- 69.42	250
	at 27°C	II	- 75.08	286
	Calculated		- 70.2	93
	in 500 H_2O	aq	- 63.2	250
	∞ H_2O	aq	- 63.15	250
	∞ H_2O	aq	- 72.0	311
$Ba(ClO_4)_2$			-192.8	250
	at 18°C		-210.0	311
	Calculated		-194.3	93
	at 18°C in 800 moles H_2O	aq	-208.0	311
		aq	-191.5	250
$Ba(ClO_4)_2 \cdot 3H_2O$			-405.4	250
	at 18°C		-423.0	311
$LiClO_4$		aq	-106.3	169

TABLE A6-2. HEAT OF FORMATION OF PERCHLORATES
H_f°, kg cal/mole (Cont'd)

Formula	Conditions	State	Value	Reference
$Mg(ClO_4)_2$			-140.6	250
		aq	-172.5	
$Mg(ClO_4)_2 \cdot 2H_2O$			-290.7	
$Mg(ClO_4)_2 \cdot 4H_2O$			-438.6	
$Mg(ClO_4)_2 \cdot 6H_2O$			-583.2	
$KClO_4$			112.5	198
	at 18°C		-112	311
	at 25°C		-103.6	329
	at 27°C		-111.29	286
	Calculated		-104.4	93
	Saturated	aq	-105	311
	at 25°C, std. state, hyp. m = 1	aq	- 91.45	250
	500 H_2O	aq	-108	311
	at 25°C, in 500 H_2O	aq	- 91.58	250
	at 25°C, in 600 H_2O	aq	- 91.55	
	at 25°C, in 700 H_2O	aq	- 91.53	
	at 25°C, in 800 H_2O	aq	- 91.52	
	at 25°C, in 900 H_2O	aq	- 91.51	
	at 25°C, in 1000 H_2O	aq	- 91.50	
	at 18°C, in 1000 H_2O	aq	- 99.8	311

TABLE A6-2. HEAT OF FORMATION OF PERCHLORATES
Hf, kg cal/mole (Cont'd)

Formula	Conditions	State	Value	Reference
$KClO_4$	at 25°C, in 1500 H_2O	aq	- 91.47	250
	at 25°C, in 2000 H_2O	aq	- 91.46	
	at 25°C, in 3000 H_2O	aq	- 91.45	
	at 25°C, in 4000 H_2O	aq	- 91.44	
	at 25°C, in 5000 H_2O	aq	- 91.44	
	at 25°C, in 8000 H_2O	aq	- 91.43	
	at 25°C, in 10,000 H_2O	aq	- 91.43	
	at 25°C, in 20,000 H_2O	aq	- 91.43	
	at 25°C, in 50,000 H_2O	aq	- 91.44	
	at 25°C, in 100,000 H_2O	aq	- 91.44	
	at 25°C, in 200,000 H_2O	aq	- 91.45	
	at 25°C, in 500,000 H_2O	aq	- 91.45	
	Dilute	aq	-112.07	115
	at 25°C, ∞ H_2O	aq	- 91.45	250
	at 18°C, ∞ H_2O	aq	- 99.4	311
$AgClO_4$			- 7.75	250
	at 18°C		- 12.2	311
		aq	- 6.10	115
	at 18°C, dilute	aq	- 14.4	311
$NaClO_4$			-100.2	198
	at 18°C		-101.	311

TABLE A6-2. HEAT OF FORMATION OF PERCHLORATES
H_f°, kg cal/mole (Cont'd)

Formula	Conditions	State	Value	Reference
$NaClO_4$	at 25°C	II	- 92.18	250
	Calculated		- 93.	93
	at 18°C, dilute	aq	- 97.0	311
	at 25°C, std. state, hyp. m = 1	aq	- 88.69	250
	at 25°C, in 400 H_2O	aq	- 88.76	
	at 25°C, in 600 H_2O	aq	- 88.73	
	at 25°C, in 1000 H_2O	aq	- 88.70	
	at 25°C, in 2000 H_2O	aq	- 88.68	
	at 25°C, in 5000 H_2O	aq	- 88.67	
	at 25°C, ∞ H_2O	aq	- 88.69	
	at 25°C, in CH_3OH		- 94.6	
	at 25°C, in C_2H_5OH	--	- 92.6	

TABLE A6-3. FREE ENERGY OF FORMATION OF CHLORATES
ΔF_f°, kg cal/mole

Formula	Conditions	State	Value	Reference
ClO_3^-	at 25°C, std. state, hyp. m = 1	aq	- 0.62	250
	at 25°C, std. state, hyp. m = 1	aq	- 3.7	173
	at -33°C, in liq NH_3	--	- 18.0	127
$LiClO_3$	at 25°C in soln.	aq	- 70.95	169
$KClO_3$	at 25°C	c	- 69.29	250
	at 25°C, std. state, hyp. m = 1	aq	- 68.09	250
	at 25°C, in liq. NH_3	--	- 69.3	127
$NaClO_3$	at 25°C, std. conditions	--	- 59.1	146
	at 25°C, std. state, hyp. m = 1	aq	- 63.21	250
	in 400 H_2O	aq	- 62.8	169

TABLE A6-4. FREE ENERGY OF FORMATION OF PERCHLORATES
ΔF_f°, kg cal/mole

Formula	Conditions	State	Value	Reference
ClO_4^-	at 25°C, std. state, hyp. m = 1	aq	- 2.57	250
		g	- 10.9	172
NH_4ClO_4	at 18°C, ∞ H_2O	aq	- 21.1	169
$LiClO_4$		aq	- 81.4	169
$KClO_4$	at 25°C	c	- 72.7	250
	at 25°C, std. state, hyp. m = 1	aq	- 70.04	250
$NaClO_4$	at 25°C, std. state, hyp. m = 1	aq	- 65.16	250

TABLE A6-5. EQUILIBRIUM CONSTANT OF FORMATION FOR CHLORATES, $Log_{10} K_f$

Formula	Conditions	State	Value	Reference
ClO_3^-	at 25°C, std. state, hyp. m = 1	aq	0.454	250
$KClO_3$	at 25°C	c	50.789	250
	at 25°C, std. state, hyp. m = 1	aq	49.909	250
$NaClO_3$	at 25°C, std. state, hyp. m = 1	aq	46.332	250

TABLE A6-6. EQUILIBRIUM CONSTANT OF FORMATION FOR PERCHLORATES, $Log_{10} K_f$

Formula	Conditions	State	Value	Reference
ClO_4^-	at 25°C, std. state, hyp. m = 1	aq	1.884	250
$KClO_4$	at 25°C	c	53.29	250
	at 25°C, std. state, hyp. m = 1	aq	51.34	250
$NaClO_4$	at 25°C, std. state, hyp. m = 1	aq	47.688	250

TABLE A6-7. ENTROPY OF CHLORATES, S, cal/degree mole

Formula	Conditions	State	Value	Reference
ClO_3^-	at 25°C, std. state, hyp. m = 1	aq	39.0	250
	at 25°C, std. state, hyp. m = 1	aq	39.3	173
	at -33°C, in liq. NH_3	--	16.0	127
$KClO_3$	at 25°C	c	34.17	250
	at 25°C, std. state, hyp. m = 1	aq	63.5	250
$AgClO_3$		s	35.8 ± 0.6	146
$NaClO_3$	at 25°C, std. state, hyp. m = 1	aq	53.4	250
	at 25°C, std. conditions	--	30.2 ± 1.0	146

TABLE A6-8. ENTROPY OF PERCHLORATES, S, cal/degree mole

Formula	Conditions	State	Value	Reference
ClO_4^-	at 25°C, std. state, hyp. m = 1	aq	46.2	172
	at 25°C, std. state, hyp. m = 1	aq	43.50	250
$KClO_4$	at 25°C	c	36.1 ± 0.4	145
	at 25°C	c	36.3	329
	at 25°C, std. state, hyp. m = 1	aq	68.0	250
$NaClO_4$	at 25°C, std. state, hyp. m = 1	aq	57.9	250

TABLE A6-9. HEAT CAPACITY OF CHLORATES
C_p, cal/degree mole

Formula	Conditions	State	Value	Reference
ClO_3^-	at 25°C, std. state, hyp. m = 1	aq	-18	250
$Ba(ClO_3)_2$		--	47.8	198
$Ba(ClO_3)_2 \cdot H_2O$	at 25°C	c	50.6	250
			cal/g soln/°C	
$LiClO_3$	at 18°C, in 5% aq soln	aq	0.953	311
	at 18°C, in 10% aq soln		0.905	
	at 18°C, in 15% aq soln		0.856	
	at 18°C, in 20% aq soln		0.804	
	at 18°C, in 25% aq soln		0.752	
$KClO_3$	at 25°C	c	23.96	250
	between 19-49°C	--	19.1	198
	between 16-98°C	--	23.5	
		--	23.8	
	at -150°C	c	14.7	311
	at -100°C	c	18.9	
	at 0°C	c	23.4	
	at 50°C	c	25.1	
	at 100°C	c	28.4	
	at 200°C	c	36.2	
	at 225°C	c	39.7	

TABLE A6-9. HEAT CAPACITY OF CHLORATES
C_p, cal/degree mole (Cont'd)

Formula	Conditions	State	Value	Reference
			cal/g soln/°C	
$KClO_3$	at 20°C, in 5% aq soln	aq	0.934	
	at 20°C, in 10% aq soln	aq	0.895	
	at 20°C, in 15% aq soln	aq	0.816	
	at 20°C, in 20% aq soln	aq	0.767	
	at 20°C, in 25% aq soln	aq	0.720	
$NaClO_3$		--	29.9	198
	Molten	liq	61.8	198
	at 280°C	liq	33.9	311
	The specific heat of solution at 25°C drops smoothly with concentration to 0.650 cal/g soln/°C for a solution containing 15.39 moles/100 moles H_2O			51

TABLE A6-10. HEAT CAPACITY OF PERCHLORATES
C_p, cal/degree mole

Formula	Conditions	State	Value	Reference
$KClO_4$	at 25°C	c	26.33	250
	at 25°C	s	26.0	51
	between 14-45°C	c	26.3	198
	at 30°C	c	26	311
	at -260.5° C	c	0.73	172
	at -256.6°C	c	1.06	
	at -253.5°C	c	1.69	
	at -251.1°C	c	2.25	
	at -249.0°C	c	2.75	
	at -246.0°C	c	3.56	
	at -239.6°C	c	5.38	
	at -236.0°C	c	6.38	
	at -227.8°C	c	8.37	
	at -218.2°C	c	10.30	
	at -214.0°C	c	11.00	
	at -210.0°C	c	11.62	
	at -206.4°C	c	12.09	
	at -201.3°C	c	12.82	
	at -199.6°C	c	13.55	
	at -192.4°C	c	13.91	
	at -183.5°C	c	14.73	

TABLE A6-10. HEAT CAPACITY OF PERCHLORATES
Cp , cal/degree mole (Cont'd)

Formula	Conditions	State	Value	Reference
$KClO_4$	at -182.6°C	c	14.77	172
	at -178.6°C	c	15.08	
	at -173.1°C	c	15.49	
	at -167.7°C	c	15.80	
	at -162.8°C	c	16.23	
	at -155.9°C	c	16.76	
	at -150.7°C	c	17.15	
	at -140.8°C	c	17.64	
	at -130.8°C	c	18.17	
	at -119.8°C	c	18.77	
	at -109.2°C	c	19.43	
	at - 97.9°C	c	20.02	
	at - 86.1°C	c	20.49	
	at - 80.6°C	c	20.81	
	at - 70.1°C	c	21.39	
	at - 59.9°C	c	22.01	
	at - 48.4°C	c	22.60	
	at - 42.1°C	c	22.61	
	at - 35.7°C	c	23.04	
	at - 29.0°C	c	23.14	
	at - 22.7°C	c	23.56	

TABLE A6-10. HEAT CAPACITY OF PERCHLORATES
C_p , cal/degree mole (Cont'd)

Formula	Conditions	State	Value	Reference
$KClO_4$	at - 16.7°C	c	23.86	
	at - 10.4°C	c	24.33	
	at - 4.1°C	c	26.16	
	at + 1.8°C	c	27.46	
	at + 7.5°C	c	25.98	
	at + 13.3°C	c	29.90	
	at + 18.5°C	c	25.82	
	at + 25.1°C	c	26.34	
$NaClO_4$	at 25°C	C, II	24.1	250
	At 24.5°C, the specific heat of solution drops smoothly with conc. to 0.568 cal/g soln/°C at 22.01 moles/100 moles H_2O			51

Formula	Temperature, °C	Value, Cal/g/°C	Reference
NH_4ClO_4	34.62	0.260	Aerojet Report 649 Feb 24, 1953 Contract NOas 52-359
	35.73	.268	
	39.46	.264	
	36.60 (avg)	0.264	

TABLE A6-11. HEAT OF SOLUTION OF CHLORATES, kg cal/mole

Formula	Conditions	Value	Reference
$Ba(ClO_3)_2$	at 10°C in 600 moles H_2O	- 6.7	311
$Ba(ClO_3)_2 \cdot H_2O$	at 18°C in 600 moles H_2O	-11.0	311
	in 600 moles H_2O	11.24	311
$KClO_3$		-10.04	198
	in 100 ml H_2O	8.9	198
	at 18°C in 400 moles H_2O	-10.03	311
$AgClO_3$	at 18°C, dilute solutions	- 7.5	311
$NaClO_3$	at 10°C	- 5.57	198
	at satn., 17 moles/100 moles H_2O	- 3.51	51
	at infinite dilution	- 5.29	51
	at 10°C, 180-360 moles H_2O	- 5.6	169
	at -33°C, in liq. NH_3	- 2.2	127

TABLE A6-12. HEAT OF SOLUTION OF PERCHLORATES
kg cal/mole

Formula	Conditions	Value	Reference
NH_4ClO_4	in 220 moles H_2O at 20°C	- 6.36	311
	in 200-400 moles H_2O at 10°C	- 6.36	198
$Ba(ClO_4)_2$	in 800 moles H_2O at 10°C	- 1.67	115
	at 18°C	- 1.42	267
$Ba(ClO_4)_2 \cdot 3H_2O$	at 18°C	-10.05	267
	in 1000 moles H_2O at 18°C	- 9.3	311
$Ca(ClO_4)_2$	at 18°C	14.2	267
$Ca(ClO_4)_2 \cdot 4H_2O$	at 18°C	- 1.285	267
$LiClO_4$	at 18°C	6.24	267
$LiClO_4 \cdot 3H_2O$	at 18°C	- 7.965	267
$Mg(ClO_4)_2$	at 18°C	36.900	267
		31.900 (avg.)	268
$Mg(ClO_4)_2 \cdot 2H_2O$		18.390 (avg.)	268
$Mg(ClO_4)_2 \cdot 4H_2O$		7.175 (avg.)	268
$Mg(ClO_4)_2 \cdot 6H_2O$		- 0.809 (avg.)	268
$KClO_4$	Saturated	-11.7	311
	in 100 moles H_2O	3.66	198
	in 200-400 moles H_2O	-12.1	198
	in 460 moles H_2O at 20°C	-12.13	169

TABLE A6-12. HEAT OF SOLUTION OF PERCHLORATES
kg cal/mole (Cont'd)

Formula	Conditions	Value	Reference
$KClO_4$	in 1800 moles H_2O at 25.1°C	-12.12	172
$AgClO_4$	at 18°C	2.2	311
	in 1600 moles H_2O	2.17	198
$NaClO_4$	at 18°C	- 3.475	267
	at satn., 30.84 moles/100 moles H_2O	- 1.16	51
	in 200-400 moles H_2O at 10°C	- 3.5	169
	in 400 moles H_2O at 10°C	- 3.6	311
	in ∞ H_2O	- 3.44	51
$NaClO_4 \cdot 2H_2O$	at 18°C	- 5.490	267

TABLE A6-13. HEAT OF DILUTION OF CHLORATES IN WATER
cal/mole

a. Heats of Dilution

Formula	Concentration, moles/l		Value		Reference
	Initial	Final	15°C	25°C	
$KClO_3$	0.00625	0.000165	10.7	26.4	4
		0.000325	7.1	17.0	
	0.0125	0.000329	12.4	24.1	
		0.00652	11.7	19.8	
	0.0250	0.000657	0	15.7	
		0.00131	- 2.6	12.1	
	0.050	0.00132	- 22.8	- 2.2	
		0.00260	-26.2	- 6.	
	0.100	0.00263	-73.2	-38.2	
		0.00519	-78.5	-42.4	
$NaClO_3$	0.1	0.00308			
		0.00311		21.3 ± 0.2(avg)	170
		0.00606			
		0.00613		14.5 ± 0.2	
	0.5	0.00154			
		0.001555		32.7	
		0.00302			
		0.00306		26.8 ± 0.1	
	0.025	0.00769			
		0.00779		32.7 ± 0.1	
		0.001515			
		0.00153		28.2 ± 0.2	
	0.0125	0.000385			
		0.000389			
		0.000389		27.6 ± 1.0	
		0.000752			
		0.000765			
		0.000765		25.5 ± 0.5	

TABLE A6-13. HEAT OF DILUTION OF CHLORATES IN WATER
cal/mole (Cont'd)

b. Heats of Integral and Differential Dilutions

Formula	Concentration, moles/l	Integral Heat of Dilution, cal/mole	Differential Heat of Dilution, cal/mole	Reference
$NaClO_3$	0.0001	3.9	0.00000356	170
	0.0009	11.8	0.0000960	
	0.0025	19.7	0.000412	
	0.0049	26.1	0.000876	
	0.0081	31.4	0.00171	
	0.0121	36.1	0.00252	
	0.0169	39.7	0.00306	
	0.0225	42.6	0.00425	
	0.0289	45.2	0.00488	
	0.0361	47.1	0.00463	
	0.0441	48.1	0.00251	
	0.0529	48.1	-0.00275	
	0.0625	47.4	-0.00566	
	0.0729	46.3	-0.0107	
	0.0841	44.9	-0.0177	
	0.0961	43.0	-0.0275	
	At 25°C, the differential heat of dilution reaches a maximum of -101 cal/mole at saturation.			51

TABLE A6-14. HEAT OF DILUTION OF PERCHLORATES IN WATER
cal/mole

Formula	Concentration, moles/l		Value		Reference
	Initial	Final	15°C	25°C	
$KClO_4$	0.00625	0.000165	0	+ 5.9	4
		0.000325	0	+ 10.8	4
	0.0125	0.000329	- 7.0	+ 4.3	4
		0.000652	- 8.1	+ 1.2	4
	0.0250	0.000657	- 31.6	- 16.4	4
		0.00131	- 32.0	- 18.3	4
	0.050	0.00132	- 82.4	- 53.5	4
		0.00260	- 84.1	- 55.1	4
	0.080	0.00209	-139.5	-	4
		0.00413	-138.5	-	4
	0.100	0.00263	-168.3	-128.5	4
		0.00519	-160.6	-129.2	4
			at 20°C		
$AgClO_4$	0.512	0.221	-100		124
	0.211	0.099	- 30		124
			at 20°C		
$NaClO_4$	0.502	0.233	-140		124

At 24.5°C, the differential heat of dilution reaches a maximum of -111 cal/mole at 19 moles/ 100 moles H_2O; at saturation, it is -27 cal/mole. 51

TABLE A6-15. HEAT OF DILUTION OF PERCHLORATES IN NONAQUEOUS SOLVENTS, kg cal/mole

Formula	Concentration, moles/l of CH_3OH at 20°C		Value	Reference
	Initial	Final		
$NaClO_4$	1.415	0.647	0.761	124
	0.647	0.287	0.559	124
	0.600	0.244	0.577	124
	0.287	0.143	0.370	124
	0.143	0.067	0.32	124
	0.067	0.032	0.23	124
	0.032	0.016	0.23	124
	0.026	0.011	0.19	124
	0.016	0.008	0.17	124
	0.008	0.0035	0.12	124
	Concentration, moles/l of CH_3NO_2 at 20°C			
	Initial	Final		
	0.017	0.008	0.06	124

TABLE A6-16. HEAT OF FUSION OF CHLORATES ΔH, kg cal/mole

Formula	Conditions	Value	Reference
$NaClO_3$	fusion at 255°C	5.4	250
	fusion	5.2	198

TABLE A6-17. ENTROPY OF FUSION OF CHLORATES
ΔS, cal/degree mole

Formula	Conditions	Value	Reference
$NaClO_3$	fusion at 255°C	10.2	250

TABLE A6-18. HEAT CAPACITY OF FUSION OF CHLORATES
ΔC_p, cal/degree mole

Formula	Conditions	Value	Reference
$NaClO_3$	fusion at 255°C	4.9	250

TABLE A6-19. HEAT OF HYDRATION OF CHLORATE ION
kg cal/mole

Formula	Conditions	Value	Reference
ClO_3^-		70.0	324

TABLE A6-20. HEAT OF HYDRATION OF PERCHLORATES
kg cal/mole

Formula	Conditions	Value	Reference
$Ba(ClO_4)_2$	at 18°C	8.63	267
		(412)?	203
$Ca(ClO_4)_2$	at 18°C	15.485	267
$LiClO_4$	at 18°C	14.200	267
$Mg(ClO_4)_2$	at 18°C	38.370	267
		32.708(avg)	268
$Mg(ClO_4)_2 \cdot 2H_2O$		19.199(avg)	268
$Mg(ClO_4)_2 \cdot 4H_2O$		7.984(avg)	268
$KClO_4$		(130)?	203
$NaClO_4$	at 18°C	-1.460	267

TABLE A6-21. HEAT OF DECOMPOSITION OF CHLORATES
kg cal/mole

Formula	Conditions	Value	Reference
$KClO_3$	crystalline decomposition at room temp., $KClO_3 \rightarrow KCl + O_2$	12.1 ± 0.3	116
	$KClO_3 \rightarrow KCl + 3O$	-9.7	198
	$4\ KClO_3 \rightarrow KClO_4 + KCl$	63.	198
$NaClO_3$		12.3	198

TABLE A6-22. HEAT OF DECOMPOSITION OF PERCHLORATES
kg cal/mole

Formula	Conditions	Value	Reference
NH_4ClO_4		+38.3	198
$KClO_4$	constant volume, room temperature, $KClO_4 \rightarrow KCl + O_2$	1.73	116
$NaClO_4$		- 3.0	198

TABLE A6-23. HEAT OF TRANSITION OF $KClO_4$
ΔH, kg cal/mole

Formula	Conditions	Value	Reference
$KClO_4$	at 299.5°C; c, II to c, I	3.29	116

TABLE A6-24. ENTROPY OF TRANSITION OF $KClO_4$
ΔS, cal/degree mole

Formula	Conditions	Value	Reference
$KClO_4$	at 299.5°C; c,II to c,I	5.74	250

TABLE A6-25. HEAT OF NEUTRALIZATION OF $NaClO_3$
kg cal/mole

Formula	Conditions	Value	Reference
$NaClO_3$		13.76	198

TABLE A6-26. FREE ENERGY OF SOLUTION OF $KClO_3$
kg cal/mole

Formula	Conditions	Value	Reference
$KClO_3$	at 25°C, in liq. NH_3	4.6	127

TABLE A6-27 HEAT OF COMBUSTION OF CHLORATE MIXTURES
kg cal/kg[276]

Mixture	Value
$Ba(ClO_3)_2$ - Mg	2018
$KClO_3$ - Al dust	2330
$KClO_3$ - Mg powd	2280
$KClO_3$ - P (red)	1417
$KClO_3$ - $C_6H_5NO_2$	1182
$KClO_3$ - S	682
$KClO_3$ - C (lampblack)	1083

TABLE A6-28. HEAT OF COMBUSTION OF PERCHLORATE MIXTURES
kg cal/kg[276]

Mixture	Value
$KClO_4$ - Al dust	2504
$KClO_4$ - Mg powd	2429
$KClO_4$ - P (red)	1477
$KClO_4$ - S (rhombic)	705
$KClO_4$ - C (lampblack)	1118
$NaClO_4$ - Al dust	2751

TABLE A6-29. LATTICE ENERGY OF CHLORATES
kg cal/mole[325]

Cation	Value
Na+	175.6
K+	159.7
Ca++	515.
Ba++	467

TABLE A6-30. LATTICE ENERGY OF PERCHLORATES
kg cal/mole[325]

Cation	Value
Na+	159.3
K+	146.1
Ca++	468
Ba++	429

TABLE A6-31. HEAT OF ACTIVATION OF VISCOUS FLOW OF $NaClO_4$ kg cal/mole[202]

Formula	Concentration, moles $NaClO_4$/l soln at 30°C	Value
$NaClO_4$	2.0	3.5
	3.0	3.67
	4.0	3.67
	5.0	3.71
	6.0	4.00
	7.0	4.68
	8.0	5.25
	9.0	8.70
	9.5	9.85

TABLE A6-32. FREE ENERGY OF ACTIVATION OF VISCOUS FLOW OF $NaClO_4$, kg cal/mole[202]

Formula	Concentration, moles $NaClO_4$/1 soln at 30°C	Value
$NaClO_4$	2.0	2.26
	3.0	2.34
	4.0	2.45
	5.0	2.59
	6.0	2.78
	7.0	2.97
	8.0	3.19
	9.0	3.45
	9.5	3.59

TABLE A6-33. ENTROPY OF ACTIVATION OF VISCOUS FLOW OF $NaClO_4$, cal/degree mole[262]

Formula	Concentration, moles $NaClO_4$/1 soln at 30°C	Value
$NaClO_4$	2.0	4.2
	3.0	4.4
	4.0	4.0
	5.0	3.7
	6.0	4.0
	7.0	5.6
	8.0	6.8
	9.0	17.3
	9.5	20.7

TABLE A6-34. MISCELLANEOUS PARTIAL MOLAR QUANTITIES FOR CHLORATES[51]

Partial Molar Heat Capacity for $NaClO_3$

Concentration	ΔC_p, cal/degree mole at 25°C
0.1 mole/100 moles H_2O	- 5.
15. mole/100 moles H_2O	+35.

Partial Molar Volume

The partial molar volume changes from 3 to 43 cc/mole at 0.25 and 16 moles/100 moles H_2O.

TABLE A6-35 MISCELLANEOUS PARTIAL MOLAR QUANTITIES FOR PERCHLORATES

Partial Molar Enthalpies and Entropies for the Phase Transitions[175] (from crystalline state to the dissolved state)

Substance	ΔH, kg cal/mole	ΔS, cal/degree mole
$Mg(ClO_4)_2 \cdot 6H_2O$	0.93	3.12
$Ca(ClO_4)_2 \cdot 4H_2O$	1.83	6.14
$Ba(ClO_4)_2 \cdot 3H_2O$	1.57	5.27

Partial Molar Heat Capacity for $NaClO_4$[51]

Concentration	ΔC_p, cal/degree mole at 24.5 °C
0.1 mole/100 moles H_2O	- 9.
4.0 mole/100 moles H_2O	-38.
22. mole/100 moles H_2O	-35.

Partial Molar Volume[51]

The partial molar volume increases with concentration from 4 to 52 cc/mole at 0.25 and 30 moles/100 moles H_2O.

TABLE A6-36. THERMOCHEMICAL RADII OF THE CHLORATE AND PERCHLORATE IONS

Ion	Radii, Å	Reference
ClO_3^-	2.00	324, 325
ClO_4^-	2.36	325

A7. EXPLOSIVE PROPERTIES

TABLE OF CONTENTS

	Page
EXPLOSIVE PROPERTIES	570
EXPLOSIVE PROPERTIES OF AMMONIUM PERCHLORATE	572

EXPLOSIVE PROPERTIES

Although many chlorates and perchlorates in a high state of purity are insensitive to shock and friction compared to many useful explosives, spontaneous explosions of these materials have occurred. Lack of a predictable response to a given set of conditions has severely limited their use as explosives. With organic matter, metal dusts, and other oxidizable substances, chlorates form erratic, powerful explosives which are notoriously sensitive to friction. The extreme sensitivity of chlorate mixtures to friction has led to their use as matches and primers. Perchlorates, mixed with oxidizable material, also form dangerous explosives. For example, the explosion of less than one ounce of a 70-30 mixture of $LiClO_4$ and Carbox wax in the hands of an investigator resulted in grave injury.* However, such mixtures employing ammonium perchlorate find wide use as solid rocket propellants. Other objectionable features of chlorates and perchlorates as explosives include the formation of toxic and corrosive fumes upon combustion, poor storage stability when combined with other materials resulting in many cases in increased sensitivity of the mixtures, tendency toward hygroscopicity, and the undependable behavior of mixtures which have taken on water. (148, 318, 317, 62, 46, 139, 4, 288, 7, 6)

* Private communication from Bu Ord, USN.

Just as the sensitivity of chlorates and perchlorates can be increased by additives, so, also, can they be desensitized by the addition of certain materials. The most famous and widely used desensitizer is castor oil.[317, 62] Despite the past widespread use of chlorate and perchlorate explosives, safer, better, less costly explosives have mostly replaced them except in the fields of matches, primers, pyrotechnics, and propellants.[148, 46]

Quantitive data on the explosive properties of pure chlorate and perchlorate compounds are very scarce. This situation is perhaps born of a falling interest in their use as a component of high explosives of general application, inadequate test methods in the explosives field, and inability to foresee uses for the explosive power of the pure compounds. Silver perchlorate, which has been recommended by some as a Friedel-Crafts reaction catalyst[35, 36], is known to explode violently at times[27, 111, 49], but its explosive properties have not been found in the literature. Likewise, the explosion of magnesium perchlorate, a useful drying agent, has been recorded[49] but not its explosive properties. The same is true for many chlorates and perchlorates: their treacherous explosive nature has been noted but experimental data have not been presented.

One exception is ammonium perchlorate. Previous use in high explosive mixes and its current use a solid rocket propellant ingredient have encouraged investigation of its explosive properties which are presented below:

EXPLOSIVE PROPERTIES OF AMMONIUM PERCHLORATE

Sensitivity

Requires the equivalent of 10 g of mercury fulminate or an XC-32 Detonator to detonate the dry material.[274]

Very insensitive as explosives go but more sensitive than the sodium, potassium and magnesium compounds; drop test, minimum: 86 in. for 11-lb weight.[275]

Insensitive to severe friction tests.[274]

Heating small quantities does not cause explosion; temperature of explosion = 1308°C; heat liberated = 344.5 cal/kg.[214]

Decomposition begins at 130°C, becoming explosive at 380°C.[274]

Brisance

Trauzl lead block test, expansion in cc = 140, 193.[313]

One-fourth that of 40% nitroglycerine dynamite.[274]

Velocity of Detonation[313]

km/sec	g/cc*	mm**	Notes
2.57	1.17	35	1,2
2.47	1.17	35	1,2
2.48	1.0	38	1,3

* Bulk density in cartridge form
** Cartridge or tube diameter

Notes:

1. In wrought iron tube
2. Primer 110 g pressed tetryl
3. Primer 25 g pressed picric acid

Velocity of Detonation[214]

km/sec

3.8 (in 60 mm diameter iron tube; detonated with five No. 8 caps)

Explosive properties of other compounds as found in the literature are:

Ammonium Chlorate

Tendency to ignite spontaneously; detonated by weakest cap.[214, 228]

Temperature of explosion = 1733°C; heat liberated = 537 cal/kg.[214]

Explodes at 100°C[49]

Trauzl lead block test, exp., cm^3 = 240.[313]

Magnesium Perchlorate

Explodes at 220°C.[49]

Potassium Perchlorate

Cannot be exploded at elevated temperatures by mild impact.[4]

Silver Perchlorate

Explodes violently and for unknown reasons at times.[27, 111, 49]

Sodium Perchlorate

Has been exploded by heating.[209]

A8. TOXIC PROPERTIES

TABLE OF CONTENTS

		Page
1.	INTRODUCTION	576
2.	CHLORATES	576
3.	PERCHLORATES	582
4.	CATIONS OF CHLORATE AND PERCHLORATE COMPOUNDS	584

1. INTRODUCTION

Data concerning the toxicity of the chlorate and perchlorate salts of sodium and potassium are reported frequently in the literature, although the lethal doses are found to vary considerably. Limited information is available on several other chlorate salts, whereas no pertinent toxic properties could be found reported concerning many of the chlorate and perchlorate compounds included within the scope of this report.

This section presents, first, the toxic properties of the chlorate and perchorate ions, followed by data about certain chlorate and perchlorate compounds, and finally, information concerning any toxicity that may be due to the cations of these compounds.

2. CHLORATES

The chlorate salts have a toxicity rating of very toxic, and an estimated lethal dose for man is about 30 gm, although a range for the probable human lethal dose is given as 50-500 mg/kg or between 1 teaspoonful and 1 oz for a 70 kg (150 lb) man. Susceptibility varies widely among men and animals. (90)

The oxidation potential is responsible for the strong toxic effects of chlorate. Chlorate penetrates the erythrocytes and attacks the hemoglobin converting it to methemoglobin through an autocatalytic process in which reduction of the chlorate is a necessary step. (46, 138, 126 254)

Methemoglobin is an abnormal form of hemoglobin. It is a combination of oxygen and hemoblobin more stable than oxyhemoglobin. The

compound dissociates very slowly. (98) It is usually associated with intoxication with chlorates as well as nitrites, aniline and others. It may be formed from exposure in industry to excess amounts of these compounds, or may result from excessive intake of drugs. Methemoglobin does not have the same capacity to take up oxygen as the normal hemoglobin, and thus the respiratory processes are imparied. (99) Damage to heart muscle has also been reported. (254)

In a part of the cases of chlorate poisoning there is a form of erythrocyte destruction and elimination of hemoglobin through the kidney, which is not essentially different from the well-known forms of hemolysis. (242) This red blood corpuscle destruction may lead to irritation of the kidneys. (254)

The symptoms and signs of chlorate poisoning may be nausea, vomiting, salivation, dizziness, headache, abdominal pain, weakness, diarrhea, diuresis, anemia, dyspnea, jaundice, cyanosis, quick feeble pulse, fall of blood pressure, anuria, extreme dyspnea, circulatory collapse, delirium, coma, and terminal convulsions. (183, 179, 126)

Data pertaining to the toxicology of some of the chlorate compounds are listed below:

(1) Potassium Chlorate

This compound is rated as very toxic. It is an oxidizing agent more toxic than the sodium salt. The probable lethal dose (human) is 50-500 mg/kg or between one teaspoonful and one oz for a 70 kg (150 lb) man. (90)

Locket[179] places the minimal lethal dose in adults at about 10 to 15 grams, but recovery has occurred after doses as large as 40 grams. Three grams has been the cause of death of a child. Kaye[144] reports the MLD to be 8 grams.

The toxic dose for potassium chlorate is stated in Merck Index, 6th edition, to be approximately 5 grams.[199]

According to Brookes and Alyea[29] the fatal dose for an adult varies from 8 to 60 grams.

One group of investigators report the administration of 1 gram of $KClO_3$ per kg per day for about 4 weeks to rabbits and rats without any serious permanent injurious effects.[151] They conclude that the salt has no cumulative action in this dosage. However, another investigator states that death of adults have followed the administration of 4-5 grams and even gargling with $KClO_3$ solution, and that it is probable that an accumulative effect can result from continued administration of small amounts of the salt.[306]

The response shown by dosages given to different kinds of laboratory animals seems to vary considerably. $KClO_3$ is non-toxic when fed daily to cats in doses as high as 0.5 gram/kg. A single dose of 1.35-1.94 gram/kg produces symptoms of toxicity and results in death.[177] Rabbits were given dosages of 0.185-0.738 gms/kg daily for 6 weeks. This

is 1.5-6.0 times what is considered a lethal dose for man.(83) Yet, the rabbits showed no ill effects. The following table shows that the minimal lethal dose for rabbits is 2.-2.5 grams/kg.(270)

Animal	Route	Dose	Dosage, grams/kg
Rat	Oral	LD	7.0
Rat	Intraperitoneal	LD	1.5
Guinea Pig	Intraperitoneal	LD	1.8
Rabbit	Oral	MLD	2.0-2.5
Dog	Oral	MLD	1.2-1.25

For sheep the fatal dose is reported as 2. to 2.5 mg/kg (which is 0.002 to 0.0025 grams/kg).(289)

Owing to the influence of different factors, the fatal dose of $KClO_3$ cannot be even approximately stated. It is certain that even a few grams can result in death.(306)

$KClO_3$ is readily absorbed from the alimentary tract, but not from the skin.(289) The general conclusion is drawn that $KClO_3$ can act toxically when taken per os.(32)

The syndrome of poisoning is rather that of a corrosive substance.(179) The chief toxic action of potassium chlorate is from the chlorate ion which produces gastritis, methemoglobinemia, methemoglobinuria, anoxia, and a toxic nephritis.(199) The slow excretion of the chlorate may lead to

cumulative poisoning if small doses of the salt are given over a long period of time.[92] Thienes and Haley state[289], however, that it is rapidly excreted unchanged by the kidneys, excretion being complete in 2 days.

(2) Sodium Chlorate

The toxic dose of $NaClO_3$ shows wide variations. It depends upon the age, the condition of the kidneys, and the amount of methemoglobin in the circulating blood. A dose of 1.77 grams is toxic to children while occasionally a dose of 30 grams is only slightly toxic to young persons.[64] One investigator gives a description of the chlorate content of the viscera of a man who died about 8-10 hours after taking 20-30 grams of $NaClO_3$.[282]

The lethal oral dose of the $NaClO_3$ for chicks is slightly greater than 5 grams per kg of body weight; for sheep it is between 2.06 and 2.50 grams per kg of body weight.[197]

Steyn found that in sheep 3 daily doses of 15 grams each produced death 20 hours after administration of the last dose; two 30 gram doses were fatal; whereas 20 daily doses of 7.5 grams produced only transient diarrhea and inappetence.[278]

In cats, the response to $NaClO_3$ was the same as found with $KClO_3$. Daily doses as high as 0.5 grams/kg are not toxic; a single dose of 1.35-1.94 grams/kg produces symptoms of toxicity and results in death.[177]

In rabbits given daily amounts up to 5 grams in a 10% solution produced no ill effects, but 10 grams in a single dose was either fatal or produced severe symptoms of poisoning. (151, 278) Clark and Hawley report a 2-4 gram/kg. dose by mouth is lethal to rabbits. (46)

A horse developed fairly severe symptoms of poisoning after the administration of 120 and 130 grams $NaClO_3$, respectively, whereas 60 grams produced only slight methemoglobinemia. (278)

A table showing the lethal dose of $NaClO_3$ for several animals is shown below: (270)

Animal	Route	Dosage, grams/kg
Rat	Oral	12.0
Rat	Intraperitoneal	6.0
Rabbit	Oral	8.0-12.0
Cat	Oral	1.35-1.94
Cat	Subcutaneous	1.0
Dog	Oral	0.7
Dog	Intraperitoneal	12.0
Dog	Intravenous	1.0 (5% soln. in water rapidly injected)

Seeds germinate in a 0.2% but not in 0.5% solutions of sodium chlorate. (46)

(3) Magnesium Chlorate

For the toxicity of this compound the data given for chlorate salts in general apply.[90] The toxicity of magnesium compounds is usually that of the anion.[254]

The LD_{50} for the rat (dosage which is lethal for 50% of the animals) is shown below:[270]

Animal	Route	Dosage, grams/kg
Rat	Oral	5.25
Rat	Intraperitoneal	1.10

(4) Aluminum Chlorate

In addition to the effects produced by the chlorate ion a local astringent action may occur due to the Al ion.[32]

(5) Calcium Chlorate

The LD_{50} for the rat is shown as:[270]

Animal	Route	Dosage, grams/kg
Rat	Oral	4.5 anhyd. salt
Rat	Intraperitoneal	0.625 anhyd. salt

3. PERCHLORATES

The perchlorate ion is a weak muscular poison. It is not cumulative, and does seem to be reduced in the animal organism.[140]

The toxic hazard rating, according to Sax, is "moderate" for irritant, ingestion and inhalation. Perchlorates are unstable materials, and are irritating to the skin and mucous membranes of the body wherever they

come in contact with it. Skin contact with these materials should be avoided.(254)

(1) Potassium Perchlorate

This compound is rated as very toxic using the system of Gleason et al(90) in assigning toxicity ratings. The probable lethal dose (human) is 50-500 mg/kg or between 1 teaspoonful and 1 oz for a 70 kg (150 lb) man.(90)

Disease in corn and other plants, traced to the presence of small percentages of $KClO_4$ and $NaClO_4$, was encountered in the early days of use of Chilean saltpeter as a fertilizer.(46)

(2) Sodium Perchlorate

When $NaClO_4$ is ingested by man it appears in the urine in 10 minutes. Fifty percent is eliminated in the urine in 5 hours and 95% in 48 hours.(46, 68)

Goldfish live indefinitely in a 0.1% solution; a 1.0% solution causes death with symptoms resembling asphyxia.(140)

Injections of $NaClO_4$ in animals cause a depression of the parasympathetic-vagal system; high doses produce complete paralysis. It is supposed that the $NaClO_4$ causes a decrease of the K ions in the blood with consequent change of the Ca:K ratio.(269) In rabbits the intravenous injection of 0.3 gram/kg produces no serious effects. Larger and repeated doses cause liver damage and violent diarrhea.(140) For rabbits the lethal dose of $NaClO_4$ is 2-4 grams/kg by mouth.(68)

As stated under potassium perchlorate, disease in corn and other plants, traced to the presence of small percentages of $NaClO_4$ and $KClO_4$, was encountered in the early days of use of Chilean saltpeter as a fertilizer.(46)

4. CATIONS OF CHLORATE AND PERCHLORATE COMPOUNDS

In addition to the toxicity of the chlorate and perchlorate ions of the compounds mentioned above, certain of the cations of these compounds may introduce an additional toxicity.

The toxicity of aluminum compounds has been thoroughly investigated, with particular reference to its use in cooking utensils. In comparison with heavy metals, aluminum is essentially non-toxic.(72, 32)

Ammonium salts cause convulsions.(99)

Barium salts, water or acid-soluble, are moderately toxic to extremely toxic.(199, 90) Barium stimulates smooth, striated and cardiac muscle; the result is violent peristalsis, arterial hypertension, muscle twitching, and disturbances in cardiac action. The central nervous system may be first stimulated and then depressed. Kidney damage has been described as a late complication, probably a result of circulatory insufficiency.(90) Ulceration of the bladder and inflamation of the bladder and urethra giving rise to painful micturation or a constant desire to micturate (strangury), often with haematuria, have been reported as occurring in poisoning by barium salts.(179) Acute toxicity varies widely with the compound, animal species, and even strain. Toxicity rating of 5, (extremely toxic), is probably the best description of clinical experience.(90)

Except for gastric irritation caused in part by osmotic disturbances, calcium per se has no significant oral toxicity.[90] Generally speaking, calcium compounds should be considered toxic only when they contain a toxic component or as calcium oxide or hydroxide.[254]

Lithium salts are rated as moderately toxic by Gleason et al.[90] Fatal cases of lithium poisoning have occurred when a lithium compound was used as a salt substitute in the diet. After a variable period of a few days to a few weeks of this type seasoning, the patients developed tremors, twitching of the muscles, hyperirritable reflexes, dizziness, apathy, confusion, difficulty in thinking, prostration, coma and death.[90, 92, 254] The toxic action of the lithium ion on the central nervous system was the cause of death in these cases.

The toxicity of magnesium compounds is classed as slight to moderate.[90, 254] Generally magnesium salts are so slowly absorbed that oral administration causes nothing more than purging. If evacuation fails to occur mucosal irritation and absorption occur. Systemically Mg^{++} produces central nervous depression, abolition of reflexes, and death from respiratory paralysis.[90] Inhalation of fumes or dust may cause irritation of respiratory tract.[199] For magnesium compounds, the maximum allowable concentration, ACGIH accepted, is 10 parts per million in air.[254]

Acute potassium intoxication from oral administration is highly improbable because large doses induce vomiting and because absorbed potassium is rapidly excreted (except in the face of pre-existing kidney damage). If the potassium ion is in excess in the tissues, however, the

rhythm of the heart is disturbed, cardiac contractility is weakened and cardiac collapse may result.[90, 92] Potassium salts are rated as moderately toxic; the probable lethal dose (human) is 0.5-5.0 grams/kg.

The ingestion of salts of silver or the inhalation of the dust of silver compounds can result in the absorption of silver compounds into the circulation and the subsequent deposition of the reduced silver in various tissues of the body. This produces a generalized greyish pigmentation of the skin and mucous membranes, a condition known as argyria.[254] It does not endanger life, but produces lifelong disfigurement.[179] Once deposited, there is no known method by which the silver can be eliminated; the pigmentation is permanent.[254] Generalized argyria appears slowly and may take up to twenty-five years to fully develop. Less severe and more localized cases can develop within two years. A grey pigmentation is usually first noticed around the eyes, and then spreads over the remainder of the face. The hands and forearms are usually involved early in the course of the disorder.[179] Inhalation of the dust of soluble silver salts or of excessive amount of metallic silver dust should be avoided.[72, 199]

BIBLIOGRAPHY

1. Accoscina, Filippo, and Schiovo, Silvia, Ann. Chim. (Rome) 43, 695-704 (1953).

2. Alonso, I. I. Fernández, and Gasco, L., C.A. 49, 7910[a].

3. Ames and Sears, J. Phy. Chem. 59, No. 1, 16-19 (1955).

4. Andauer, M., and Lange, E., C.A. 27, 4473[6].

5. Andreae, J. L., C.A. 7, 1654[7].

6. Anon., C.A. 14, 3157[1].

7. Anon., C.A. 15, 3700[2].

8. Ansidei, Reginaldo Manzoni, C.A. 34, 5756[3].

9. Banks, W. H., Ighellato, E. C., and C. W. Davies, Trans. Farady Soc., 27, 621-7 (1931).

10. Barcia, J. Gonzalez De, and Moles, E., C.A. 30, 6299[7].

11. Barker, Th. V., C.A. 1, 2674[7,8,9].

12. Basche, W., and Mark, H., C.A. 20, 3597[6].

13. Beauvilain, Maurice, Ann. Phys. 6, 502-60 (1936).

14. Beckenkamp, J., C.A. 14, 3354[1].

15. Bechmann, R., C.A. 46, 9920[h].

16. Bell, H. C., C.A. 18, 609[6].

17. Benrath, A., Hartung, P., and Wilden, M., C.A. 30, 367[2].

18. Berg, L., C.A. 21, 214[7].

19. Berg. L., C.A. 22, 737[7].

20. Bhagavantam, S., and Suryanarayan, D., C.A. 41, 4019[g].

21. Bhatnagar, S. S., and Kapur, Pyara L., C.A. 27, 215[6].

22. Boldivirev, A. K, C.A. 18, 1973[1].

23. Bonino, G. B., Manzoni-Ansider, R., and Pratesi, C. A. 27, 4736[5].

24. Bottcher, C.J.F., C.A., 40, 4586[7],

25. Bray, P. J., C.A. 49, 10737[e].

26. Brester, A., C.A. 21, 2836[8].

27. Brinkley, S. R., J.A.C.S., 62, 3524 (1940).

28. Bronsted, J.N., Z. Physik. Chem., 82, 621-40 (1913).

29. Brookes, V. J., and Alyea, H N., Poisons, 1946, D. Van Nostrand Co., N. Y.

30. Cady, H. P., and Taft; R., J. Phys. Chem., 29, 1057-74 (1925).

31. Cady, H.P. and Taft, R., J Phys. Chem., 29, 1075-85 (1925).

32. Caesar, Egbert, C.A. 13, 341[4].

33. Carnelley, Hill and Miller, J.A.C.S., 47, 2703 (1925).

34. Carpenter, C. D., C.A. 15, 1645[2].

35. Cauquil, G., Barrera, H., and Barrera, R., C.A. 49, 3038[d].

36. Cauquil, G., Barrera, H., and Barrera, R., C.A. 50, 2487[a].

37. Cavallaro, Leo, Gazz. Chim. Ital., 71, 63-72 (1941).

38. Cavallaro, Leo, Gazz. Chim. Ital., 71, 135-8 (1941).

39. Cavallaro, Leo, Gazz. Chim. Ital., 71, 269-88 (1941).

40. Cavallaro, Leo, Ber., 76B, 656-63 (1943).

41. Chandrasekharan, V., C.A. 47, 7325[b].

42. Chandrasekhar, S., C.A. 47, 8447[f].

43. Chaney, A. L., and Mann, C. A., J. Phys. Chem., 35, 2289-2314(1931)

44. Chapelle, Jean, and Gaby, Andre, C.A. 47, 7896[e].

45. Chatterji, A. C., and Kastogi, R. P., J. Indian Chem. Soc. 31, 63-8 (1954).

46. Clark and Hawley (Editors), The Encyclopedia of Chem., 237, 709 (1957).

47. Clausen, H., Annalen der Physik, 37, 51-67 (1912).

48. Clérin, Jacques, C. A. 40, 3966[3], 1946.

49. Clift, G. D., and Fedoroff, B. T., A Manual for Explosives Laboratories, Vol II, Lefax Soc. Inc., Phil. Pa. (1943).

50. Cohen, Ernst, and Cohen-De Meester, W. A. T., C.A. 27, 2076[8].

51. Colomina, M., and Nicolas, J., C.A. 44, 923[b].

52. Copaux, H., C.A. 1, 1242[9].

53. Copeland and Bragg, J. Phys. Chem., 58, No. 12, 1075-7 (Dec. 1954).

54. Copley, E. D., and Hartley, (Sir) Harold, J. Chem. Soc. 1930, 2488-91 (1930).

55. Copley, E. D., Murray-Rust, D. M., and Hartley, (Sir) Harold, J. Chem. Soc. 1930, 2492-8 (1930).

56. Cordes, H. F., and Fetter, N. R., J. Phys. Chem., 62, 1340 (1958).

57. Corey, Victor B., Phys. Rev., 64, 350-7 (1943).

58. Cornec, E., and Dickely, J., Compt. rend., 184, 1555 (1927).

59. Couture, Lucenne, and Mathieu, Jean-Paul, C.A. 43, 3294[d].

60. Davies, C. W., Trans. Faraday Soc., 23, 351 (1927).

61. Davies, C. W., Endeavour 4, 114-19 (1945).

62. Davis, T. L., The Chemistry of Powder and Explosives, I and II, 354-367, John Wiley and Sons, Inc., N. Y. (1953).

63. Dawson, L. R., Lester, G. R., and Sears, P. G., J. Am. Chem. Soc., 80, No. 16, 4233-5 (1958).

64. Derat, Maurice; Dérobert, Léon; Gerard, Maurice; Dupeyron, Therese, and Méroger, M. J., C. A. 45, 7696[f].

65. Dickinson, Roscoe G., and Dillon, Robert T., C. A. 23, 5107[9].

66. Dobroserdov, D., C. A. 22, 1112[7].

67. Dobroserdov, D., and Pshenichni, A., C. A. 21, 3841[6].

68. Durand, Jules, C. A. 32, 6674[8].

69. Duval, Clement, C. A. 42, 8698[c, d].

70. Duveau, Nanine, C. A. 38, 2566[2, 3].

71. Ekelin, Karin, and Sillen, Lars G., Acta. Chem. Scand., 7, 987-1000 (1953).

72. Elkins, H. B., The Chemistry of Industrial Toxicology, John Wiley and Sons, N. Y., 1950.

73. Euctien, A., Ann. Physik 34, 185-222.

74. Fajana and Johnson, J. A. C. S., 64, March, 668-78 (1942).

75. Ferrari, A., and Fontana, G. G., C. A. 22, 1257[5].

76. Flügel, F., Z. Physik Chem., 79, 577-91.

77. Fogg, P. G. T., J. Chem. Soc., 1958, 4111 (1958).

78. Forbes, Geo. S., and Elkins, H. B., J. A. C. S., 56, March, 516-21 (1934).

79. Fredenhagen, Karl, and Cactenback, Gustav, C. A. 24, 2938[5].

80. Frevel, L. K., Rinn, H. W., and Anderson, H. C., Ind. Eng. Chem., Anal. Ed., 18, 83-93 (1946).

81. Frivold, O. E., J. Franklin Inst., 208, 627-42 (1929).

82. Frivold, O. E., and Sogn, H., Ann. Physik, 23, 413-24 (1935).

83. Gajatto, Sante, C. A. 41, 1037[f].

84. Ganz, Ernst, Z. Physik, Chem., B33, 163-78 (1936).

85. Ganz, Ernst, and Gerlach, Walther, Physik Z., 37, 358-9 (1936).

86. Geffcken, W., Z. Physik. Chem., Abt. B., 5, 81-123 (1929).

87. Giacomini, Amedeo, and Pesce, Biazio, Ricerca sci., II, 605-18 (1940).

88. Gibson, R. E., J. Am. Chem. Soc., 57, 284-93 (1935).

89. Girard, Ch., Mon. sci., 23(4), 217.

90. Gleason, M. N., Gosselin, R. E., and Hodge, H. C., Clinical Toxicology of Commercial Products, Williams and Wilkins, Baltimore, 1957.

91. Gloy, Hermann, Physikalische, Berichte 9, 1082 (1928).

92. Gonzales, T. A., Vance, M., Helpern, M., and Umberger, C. J., Legal Medicine -Pathology and Toxicology, 2nd Edition, Appleton-Century-Crofts, Inc., N. Y., 1954.

93. Goodeve, Charles F., and Marsh, Arthur E. L., J. Chem. Soc., 1816-19 (1937).

94. Goodwin, H. M., and Kolmus, H. T., C.A. 3, 741-7.

95. Gopalokrishnan, C. P., J. Indian Inst. Sci., 39A, 13-18 (1957).

96. Gordon, Saul, and Campbell, Clement, Anal. Chem., 27, 1102-9 (1955).

97. Gottfried, C., and Schusterius, C., C.A. 27, 1795^{7}.

98. Gradwohl, R. B. H, Legal Medicine, C V. Mosby Co., St. Louis, 1954.

99. Gradwohl, R. B. H., Clinical Lab. Methods and Diagnosis, 5th Ed., II, C. V. Mosby Co., St. Louis, 1956.

100. Griffiths, V. S., Lawrence, K. S., and Pearce, M. L., J. Chem. Soc., 1958. 3998 (1958).

101. Griffiths, V. S., and Pearce, M. L. J. Chem. Soc., July, 3243-6 (1957).

102. Guareschi, I., C.A. 13, 689^{2}.

103. Hackenberg, E. G., and Ulich, H., Z. Anorg. Allgem. Chem., 243, 99-109 (1939).

104. Hagenmuller, Paul, Compt. rend., 232, 970-1 (1951).

105. Hanic, František, C.A. 50, 12569[i].

106. Harang, Leiv, C.A 22, 20889.

107. Harned, Parker, and Blander, J.A.C S., 77, April, 2071-3 (1955).

108. Hartley, H., and Barrett, W. H., J. Chem. Soc., 123, 398-401 (1923).

109. Hayek, E., and Schnell, E., C.A. 49, 60188.

110. Hearmon, R. F. S., C.A. 46, 64568.

111. Hein, Franz, C.A. 51, 10061g.

112. Hermann, Carl, C.A. 17, 36317.

113. Herrmann, K., and Ilge, W., C.A 25, 1420[2].

114. Hill, Arthur E., J. Am. Chem. Soc., 43, 254-68 (1921).

115. Hodgman, C. D., Handbook of Chem. and Physics, 39th Ed., Chem. Rubber Co., Cleveland, Ohio (1957).

116. Hofmann, K. A., and P. H. Marin, C.A. 27, 1264[1, 2].

117. Hölemann, P., and Kohner, H., Z. Physik. Chem., B 13, 338 (1931).

118. Hood, G. Raymond, J. Rheology, 3, 236-33 (1932).

119. Hooper, G. A., and Kraus, C. A., J.A.C.S., 56, Nov., 2265-8 (1934).

120. Hughes, Ward, and Hasty, J. of Ala. Acad. of Sci., 30, 20 (Oct. 1958).

121. Ievins, A., and Ozols, J., C.A. 50, 1405[b].

122. Ievins, A., and Ozols, J , C.A. 49, 8655[e].

123. Isbin, Herbert S., and Kobe, Kenneth A., J. Am. Chem. Soc., 67, 464-5 (1945).

124. Jackson, N. S., Smith, A. E. C., Gatty, O., and Wolfenden, J. H., J. Chem. Soc., 1376-9 (1934).

125. Jander, Gerhardt, and Kraffczyk, Karl. Z. annay. u. allegm. Chem. 282, 121-40 (1955).

126. Jennings, B. H., Hazardous Vapors and Dusts in Industry, Ventilating and Air Conditioning Contractors Ass'n. of Chicago, Chicago, Ill., 4-57 (1957).

127. Jolly, Wm. L., Chem. Revs., 50, 351-61 (1952).

128. Jona, Franco, C.A. 45, 3675e.

129. Jones, H. C., et al, Carnegie Inst. of Wash. Publ., No. 170, 16 (1912).

130. Jones, J. H., J.A.C.S., 65, July, 1353-4 (1943).

131. Jones, J. H., J.A.C.S., 67, May, 855-7 (1945).

132. Jones, J. H., J. Phys. Chem., 51, 2, 516-21 (1947).

133. Jones, J. H., J.A.C.S., 69, Aug. No. 8, 2065-6 (1947).

134. Jones, J. H., and Froning, H. B., J.A.C.S., 66, Oct., 1672-4 (1944).

135. Jones, G., and Ray, W. A., J.A.C.S., 63, Jan., 288-94 (1941).

136. Jones, G., and Talley, S. K., J.A.C.S., 55, Feb. 624-42 (1933).

137. Joy, W.E., and Wolfenden, J. H., Proc. Roy. Soc. (London), A134, 413-27 (1931).

138. Jung, Fritz, C.A. 43, 5864b.

139. Kabik, Irving, C.A. 41, 4311e.

140. Kahane, Ernest, C.A. 30, 3882l.

141. Kamiyoshi, Kan-ichi, C.A. 45, 5992a.

142. Kamiyoshi, Kan-ichi, C. A. 46, 1315[i].

143. Kartha, Gopinath, C. A. 46, 4312[c].

144. Kaye, Sidney, Handbook of Emergency Toxicology, Chas. C. Thomas, Springfield, Ill., 1954, p. 144.

145. Kelley, K. K., Bur. Mines, Bull., 350, 63 pages (1932).

146. Kireev, V. A., C. A. 41, 2976[h].

147. Kiriyama, Ryôichi, C. A. 45, 2278[d, e].

148. Kirk, R. E., and Othmer, D. F., Encyclopedia of Chemical Technology, 6, 1-90 (1951), The Interscience Encyclopedia, Inc., N. Y.

149. Kiss, Árpád, and Sándorfy, Camille, C. A. 44, 7652[a]

150. Kiyano, Setsuo, C. A 48, 8038[e].

151. Kleiner, Israel S., and Dotti, Louis B., C. A. 35, 1871[4].

152. Klochko, M. A., and Grigor'ev, I. G., Izvest. Sektora Fiz.-Khim. Anal., Inst. Obshchei Neorg. Khim. Akad. Nauk. S. S. S R., 21, 288-302 (1952).

153. Klochko, M. A., and Uchurkhanov, M. M., Izvest. Sektora Fiz-Khim, Analiza, Inst. Obshchei i Neorg. Khim. Akad Nauk, S. S. S. R., 22, 298-312 (1953).

154. Klochko M. A., and Uchurkhanov, M. M., Izvest. Sektora Fiz-Khim., Analiza, Inst. Obshche i Neorg. Khim. Akad. Nauk, S. S. S. R., 22, 313-19 (1953).

155. Klochko, M. A., and Uchurkhanov, M. M., Izvest. Sektora Fiz-Khim. Anal, Inst. Obshchei i Neorg. Khim., Akad Nauk S. S. S R., 22, 320-6 (1953).

156. Klochko, M. A., and Uchurkhanov, M. M., Izvest. Sektora Fiz-Khim. Anal., Inst. Obshchei i Neorg. Khim., Akad. Nauk S. S. S. R. 22, 326-36 (1953).

157. Klottman, Fr., C. A. 22, 1514[7, 8].

158. Koch, Sture, and Frivold, O. E., C. A. 40 6006[8].

159. Kohlrausch, F., Holborn, L., and Diesselhorst. H., Weid. Ann. Physik, 64, 417 (1898).

160. Kohner, H., Z. Physik. Chem., Abt. B, 1, 427-55 (1928).

161. Kojima, Shoji, Koto, Kiyoe, and Annaka, Shoichi, C.A. 51, 4819[c].

162. Kojima, S., Tsukada, K., Ogawa, S., and Shimauchi, A., C.A. 48, 4969[d].

163. Kraus, Charles, A., and Hooper, Gilman S., Proc. Nat. Acad. Sci., 19, 939-43 (1933).

164. Krishnamurti, P., C.A. 25 1160[2].

165. Kumari, C. Shanta, C.A. 43, 8880[f].

166. Kumari, C. Shanta, C.A. 45, 39[a].

167. Kumari, C. Shanta, Proc. Indian Acad. Sci., 32A, 177-83 (1950).

168. Kumari, C. Shanta, C A. 45, 948[h].

169. Lange, N. A., Handbook of Chem., 8th Ed., Handbook Pub. Inc., Sandusky, Ohio (1952).

170. Lange, E., and Robinson, A. L., Z. Physik, Chem. Abt. A, 148, 97-111 (1930).

171. Laski, G., C.A. 23, 1351[8].

172. Latimer, Wendell M, and Ahlberg, J. Elston, J. Am. Chem. Soc., 52, 549-53 (1930).

173. Latimer, Wendell M., Schutz, Philip W, and Hicks, Jr., J. F. G., J. Am. Chem. Soc., 56, 88-9 (1934).

174. Lester, Gover, and Sears, J. Phy. Chem., 60, No. 8, 1076-9 (1956).

175. Lilich, L. S., and Dzhurinskiĭ, B. F., Zhur. Obscheĭ Khim., 26, 1549-53 (1956).

176. Lilich, L S., and Mogilev, M. E., J. Gen. Chem. U.S.S.R., 26, 331-5 (1956)(Eng. Trans.).

177. Lipschitz, Werner, C. A. 26, 3297[8].

178. Lochet, Robert. Compt. rend., 231, 437-9 (1950).

179. Locket, S., Clinical Toxicology, 1957, C. V. Mosby Co., St Louis, pp. 74-76, 518, 591, 593, 598, 602.

180. Luder and Kraus, J. A. C. S., 69, No. 10, 2481-3 (1947).

181. Luder, Kraus, Kraus, Fuoss, J. A. C. S., 58, February, 255-8 (1936).

182. Lunden, Bertil, Svensk. Kemisk Jidskreft, 53, 86-96 (1941).

183. Lyght, C. E., Merck Manual, 9th Edition, 1956, Merck and Co., Inc., Rahway, N. J.

184. Manzoni-Ansidei, Reginaldo, C. A 36, 6082[9], 1942.

185. Mathieu, Jean Paul, and Couture C. A. 42, 8653[i].

186. Mathieu, Jean P., C. A 42, 8651[h].

187. Mathieu, Jean Paul, C. A. 44, 439[a].

188. Mathieu, J. P., C. A. 49, 56[e].

189. Mathieu, M. P., C. A. 45, 8326[e].

190. Mathieu, Lucienne Couture-, and Mathieu, Jean Paul, C. A. 46, 10765[g].

191. Mathieu, Paul, and Mathieu, Lucienne Couture-, C. A. 48, 1153[e].

192. Mathieu, Lucienne Couture-, Poulet, Henri, and Mathieu, Jean Paul, C. A. 46, 7876[i].

193. Mazzucchelli, A., and Anselmi, S., Gazz. Chim, Ital., 52, I, 147-52 (1922).

194. Mazzucchelli, Arrigo, and Pro, Drusilla, Gazz. Chim. Ital., 56, 99-111 (1926).

195. Mazzucchelli, A., and Rossi, Alba, Gazz. Chim. Ital., 57, 383-90, (1927).

196. McCrone, Walter C., C.A. 44, 9209c.

197. McCulloch, Ernest C., C.A. 34, 1387-7.

198. Mellor, J. W., Inorganic and Theoretical Chemistry, 1952, Longmans, Green and Co , London, II (1952).

199. The Merck Index, 6th Edition, Merck and Co., Inc., Rahway, N. J., 1952.

200. Mille, Luis Miraviteles, C A. 44, 3336g.

201. Miller, Foil A., and Wilkins, Charles H., Anal. Chem., No. 24, 1253-94 (1952).

202. Miller, M. L., and Sheridan, C. L. (I); Miller and Doran (II); Miller (III), J. Phys. Chem., 60, No. 2, 184-92 (1956).

203. Mishchenko, K. P., C.A. 47, 6225c-i 6226a-f.

204. Mochalov, K. N., C.A 29, 3241[2].

205. Moles, E., and Barcia, J. Gonzalez de, C.A. 31, 6830[1].

206. Monk, C. B., J.A.C.S., 70, Oct., 3281-3 (1948).

207. Mookherji, A., C.A. 49, 2136a.

208. Mookherji, A., Acta Cryst., 10, 25-6 (1957).

209. Moureu, H., and Mursch, H., C.A. 45, 5929h.

210. Murray, M. J., and Cleveland, Forrest F., C.A. 38, 300[3].

211. Murray-Rust, D.M., Hadow, H. J., and Hartley, Harold, J. Chem. Soc., 1931, 199-214 (1931).

212. Murray-Rust, D. M., Hadow, H. J., and Hartley, Harold, J. Chem. Soc., 1931, 215-19 (1931).

213. Nallet, Albert, and Paris, Rene A., C.A. 50, 9128d.

214. Naoum, P., and Aufschläger, R., C.A. 18, 3721[2].

215. Narasimhamurty, T. S., C.A. 49, 4400c.

216. Nicholson, Dan E., and Felsing, W. A., J. Amer. Chem. Soc., 72, 4469-71 (1950).

217. Nicholson, and Felsing, J.A.C.S., 73, No. 7, 3520-1 (1951).

218. Ollano, Z., C.A. 26, 5259[1].

219. Pacault, Adolphe, and Stoltz, Madeleine, C.A. 43, 5689[a, b, c].

220. Parker, H. C., and Parker, E. W., J.A.C.S., 46, 312 (1924).

221. Pascal, P., Pacault, A., and Jamet, C., C.A. 42, 6184[a, b, c].

222. Perucca, Eligio, C.A. 9, 407[7].

223. Perucca, Eligio, C.A. 14, 1478[8].

224. Pistorius, C.W. F. T., C.A. 52, 9763[b].

225. Platonov, F. P., C.A. 44, 9237[f].

226. Pócza, Jeno, C.A. 35, 5763[6].

227. Porter, Mary. W., C.A. 24, 4438[8].

228. Potjewijd, T., C.A. 29, 1985[8].

229. Prasad, Mata, and Desai, D. M., C.A. 44, 389[h].

230. Prasad, Mata, Dharmatti, S. S., and Biradar, N. S., C.A. 43, 4528[f].

231. Pullin, A. D. E., and Pollock, J. McC., Trans. Faraday Soc., 54, 11-18 (1958).

232. Rakshit, Jitendra Nath, Z. Elektrochem., 31, 97-101 (1925), cf., C.A. 17, 2808.

233. Rakshit, J. N., Z. Electrochem., 32, 276-81 (1926), cf., C.A. 19, 3195.

234. Ramachandran, G. N., C.A. 46, 10750[f].

235. Ramachandran, G. N., and Lonappan, M. A., Acta Cryst., 10, 281-7 (1957).

236. Ramaseshan, S., Proc. Indian Acad. Sci., 31A, 172-82 (1950).

237. Ramdas, A. K., C.A. 46, 10892[d].

238. Ramdas, A. K., C.A. 47, 2040[b].

239. Rao, C. Sambasiva, C.A. 31, 7314[4].

240. Rao, D. A. A. S, Narayana, C.A. 44, 10404[a].

241. Redlich, O., and Bigeleisen, J., J.A.C.S., 64, April, 758-60 (1942).

242. Riess, L., C.A. 3, 209[7], 1909.

243. Robertson, John B., S. African J. Sci., 30, 187-95 (1933).

244. Robertson, P.W., Dixon, R. M., Goodwin, W. G., McDonald, I. R., and Scaife, J. F., J. Chem. Soc., 294-9 (1949).

245. Robinson, R. A., Lim, C. K., and Ang, K. P , J. Am. Chem. Soc., 75, 5130 (1953).

246. Robinson, R. A., and Stokes, R. H., Trans. Faraday Soc., 45, 612-24 (1949).

247. Rocchiccioli, Claude, C. A. 50, 15236[e].

248. Rolla, M., C. A. 34, 4664[3].

249. Rosenfels, R. S., and Crafts, A. S., C.A. 36, 4277[6].

250. Rossini, F. D., et al, Selected Values of Chemical Thermodynamic Properties, N.B.S Cir 500, Feb. 1, 1952, Supt. of Docs., U. S. Printing Office, Wash. 25, D.C.

251. Rousset, Auguste, Laval, Jean, and Lochet, Robert, C.A. 39, 2930[1], 1945.

252. Rowley, H. H., and Seiler, Frank J., C.A. 35, 7266[8].

253. Rufer, Walter, Ann. Physik, 41, 301-12 (1942).

254. Sax, N. I , Dangerous Properties of Industrial Materials, Reinhold Publishing Corp., N. Y. (1957).

255. Scatchard, Geo., and Prentiss, S. S., J. A. C. S. 56, April, 807-11 (1934).

256. Scatchard, Geo., Prentiss, S. S., and Jones, P. T., J. A. C. S., 56, 805-7 (1934).

257. Schäfer, Kl., Masio, A. Perez, and Jüntgen, H., Z. Electrochem., 59, 425-34 (1955).

258. Schaefer, Clemens, Matossi, F., and Aderhold, H., C. A. 25, 1158[8].

259. Schreiner, E., and Frivold, O. E., Z. Physik. Chem., 124, 1-15 (1926).

260. Sears, Paul G., Lester, Geo. R., and Dawson, Lyle R., J. Phys. Chem., 60, 1433-6 (1956).

261. Seidell, A., Solubilities of Inorganic and Metal Organic Compounds, 3rd Ed. and Supplement, D. Van Nostrand Co., Inc., N. Y. (1940). Supp. (1952).

262. Sharma, S. S., C. A. 44, 8188[f].

263. Shatenstein, A. I., and Viktorov, M. M., C. A. 32, 7801[2].

264. Shen, S T., Yao, Y. T., and Wu, Ta-You, Phys. Rev., 51, 235-8 1937.

265. Sidgwick, N. V, The Chemical Elements and Their Compounds, Oxford Univ. Press, II, 1233 (1950).

266. Silveira, A., C. A. 26, 4254[4].

267. Smeets, C., C A. 27, 5267[2, 4].

268. Smith, G. Frederick, Rees, O. W., and Hardy, V. R., J. Am. Chem. Soc., 54, 3513-23 (1932).

269. Spagnol, Geronimo, C. A. 27, 1945[6].

270. Spector, Wm. S., Handbook of Toxicology, Acute Toxicities, Vol. I, 58, 180, 242, 270. W B. Saunders Co., Phila, 1956.

271. Spence, R. D., C. A. 49, 12124[a].

272. Stelling, Otto, C. A. 21, 1929[5].

273. Stelling, Otto, C. A. 23, 5411[9].

274. Stern, David R., The Explosive Sensitivity and Brisance of Ammonium Perchlorate, Tech. Rept. of Western Electrochemical Co., R. and D. Labs, July 1951.

275. Stern, David R., Impact Sensitivity of Ammonium Perchlorate, Tech. Rept. of Western Electrochemical Co., R. and D. Labs, July 1951.

276. Stettbacher, Alfred, C. A. 39, 2203[3, 4].

277. Steulmann, Gert, C. A. 26, 5802[6].

278. Steyn, D. G., C. A. 28, 2790[4].

279. Stokes, R. H., Trans. Faraday Soc., 44, 295-307 (1948).

280. Stokes, R. H., and Levien, Barbara J., C. A. 40, 2718[5].

281. Stocker, H., Z. Physik. Chem., 94, 149-80 (1920).

282. Strzyzowski, Casimir, C. A. 25, 5711[2].

283. Sutra, G., J. Chim. Phys., 43, 279-89 (1946).

284. Swanson, Howard E., Fuyat, Ruth K., and Ugrinic, George M., C. A. 48, 11184[g].

285. Teimni, I. K., J. Phys. Chem., 32, 604-15 (1928).

286. Tavernier, Paul, Mem. poudres, 38, 267-99 (1956), cf. C. A. 49, 12832[i]; 51, 1609[b], 1610[a].

287. Taylor, A. M., C. A., 24, 551[9].

288. Taylor, Guy B., and Cope, W. C., C. A. 9, 2799[7].

289. Thienes, C. H., and Haley, T. J., Clinical Toxicology, 168 (1955), Lea and Febiger, Phila.

290. Toubin, M. V., and Krasnova, S. I., C. A. 45, 5493[d].

291. Treadwell, W. D., and Ammann, A., Helv. Chem. Acta, 21, 1249-65 (1938).

292. Trew, V. C. G., Trans. Faraday Soc., 37, 476-92 (1941).

293. Trimble, Jr., R. F., J. Phys. Chem., 63, 318 (1959).

294. Tutton, A. E. H., C.A. 20, 3105[6].

295. Van Ruyven, B. H., Rec. Trav. Chim., 72, 739-62 (1953).

296. Van Rysselberghe, Pierre, and Fristrom, Robert M., J. Am. Chem. Soc., 67, 680-2 (1945).

297. Van Rysselberghe, P., and Hunt, G. J., J.A.C.S., 66, Sept., 1488 (1944).

298. Van Rysselberghe, P., and McGee, J. M., J.A.C.S., 65, April, 737-8 (1943).

299. Vegard, L., C.A. 17, 1356[6].

300. Vegard, L., C.A. 43, 4074[a]

301. Venkateswaran, C.S., C.A. 32, 5703[7].

302. Venkateswarlu, K., and Sandaram, S., J. Chem. Phys., No. 23, 2365-7 (1955).

303. Venkateswarlu, K., and Sandaram, S., Proc. Phys. Soc., 69A, 180-3 (1956).

304. Vitoria, Augusto Pérez, C.A. 24, 773[1].

305. Vorlander, D., and Kaascht, Erich, C.A. 17 2682[4, 5].

306. Wagner, Kurt, C.A. 30, 5304[9].

307. Walden, P., Ulich, H., and Busch, G., Z. Physik. Chem., 123, 429-71 (1926).

308. Washburn, E. W., International Critical Tables of Numerical Data, Physics, Chemistry, and Technology, Vol. I, McGraw-Hill Book Co., Inc. N. Y. (1926).

309. Washburn, E. W., International Critical Tables of Numerical Data, Physics, Chemistry, and Technology, Vol. III, McGraw-Hill Book Co., Inc., N. Y. (1928).

310. Washburn, E. W., International Critical Tables of Numerical Data, Physics, Chemistry, and Technology, Vol. IV, McGraw-Hill Book Co., Inc., N. Y. (1928).

311. Washburn, E. W., International Critical Tables of Numerical Data, Physics, Chemistry, and Technology, Vol. V, McGraw-Hill Book Co., Inc., N. Y. (1929).

312. Washburn, E. W., International Critical Tables of Numerical Data, Physics, Chemistry, and Technology, Vol. VI, McGraw-Hill Book Co., Inc., N. Y. (1929).

313. Washburn, E. Q., International Critical Tables of Numerical Data, Physics, Chemistry, and Technology, Vol. VII, McGraw-Hill Book Co., Inc., N. Y. (1930).

314. Weil, Annette, and Mathieu, Jean Paul, C. A. 49, 2190[d].

315. Weld, L. D., Phys. Rev., 7, 421-30 (1916).

316. West, C. D., C. A. 28, 5733[6].

317. Whiteley, M. A., Thorpe's Dictionary of Applied Chemistry, Vol. II, 525 (1946), Longmans, Green, and Co., London, N. Y.

318. Whiteley, M. A., Thorpe's Dictionary of Applied Chemistry, Vol. IV, 453-552 (1946), Longmans, Green, and Col, London, N. Y.

319. Willard, H. H., and Smith, G. F., J. Am. Chem. Soc., 44, 2255 (1922).

320. Williams, J. W., C. A. 22, 1897[5].

321. Williams, J. W., and Allgeier, R. J., J. A. C. S., 49, Oct., 2416-22 (1927).

322. Wolfsberg, Max, and Helmholz, Lindsay, C. A. 47, 2036[d].

323. Wulff, G., C. A. 17, 2375[6].

324. Yatsimirskiĭ, K. B., C. A. 42, 8604[d].

325. Yatsimirskiĭ, K. B., Zhur. Obschcheĭ Khim., 26, 2376-8 (1956).

326. Zachariasen, W. H., C A. 23, 5371[7, 8].

327. Zachariasen, W. H., C. A. 24, 4438[9].

328. Zachariasen, W. H., Phys. Rev., 36, 1693 (1931).

329. Zhuk, N. P., U S.S.R., Journal of Physical Chemistry, 28, 1690-7 (1954).

APPENDIX B

ANALYSIS OF CHLORATES AND PERCHLORATES

APPENDIX B. THE ANALYSIS OF CHLORATES AND PERCHLORATES

B1.1 Introduction

Since numerous elements may furnish the metallic, or basic, components of chlorate and perchlorate compounds, to present comprehensive analytical methods for the possible cationic partners in these compounds would result in an unwieldy volume. Many well organized schemes for the detection and estimation of the commonly met cations exist and are easily procurable. Therefore, the contents of this chapter are devoted, primarily, to qualitative and quantitative methods of analysis for the anions, chlorate and perchlorate.

B1.2 Pure Compounds

Chlorate and perchlorate ions may be reduced by various substances to chloride ions. Measurement of the quantity of the chloride ions produced, or of the amount of the reducing agent consumed, is the basis of the most widely used quantitative analytical methods. Because the chlorate ion is more susceptible to reducing action than the perchlorate ion, chlorates may be determined in the presence of perchlorates, and vice versa, by the proper choice of reducing agents and procedures. Once the reduction of chlorates or perchlorates has been carried out, the addition of silver nitrate to the resultant chloride solution gives qualitative determination by the precipitation of silver chloride. Reliable procedures for these

determinations, in the absence of interfering substances, are as follows:[a]

Chlorate

Dissolve 0.3 g of chlorate in 100 ml of water, add 50 ml of a 10 percent solution of crystallized ferrous sulfate, heat with constant stirring till the solution begins to boil, and keep at this temperature for 15 minutes. After cooling, add nitric acid until the deposited basic ferric salt is dissolved, and precipitate the chloride by means of silver nitrate. Allow the precipitate to settle in a dark place, filter through a Gooch crucible, and wash with water. Dry the precipitate at 100° and finally at 130° till a constant weight is obtained.

Perchlorate[b]

By twice igniting an intimate mixture of 0.5 g potassium perchlorate with 1.5-2 g of ammonium chloride in a platinum crucible covered with a watch glass, the perchlorate is completely changed to chloride. Care should be taken not to melt the residual chloride, for then the platinum is attacked, although the accuracy of the results is not affected. The reduction cannot be accomplished completely in a porcelain crucible unless platinum is present as a catalyzer. If 0.5 g of alkali perchlorate is mixed with 1 g of ammonium chloride, and 1 ml of chloroplatinic acid solution(0.0918 g Pt) is added, a complete reduction can be accomplished by igniting and repeating with two more additions of ammonium chloride.**(146)

---

a The portion of these procedures down to ** is reprinted with permission from F.P. Treadwell and William T. Hall, Analytical Chemistry, Vol. II, 9th English Ed., 5th Printing, (1947), John Wiley and Sons, Inc.

b When the perchlorate to be analyzed is ammonium perchlorate, this procedure must be altered. Reduction of the perchlorate to chloride is accomplished by fusion with sodium carbonate. This prevents the loss of the chloride equivalent to the quantity of perchlorate in the sample through volatilization as ammonium chloride. The procedure for ammonium perchlorate is given in the section on Industrial Specifications.

The residue should be taken up in water, made slightly acid with nitric acid, and the chloride precipitated with a solution of silver nitrate. Treat the silver chloride precipitated as stated in the chlorate procedure.

The general procedures given above may be followed for the analysis of the pure chlorate and perchlorate compounds of first interest in this work, viz., sodium, potassium, ammonium, lithium, aluminum, barium, calcium, magnesium, and silver. The high solubility of these compounds and the ease with which chlorate and perchlorate ions may be reduced, compared to their associated cation, permit a variety of analytical procedures which are listed later in this chapter. Also, based upon their oxidation-reduction potential, it would appear that chlorate and perchlorate compounds of secondary interest, such as those of cadmium, cesium, copper, lead, iron, nickel, rubidium, zinc, etc., might be analyzed by the same procedures, but those of cobalt, gold, chromium, manganese, and perhaps mercury, offer the possibility of cationic interference in the reduction step of any volumetric procedure. This interference could be overcome, however, by reducing the chlorate or perchlorate to chloride by ignition with ammonium chloride or sodium carbonate, followed by the determination of the chloride by a suitable method.

B1.3. Interferences

Among the matter which may interfere with chlorate and perchlorate determinations are: oxidizing substances, particularly other oxyhalogens; halides; and reducing substances, such as organic matter, which may lie

inactive in a mixture with chlorate or perchlorate until the analysis is underway.

When interfering substances are present, modification of procedures is required if the accurate determination of one or more sample constituents is desired. For example: perhaps one of the simplest cases which might be considered would be the existence of chloride, chlorate, and perchlorate in a material to be anlyzed. One way to analyze this mixture would be to determine the amount of chloride present in the sample originally, the amount present after reduction of the chlorate with ferrous sulfate, and the amount present after ignition with ammonium chloride (or sodium carbonate, if required). Each determination would be carried out on a separate portion of the sample, and from the results obtained, it is possible to calculate the chlorine present in the sample as chloride, chlorate, or perchlorate.

B1.4. Choosing an Analytical Method

Choice of a method of analysis may be influenced not only by the real or suspected presence of interfering substances, but, also, by accuracy required, speed of method, availability and cost of instrumentation, equipment, and analytical materials, skill of the analysts involved, safety, size and worth of the sample, and general acceptance of the method for the application. In research and development work, the need for a new method, or for the modification of a known method for a new application, may be encountered. It follows, then, that it is not possible to envision all of the analytical problems which could be associated with chlorates and perchlorates, nor to prescribe for these substances methods of analysis without

limits. To aid the chemist who must select a method of analysis or develop a new method of analysis for chlorates or perchlorates, the findings of an extensive search of the abstracts of the literature, and certain standard analytical works, pertaining to the analysis of these two anions are summarized in Tables B1-1 through B1-4. The methods for both chlorate and perchlorate are separated into qualitative and quantitative schemes, and when available from the abstract source, applications and interfering substances are noted. There is some overlap of methods since chlorates and perchlorates react identically in some instances. Where interferences are not specified, it is likely that one or more of the substances named earlier will provide analytical complications, if present. The use of blanks and knowns for comparison purposes is recommended for all analytical work wherever the slightest doubt exists as to the effect of a test reagent, sample constituent, or condition.

B1.5. Specification Test Methods

The military services specify reliable, practical tests which are performed in order to ensure that chlorates and perchlorates of certain chemical quality are being delivered. Currently, the compounds of greatest military use are ammonium perchlorate, potassium perchlorate, and potassium chlorate. Tests for these items, taken from the indicated military specification, are given below.

1. Military Specifications

a. MIL-P-150A Potassium Chlorate

(1) Moisture content. A carefully weighed portion of of the sample of approximately 10 grams (gm) shall be dried for 5 hours in an oven at 100° to 105°C, cooled in a desiccator, and reweighed. The loss in weight shall be calculated to percentage of moisture in the sample. This

TABLE B1-1. QUALITATIVE ANALYTICAL METHODS FOR CHLORATE

Method and Application	Interfering Substances	Reference Number
1. Reduction of chlorate by ferrous sulfate or a number of other reducing substances and adding silver nitrate to the acidified solution to precipitate silver chloride.	Oxyhalogens, halides	121, 146, 92
2. Heat sample with concentrated sulfuric acid; yellow fumes and detonations result.	*	121
3. Redox reaction with hydriodic acid, forming elementary iodine.	*	45
4. Reduction with sodium nitrite in acidic solution followed by the addition of silver nitrate to form silver chloride.	Bromate and iodate (remove with silver nitrate in a solution barely alkaline to phenolphthalein)	93
5. Heat sample with concentrated sulfuric acid. The chlorine dioxide given off is detected with benzidine acetate, diphenylamine, or starch-iodide paper. When benzidine acetate is used, up to 2500 parts of nitrate may be tolerated. Limit of identification is 1 gamma; concentration limit is $1:10^4$.	Nitrite (remove with sodium azide and acetic acid); halides and oxyhalides (remove with silver nitrate)	60
6. Blue color with diphenylamine is a positive test for oxidizing substances in a water extract of soil.	See Method 4	58

* Interfering substances not given.

TABLE B1-1. QUALITATIVE ANALYTICAL METHODS FOR CHLORATE (Cont'd)

Method and Application	Interfering Substances	Reference Number
7. Add copper phthalocyanine in concentrated sulfuric acid to test for oxidizing agents, including chlorate.	Sulfide, thiosulfate, thiocyanate, bromide, and iodide. Remove with mercuric acetate and barium chloride; arsenite interferes with removal.	19
8. Chlorate, bromate, and iodate in a 4:1 mixture of acetone-ammonium hydroxide separated by paper chromatography. Also, chlorate and chloride in 5:2:3 butyl alcohol to acetone to water.	*	100, 122, 123, 170
9. An unconventional systematic qualitative scheme for a mixture of certain cations and anions, including chlorates and perchlorates.	*	114
10. Urine containing chlorates, and other solutions of chlorate, turn aniline chloride-hydrochloric acid solution purple or blue, then green. Colorimetric estimation of chlorate is possible. Addition of certain solvents aids color development and retention.	Oxidizing compound, iodides, bromides	70, 83, 98, 154, 155

* Interfering substances not given.

TABLE B1-1. QUALITATIVE ANALYTICAL METHODS FOR CHLORATE (Cont'd)

Method and Application	Interfering Substances	Reference Number
11. Detection of chlorate in presenc of bromate and iodate by reduction with zinc in sulfuric acid solution, boiling to remove iodine, and precipitation of chloride with silver nitrate.	*	25
12. Solution of chlorate evaporated to dryness with ammonium thiocyanate, then heated to 140-50° to give orange-red color. Perchlorates do not give color.	Iodates, hypobromites, persulfates, and molybdates	99
13. The color of a solution of hydrochloric acid, sulfite, and indigo-carmine is changed by chlorate. Can detect chlorate in milk.	Hypochlorite, bromate, iodate, sulfite	61, 62, 78
14. To a solution of chlorate, add aniline sulfate, then sulfuric acid; at the liquid interface a blue color will appear. May be used on blood or urine samples.	Nitrates and iodates give a brownish-red color	28, 102
15 To a solution of chlorate. add benzidine sulfate, then sulfuric acid; at the liquid interface an orange color will appear.	Nitrates and iodates give the same color.	102

* Interfering substances not given.

NAVORD REPORT 7147 (VOLUME 1)

TABLE B1-1. QUALITATIVE ANALYTICAL METHODS FOR CHLORATE (Cont'd)

Method and Application	Interfering Substances	Reference Number
16. Finely powdered chlorate is treated with freshly prepared hydrogen sulfide water. A turbidity due to sulfur develops. May be used in presence of perchlorates and nitrates.	*	103
17. Chlorates, nitrites, and nitrates give colors with 1 and 2 anilinonaphthalenes, 1, 1' and 2, 2' dinaphthylamines, and phenyldihydrodibenzacridine.	*	110
18. Schemes for determining chlorate, bromate, and iodate in the presence of chloride, bromide, iodide, and sulfate ions.	*	69, 139
19. A method employing microorganisms for determining residual chlorate in soil samples.	*	136
20. Spot test for chlorate and periodate by the formation of inorganic phosphate.	*	43
21. A 1% solution of methylene blue added to a 1% solution of a chlorate precipitates dichroic (from blue to rose), doubly-refracting prisms.	*	2

* Interfering substances not given

NAVORD REPORT 7141, VOLUME 1)

TABLE B1-1. QUALITATIVE ANALYTICAL METHODS FOR CHLORATE (Cont'd)

Method and Application	Interfering Substances	Reference Number
22. Use of pyridine and sulfuric acid to detect chlorate in weed killers and nutrient water cultures. Nitrate, chloride, sulfate, and phosphate do not interfere.	*	107

* Interfering substances not given.

TABLE B1-2. QUANTITATIVE ANALYTICAL METHODS FOR CHLORATE

	Method and Application	Interfering Substances	Reference Number
1.	Reduction of chlorate by ferrous sulfate or a number of other reducing substances and a volumetric or gravimetric determination of the chloride produced.	Oxyhalogens, halides	121, 146
2.	Chlorate is determined by reduction with ferrous sulfate in the presence of bromate, hypochlorite, hypobromite, chloride, and bromide, which must be determined separately for calculation purposes. Chlorate is obtained by difference. Instead of titrating the excess ferrous ion, the ferric ion may be titrated with reducing agents. Also, conductimetric methods may be used.	*	1, 8, 15, 38, 59, 72, 125, 150, 167
3	By proper adjustment of reaction conditions, sodium arsenite may be used to determine chlorate, chlorite, and hypochlorite in a sample.	*	4, 50, 64, 95
4.	Reduction of chlorate with ferrous ethylene diamine sulfate and titration of excess reductant with potassium permanganate, potassium dichromate, or ceric sulfate.	*	126, 128, 129

* Interfering substances not given.

TABLE B1-2. QUANTITATIVE ANALYTICAL METHODS FOR CHLORATE (Cont'd)

	Method and Application	Interfering Substances	Reference Number
5.	Reduction of chlorate by direct titration with ascorbic acid. Perchlorate, chloride, and many other ions do not interfere.	Bromide, iodide, nitrate, hypochlorite, and other strong oxidizing or reducing agents	34, 35, 36, 37
6.	Reduction of chlorate to chloride with sodium sulfite and titration of the chloride with silver nitrate. Sodium sulfite may be used as the titrant. Modified procedures have been developed using potassium bisulfite.	*	97, 120, 158
7.	A rapid approximation (1-2% accuracy) of low concentrations (10-100 gamma/ml) of chlorate can be made by titration with standard solution of methyl orange.	*	20
8.	Spectrophotometric determination of traces of ammonium chlorate in ammonium perchlorate. Color is developed in water solutions by adding sulfuric acid and brucine.	*	32, 123
9.	Ion exchange of hydrogen ion for the cations associated with chlorates and titration of the acidic effluent with sodium hydroxide.	*	113

* Interfering substances not given.

TABLE B1-2. QUANTITATIVE ANALYTICAL METHODS FOR CHLORATE (Cont'd)

Method and Application	Interfering Substances	Reference Number
10. Reduction of chlorate with excess arsenous oxide and titration of the excess with ceric sulfate. Osmium tetroxide is necessary as a catalyst. Perchlorate does not interfere. Potassium permanganate or potassium bromate may be used as titrants.	Chloride (remove by adding mercuric perchlorate)	24, 50, 51, 96, 149, 151
11. Colorimetric estimation of chlorates using aniline chloride and standard chlorate solutions.	Oxidizing agents, strong reducing substances, compounds which produce colors in solution	153, 156, 157
12. A mixture of chlorate, chlorite, and hypochlorite may be analyzed with approximate accuracy by titrating iodine liberated from potassium iodide at controlled pH values	*	7, 18, 21, 76, 84, 108, 111, 137, 138, 141, 168
13. Reduction of chlorate with sulfur dioxide or sulfurous acid to chloride and determination of the chloride as silver chloride in mixtures of chlorate and perchlorate, railroad torpedoes, etc.	*	33, 84, 105, 117, 134

* Interfering substances not given.

TABLE B1-2. QUANTITATIVE ANALYTICAL METHODS FOR CHLORATE (Cont'd)

Method and Application	Interfering Substances	Reference Number
14. Reduction of chlorate with titanous salt and an electrometric titration or regular titration for excess titanous salt.	*	5, 57, 74, 163
15. Reduction of chlorate with ferrous chloride and titration of the ferric ion produced.	*	68
16. Reduction of chlorate to chloride with a cadmium reductor and titration of the chloride.	*	145
17. Chlorates and perchlorates may be reduced to chloride in mixtures with nitrate by copper powder. Chloride is titrated. To reduce chlorate only, substitute magnesium powder.	*	115, 116
18. Reduction of chlorate with hydrobromic acid. Released bomine is reacted with potassium iodide and liberated iodine titrated.	*	47, 89, 161
19. A comparison of several methods for determining chlorate.	*	162

* Interfering substances not given.

TABLE B1-2. QUANTITATIVE ANALYTICAL METHODS FOR CHLORATE (Cont'd)

Method and Application	Interfering Substances	Reference Number
20. Reduction of chlorate with formaldehyde and potassium persulfate to chloride and determination of chloride by a usual method. Perchlorates do not interfere. Modified procedures have been developed.	*	17, 106, 143
21. Reduction of chlorate with ferrous ammonium sulfate and titration of the ferric ion produced with stannous chloride or titration of the excess ferrous material with ceric sulfate.	*	65, 109
22. Reduction of chlorate with sodium nitrite and determination of the chloride by titration. Useful in mixtures with chlorides and hypochlorites.	*	3, 5, 48
23. Reduction of chlorate to chloride by zinc in acid solution and titration of the chloride. Can be used in mixtures with chloride and perchlorate. Zinc amalgam may be used in reduction step.	*	49, 56, 66, 101, 140, 143, 144
24. Reduction of chlorate with vanadous sulfate and titration of excess with potassium permanganate.	*	6, 172

* Interfering substances not given.

TABLE B1-2. QUANTITATIVE ANALYTICAL METHODS FOR CHLORATE (Cont'd)

Method and Application	Interfering Substances	Reference Number
25. Reduction of chlorate with thiourea and titration of the excess thiourea with potassium permanganate, etc.	*	85
26. Determination of chlorate by a polarographic method.	*	79
27. Reduction of chlorate with hydriodic acid in presence of ferrous sulfate catalyst.	*	46
28. Reduction of chlorate with cuprous chloride by direct titration or by adding an excess which is determined by titration with potassium dichromate. Useful in mixtures with hypochlorite.	*	147
29. Ion exchange method which adsorbs chlorate quantitatively; chlorate, bromate, and iodate may be separated in alkaline solutions.	*	73, 123
30. Reduction of chlorate with excess stannous chloride and titration of the excess with potassium permanganate.	*	56

* Interfering substances not given.

TABLE B1-3. QUALITATIVE ANALYTICAL METHODS FOR PERCHLORATE

	Method and Application	Interfering Substances	Reference Number
1.	Reduction of perchlorate by fusing with sodium carbonate and adding silver nitrate to the acidified solution to precipitate silver chloride.	Oxyhalogens, halides	92, 121
2.	Generation of oxygen during dry state heating of alkali perchlorates.	*	45
3.	Microscopic identification of the violet, lavender, or blue crystals of cupric tetrapyridine diperchlorate formed from dilute solutions.	*	124, 160
4.	α-Phenyl-β-diethylamminoethyl-p-nitrobenzoate forms difficultly soluble salts with nitric and perchloric acids.	Iodides, oxalates, thiocyanates, and dichromates	87
5.	A micro method depending upon the formation of rubidium perchlorate and its coloration by potassium permanganate. Useful in presence of chloride.	*	94

* Interfering substances not given.

TABLE B1-3. QUALITATIVE ANALYTICAL METHODS FOR PERCHLORATE (Cont'd)

	Method and Application	Interfering Substances	Reference Number
6.	Fusion of an alkali perchlorate with cadmium chloride yields chlorine which, in the gas phase, gives a blue color with the thio analog of Michler's ketone, or a red color with fluorescein-bromide mixtures. Detects 1-5 gamma of perchlorate in presence of 1000 gamma of nitrate or chlorate.	Any halogenate or nitrate (remove by a preliminary fuming and concentrated hydrochloric acid)	44
7.	Perchlorate and chlorate may be detected by means of fluorescence indicators.	*	52
8.	The crystals obtained when perchlorate and pyroantimonate are added to a saturated aqueous solution of iso-xanthocobaltic chloride are sufficiently characteristic for the identification of these ions.	*	171
9.	Titanium chloride in the presence of perchlorate and potassium iodide gives free iodine.	Chlorates	90

* Interfering substances not given.

TABLE B1-3. QUALITATIVE ANALYTICAL METHODS FOR PERCHLORATE (Cont'd)

Method and Application	Interfering Substances	Reference Number
10. Methylene blue with perchlorates forms a violet precipitate which, when filtered and ignited, decomposes with deflagration. Use in mixtures with persulfates and chlorates.	*	90
11. Chromatographic adsorption on aluminum hydroxide.	Chlorides, sulfates, heavy metals	118

* Interfering substances not given.

TABLE B1-4. QUANTITATIVE ANALYTICAL METHODS FOR PERCHLORATE

Method and Application	Interfering Substances	Reference Number
1. Reduction of perchlorate by fusing with sodium carbonate followed by a volumetric or gravimetric determination of the chloride produced.	Oxyhalogens, halides	27, 81, 121, 146
2. Use of tetraphenylarsonium chloride to precipitate the perchlorate ion by gravimetric or volumetric procedures. In similar methods, tetraphenylphosphonium chloride and tetraphenylstibonium chloride are used.	Oxidizing agents, halides, and certain metallic ions	164, 165
3. Reduction of perchlorate with titanous sulfate titration of the excess titanous ion with ferric ammonium sulfate in presence of ammonium thiocyanate. In modified methods, the chloride is titrated.	*	67, 77, 75, 142, 144, 152
4. Reduction of perchlorate with excess titanous chloride and titration of the excess with ferrous sulfate in the presence of thiocyanate. Useful for small quantities of perchlorate. Other titrants may be used.	Air must be excluded	31, 53, 63, 88, 91, 104, 134, 142, 152, 169

* Interfering substances not given.

TABLE 1-4. QUANTITATIVE ANALYTICAL METHODS FOR PERCHLORATE (Cont'd)

Method and Application	Interfering Substances	Reference Number
10. A chromatographic method employing an alumina column for adsorbing perchlorate.	*	80
11. A microgravimetric method for perchlorate using 3, 5, 6, 8-tetramethyl-1, 10-phenanthroline.	*	16
12. Determination of perchlorate in nitrate ore by heating with sodium oxalate and titrating the chloride produced with silver nitrate.	Steps for removing interferences of iodates, chlorates, and iron are given.	54
13. Determination of perchlorate in nitrate ore by precipitation with nitron in a gravimetric procedure.	Chlorate and nitrate must first be removed by reduction with Devarda's alloy.	159
14. Determination of perchlorate in nitrate ore by colorimetric procedures involving the reaction of perchlorate with the quaternary ammoniacal group of methylene blue, crystal violet, or malachite green.	Free iodine must be removed by boiling or reduction.	41, 42, 55, 71, 148

* Interfering substances not given.

TABLE B1-4. QUANTITATIVE ANALYTICAL METHODS FOR PERCHLORATE (Cont'd)

Method and Application	Interfering Substances	Reference Number
15. Reduction of perchlorate with excess ferrous ethylenediamine sulfate and titration of the excess with ceric sulfate in a potentiometric procedure.	Air must be excluded.	127
16. Determination of perchlorate, chlorate, and chloride in a mixture by fusion with sodium carbonate, fuming with nitric acid, and titration of chloride. Chlorate is obtained by difference.	*	86
17. Determination of perchlorate by heating with manganese dioxide.	*	82
18. Use of ferrous hydroxide to reduce perchlorate.	Sulfates and phosphates	142
19. Reduction of perchlorate to chlorine by starch and sulfuric acid, absorption and reduction of the chlorine to chloride by arsenous oxide, and gravimetric determination of the chloride as silver chloride	*	166
20. A comparison of several methods for perchlorate.	*	26, 39, 40

* Interfering substances not given.

TABLE B1-4. QUANTITATIVE ANALYTICAL METHODS FOR PERCHLORATE (Cont'd)

Method and Application	Interfering Substances	Reference Number
21. Reduction of perchlorate by potassium persulfate, nitrate, or dichromate in sulfuric acid, absorption and reduction of the chlorine formed in sodium sulfite or arsenite, and titration with silver nitrate.	*	11
22. Determination of perchlorate by precipitation with excess methylene blue chloride and titration of the excess with picric acid solution.	*	14
23. Gravimetric determination of perchlorate by precipitation with potassium acetate in alcohol. This is a modification of a previous differential solubility method.	Steps to eliminate the interferences of chloride, chlorate, and nitrate are given.	130, 131, 132
24. Reduction of perchlorate with sulfur and sulfuric acid, absorption of the hydrogen chloride evolved in sodium sulfite, and determination of chloride as silver chloride. Useful method for biological substances.	*	30
25. Reduction of perchlorate with chromic oxide and determination of the chloride by volumetric means. A comparison of several methods is given.	*	10

* Interfering substances not given.

TABLE B1-4. QUANTITATIVE ANALYTICAL METHODS FOR PERCHLORATE (Cont'd)

Method and Application	Interfering Substances	Reference Number
26. Reduction of perchlorate with bismuth amalgam and titration of the chloride formed.	*	133

* Interfering substances not given.

dried material shall be retained for determination of potassium chlorate [see (2)].

(2) Potassium chlorate. Approximately 0.15 gm of the of the dried sample retained from the moisture test [see (1)] shall be weighed accurately and dissolved in 100 milliliters (ml) of distilled water in a 500-ml Erlenmeyer flask. Five ml of sulfuric acid, and exactly 50 ml of an 8-percent solution of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (Mohr's Salt, or substantial equal) shall be added. A Bunsen valve shall be inserted in the flask and the solution heated to boiling. Two minutes after steam is emitted from the Bunsen valve, the source of heat shall be removed, and the flask and its contents cooled rapidly to room temperature. The Bunsen valve shall then be removed. Ten ml of Zimmerman-Reinhardt reagent (7 gm of $MnSO_4 \cdot 4H_2O$ are dissolved in 50 ml of water; cautiously add 12.5 ml of sulfuric acid and 12.5 ml of phosphoric acid, and dilute to 100 ml with water) shall be added. The excess of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in the solution shall be titrated with a standardized, approximately N/10 solution of potassium permanganate. Concurrently the blank value for exactly 50 ml of the $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ solution shall be determined. A 100-ml buret, with 50-ml bulb, accurately calibrated, with 0.1 ml subdivisions is most convenient for this titration. The potassium chlorate content shall be calculated as follows:

$$\text{Percent } KClO_3 = \frac{2.043\,(V - v)N}{W}$$

where:

V = ml of $KMnO_4$ required for blank.

v = ml of $KMnO_4$ required for sample.

N = normality of $KMnO_4$ solution.

W = dry weight of sample, in grams.

(3) Water-insoluble material. A carefully weighed portion of approximately 50 gm of the sample shall be dissolved in approximately 650 ml of warm water. The solution shall be filtered through a tared filtering crucible, and the residue washed with 5 portions of hot water. The crucible shall be dried for 1 hour at 105° C, cooled in the desiccator, and weighed. The increase in weight of the crucible shall be calculated to percentage of water-insoluble material. The filtrate, as well as the residue, shall be retained for subsequent determinations.

(4) pH value. The filtrate retained from the determination of water-insoluble material [see (3)] shall be cooled to room temperature, transferred to a 1000-ml volumetric flask with the aid of distilled water, and diluted to the mark. A portion of this solution shall be used to determine the pH value by means of a suitable standardized pH meter.

(5) Hypochlorites. A strip of potassium iodide-starch paper shall be added to the solution previously tested for pH value [see (4)] (This paper shall be of the same quality as furnished by the Naval Proving Grounds, Indian Head, Md for use in carrying out the standard KI test on pyrocotton, etc.). The immediate appearance of a blue coloration shall be considered to indicate the presence of hypochlorites. If no hypochlorites are

present, when testing grade A material, this solution shall be retained to test for chlorites. If hypochlorites are present the test for chlorites shall be disregarded.

(6) Chlorites. If a negative test for hypochlorites has been obtained by the test specified in (5), 2 ml of approximately N/10 sulfuric acid shall be added to the solution to determine presence of chlorites. Chlorites shall be reported absent if the standard potassium iodide-starch paper does not immediately turn blue.

(7) Chlorides. By means of an accurately calibrated pipette a 100-ml aliquot of the solution prepared for determining the pH value [see (4)], shall be transferred to a white porcelain dish, and 1 ml of a 5-percent solution of potassium chromate shall be added. The solution shall be titrated with a solution of silver nitrate containing exactly 4.791 gm of pure, dry $AgNO_3$ per liter of solution, to the first perceptible color change. The indicator blank shall be determined by titrating under the same conditions of lighting and background, 100 ml of distilled water containing 1 ml of the same potassium chromate solution, to the same color change. The percentage of chlorides, as potassium chloride, shall be calculated as follows:

$$\text{Percent KCl} = \frac{(V - v)0.21}{0.1W}$$

where:

V = volume of $AgNO_3$ required for sample.

v = volume of $AgNO_3$ required for blank.

W = weight of sample in (3)(moisture free basis).

(8) Bromates. By means of a pipette, a 200-ml aliquot shall be transferred from the solution prepared as specified under pH value [see (4)] to a 500-ml glass-stoppered iodine flask. Five ml of approximately 1:9 hydrochloric acid solution, 5 ml of freshly prepared 10-percent KI, and 5 ml of starch indicator solution shall be added. The flask containing the sample and reagents shall be stoppered and set in a dark place for 1 hour. The solution shall be titrated with approximately 0.02N $Na_2S_2O_3$ solution until the blue color disappears. A blank using 200 ml of the same distilled water used to prepare the solution and the same reagents shall be run concurrently. The percentage of potassium bromate in the sample shall be calculated as follows:

$$\text{Percent } KBrO_3 = \frac{2.783\,(V - v)N}{W}$$

where:

V = ml of $Na_2S_2O_3$ solution used for sample.

v = ml of $Na_2S_2O_3$ solution used for blank.

N = normality of $Na_2S_2O_3$ solution.

W = dry weight of sample in aliquot.

(9) Heavy metals. A 25-ml aliquot part of the solution, prepared as described in (4), shall be made acid with 1 ml of N/10 hydrochloric or sulfuric acid and hydrogen sulfide gas passed through the solution for about 30 seconds. No precipitation or coloration shall result.

(10) Alkaline earths. A 25-ml aliquot part of the solution prepared as described in (4) shall be made alkaline with 1 ml of a 10-percent solution of ammonium hydroxide. Five ml of a 10-percent solution of

ammonium oxalate shall be added and the solution heated nearly to boiling. Report the absence of alkaline earths if no precipitate is found when the liquid is cooled.

(11) Sodium salts.

(a) Magnesium uranyl acetate reagent preparation. Magnesium uranyl acetate reagent shall be prepared as follows: Solution A shall be prepared by dissolving 90 gm of uranyl acetate, $UO_2(C_2H_3O_2)_2 \cdot 2H_2O$, in 60 ml glacial acetic acid and sufficient distilled water to make a volume of 1 liter by heating to 70° C, and stirring until solution is complete. Solution B shall be prepared by dissolving 600 gm of magnesium acetate, $Mg(C_2H_3O_2)_2 \cdot 4H_2O$, in 60 ml of glacial acetic acid and sufficient distilled water to make a volume of 1 liter by heating to 70° C, and stirring until solution is complete. Solutions A and B shall be mixed together while at 70° C, and the mixture cooled to 20° C. The mixture shall be allowed to stand at this temperature for 2 hours or longer and then filtered through a dry filter paper into an amber-colored bottle. The bottle containing the solution shall be stored where it is not exposed to direct sunlight. If a precipitate appears on standing, the solution shall be filtered again prior to use.

(b) Alcohol wash liquid preparation. Ninety-five percent ethyl alcohol, at 29° C, shall be saturated with dry sodium magnesium uranyl acetate, and filtered prior to use.

(c) Procedure. A portion of the sample shall be ground to a fine powder and a weighed portion of approximately 20 gm of the ground material transferred to a beaker. Fifty milliliters of distilled water

shall be added and the solution heated to boiling. The solution shall be allowed to cool to room temperature and decanted through a filter, catching the filtrate in a small beaker. The solid residue shall be rinsed with two 5-ml portions of distilled water and these decanted through the filter, uniting the filtrate and washings. The solution shall be evaporated to a volume of 5 ml and cooled to room temperature. The supernatant liquid shall be filtered into a beaker, and the solid residue washed with 2-ml portions of distilled water, uniting the filtrate and washings. The solution shall be evaporated to a volume of approximately 5 ml and cooled to 20° ± 1° C. A 100-ml portion of magnesium uranyl acetate solution which has been held at 20° ± 1° C shall be added rapidly. The vessel containing the mixture shall be partially immersed in a bath maintained at 20° ± 1° C and the mixture stirred vigorously for 1 hour. The solution shall be filtered through a tared filtering crucible, using slight suction, and the precipitate transferred to the crucible by means of magnesium uranyl acetate solution. The precipitate in the crucible shall be washed with 5-ml portions of alcohol wash liquid, and the crucible sucked dry after each washing. The crucible and the contents shall be dried in an oven at 105° to 110° C for 30 minutes, cooled in a desiccator, and then weighed. To determine compliance with specifications, the weight of precipitate, sodium magnesium uranyl acetate, $NaMg(UO_2)_3(C_2H_3O_2)_5 \cdot 6\text{-}1/2H_2O$ shall be calculated to percentage of sodium chlorate in the sample as follows:

$$\text{Percent } NaClO_3 = \frac{7\ 07A}{W}$$

where:

A = weight of precipitate.

W = weight of sample (moisture-free basis).

(12) Grit. The residue obtained from the determination of water insoluble material [see (3)] shall be placed on a smooth glass plate and pulverized with the smooth steel blade of a spatula. To determine compliance with requirement any rough, foreign particles which tend to give the characteristic tactile sensation experienced when sand is ground between glass and steel in a similar manner shall be considered as grit.

(13) Granulation.

(a) Classes 1, 2, 3, 4, 5, and 7. An accurately weighed portion of about 100 gm of sample shall be placed on the specified nest of sieves complying with Specification RR-S-366, properly superimposed and assembled with a bottom pan. Lumps due to moisture shall be broken up by gentle brushing with a camel's hair brush. The sieves shall be covered and shaken for 10 minutes by hand or 5 minutes by means of a mechanical shaker geared to produce 300 ± 15 gyrations and 150 ± 10 taps of the striker per minute. The portions retained or passed by the various sieves shall be weighed and the results calculated to a percentage basis as required to determine compliance with requirements.

(b) Class 6 only.

Preparation of iso-propylalcohol wash solution.

A portion of approximately 5 gm of the sample shall be transferred to a 250-ml Erlenmeyer flask, and 150 ml of isopropyl alcohol added. The flask shall

be placed on a shaking machine and shaken for one hour at a temperature of 25° ± 5° C, then allowed to stand overnight at a temperature of 25° ± 5° C. The solution shall be decanted and filtered through a No. 41 Whatman filter paper. Reserve this solution for the determination of granulation of class 6 potassium chlorate.

Procedure. Accurately weighed portion of approximately 10 gm of the sample shall be placed on a 3-inch diameter No. 325 U. S. Standard sieve complying with Specification RR-S-366. The material on the sieve shall be washed with a steady, gentle stream of the saturated iso-propyl alcohol [see (2)] at a temperature of 25° ± 5° C, from a wash bottle, breaking up any lumps formed by touching them with a glass rod. Washing shall be continued until no more sample passes through the sieve. The washings shall be caught in a beaker. (Waste alcohol should be discarded in a waste solvent can.) During the washing the sieve shall be shaken gently and occasionally the bottom of the screen shall be tapped with a glass rod. The sieve shall be dried on a stream bath until the odor of alcohol can no longer be detected and then dried in an oven at 100° to 105° C for 15 minutes, cooled in a desiccator and the residue weighed.

(14) Magnesium carbonate in potassium chlorate (applicable to grade C only).

(a) Reagents and solutions.

Standard disodium dihydrogen ethylenediaminetetraacetate dihydrate (disodium versenate) (about 0.1M) - Dissolve 8.00 g disodium versenate in 2 liters of water. Standardize as in (14b).

Standard magnesium solution (1 mg per ml) - Dissolve 0.5000 g polished magnesium metal ribbon in 50 ml (1:10) HCl solution. Dilute to 500 ml with water.

Ammonium hydroxide - ammonium chloride buffer. - Dissolve 60 gm NH_4Cl in about 200 ml of water, add 570 ml of concentrated NH_4OH, and dilute to 1 liter with water.

F-241 indicator solution. - Dissolve 0.15 gm F-241 (Eriochrome Schwartz T) and 0.50 gm $Na_2B_4O_7 \cdot 10H_2O$ in 35 ml methanol. Warm to effect solution.

(b) Procedure.

Standardization of disodium versenate solution. Pipet 10 ml standard magnesium solution into 250-ml Erlenmeyer flask. Add 25 ml water. Add 10 ml NH_4OH-NH_4Cl buffer plus 3 or 4 drops F-241 indicator solution. Titrate against a white background under an incandescent light with disodium versenate solution to a pure blue end point (no trace of pink). Calculate the molarity of the disodium versenate solution as follows:

$$M = \frac{0.4112}{V}$$

where:

M = molarity of disodium versenate solution.

V = ml disodium versenate solution used in titration.

Determination of $MgCO_3$. Weigh a 1-gram sample to the nearest milligram into a 250-ml Erlenmeyer flask. Dissolve in 10 ml 1:10 HCl solution. Add 25 ml water and 10 ml NH_4OH - NH_4Cl

buffer plus 3 or 4 drops F-241 indicator solution. Titrate as in the paragraph immediately preceding.

$$\text{Percent } MgCO_3 = \frac{8.433\ VM}{W}$$

where:

M = molarity of disodium versenate solution.

V = ml disodium versenate solution used in titration of sample.

W = weight of sample in grams.

b. Proposed Specification for Ammonium Perchlorate[a, b]

(1) Moisture. Determine the moisture content according to method 3253 of Federal Test Method Standard No. 791, using benzene in place of the special solvent. The moisture content of the benzene must be determined and the necessary corrections applied.

(2) Water insoluble material. Weigh to the nearest milligram (mg) a 50-gram (gm) specimen and dissolve in 350 to 400 milliliters (ml) of water, warming slightly if necessary. Filter through a tared filtering crucible and wash with small portions of hot water. Dry for one hour at 105° C. Calculate the percent of water insoluble material as follows:

$$\text{Percent water insoluble material} = \frac{100\ A}{W}$$

a MIL-A-192A

b Distilled water and analytical reagent grade chemicals shall be used throughout the tests. Where applicable blank determinations shall be run and corrections applied where significant.

where:

A = weight of residue, in gm.

W = weight of specimen used, in gm.

(3) Sulfated ash. Transfer a weighed portion of approximately 5 gm of the specimen to a tared crucible and carefully heat over a bunsen flame. Keep the crucible partially covered until danger of loss due to splattering is eliminated and then complete the volatilization of ammonium salts in a furnace below red heat. Add a few drops of concentrated sulfuric acid, heat to remove excess acid, raise the temperature to a bright red heat. Cool in a desiccator and weigh. Calculate the weight of the residue as percent of sodium perchlorate in the sample as follows:

$$\text{Percent } NaClO_4 = \frac{172\ A}{W}$$

where:

A = weight of residue.

W = weight of specimen used.

(4) Chlorate.

(a) Ortho tolidine reagent preparation. Add 1 gm of ortho tolidine in small portions to 1 liter of 10 percent hydrochloric acid.

(b) Standard solution preparation. Dissolve 0.210 gm of sodium chlorate in water and dilute to 1 liter.

Grades A and B. For grades A and B take 0.2 ml of the standard [see (4b)] and dilute to 50 ml with water.

Grade C. For grade C take 1 ml of the standard [see (4b)] and dilute to 10 ml with water. Take 0.35 ml of this diluted material and dilute to 50 ml with water.

Grade D. For grade D take 1 ml of standard [see (4b)] and dilute to 50 ml with water.

(c) Procedure. Weigh 2 gm of specimen and dissolve in 50 ml of water. Take an applicable standard [see (4b)] and the dissolved specimen and to them add 49 ml of 1 to 1 hydrochloric acid and 1 ml of ortho tolidine solution. If after 5 minutes the specimen is darker than the standard, the specimen contains excess chlorate.

(5) Bromates. Transfer approximately 5 gm of the specimen weighed to the nearest gm, to a glass-stoppered Erlenmeyer flask and dissolve with approximately 150 ml of cool, freshly-boiled, water. Add 1 gm of potassium iodide, 5 ml of a 20-percent solution of hydrochloric acid, and 5 ml of 0.2-percent starch solution. Stopper the flask, agitate the solution, and allow to stand in a dark place for 1 hour. Titrate with 0.01 N sodium thiosulfate solution until the blue color disappears. Calculate the percent of bromates in the specimen as ammonium bromate, as follows:

$$\text{Percent of ammonium bromate} = \frac{2.432\ NV}{W}$$

where

N = normality of sodium thiosulfate solution

V = volume of sodium thiosulfate solution used for specimen in ml

W = weight of specimen used, in gm

(6) Chlorides. Transfer approximately 10 grams (gm) of the specimen, weighed to the nearest mg to a 1-liter beaker, add 200 ml

of water and heat until dissolved. Dilute to approximately 600 ml, add 10 ml of a 10 percent solution of silver nitrate, and stir vigorously. Heat to boiling, allow to stand for 30 minutes in a dark place and filter through a tared filtering crucible. Calculate the weight of residue, as percent ammonium chloride, as follows:

$$\text{Percent ammonium chloride} = \frac{37.3\,A}{W}$$

where

A = weight of residue, in gm

W = weight of specimen used, in gm

(7) Sulfates. Weigh approximately 10 gm of the specimen to the nearest milligram and dilute to 100 ml. Add 5 ml of a 10 percent hydrochloric acid solution, boil, add 10 ml of a 10 percent barium chloride solution, and allow to stand overnight. Filter through a tared crucible, wash, dry for one hour at 150° C, cool and weigh. Calculate the percent ammonium sulfate as follows:

$$\text{Percent } (NH_4)_2\,SO_4 = \frac{56.7\,A}{W}$$

where

A = weight of barium sulfate

W = weight of specimen

(8) Iron.

(a) Preparation of Specimen. Dissolve approximately 50 gm of specimen weighed to the nearest 0.01 gm in 300 ml of hot water. Cool and dilute to 500 ml in a volumetric flask.

(b) Preparation of Standard. Prepare a standard iron solution by dissolving 2.55 gm of ferrous ammonium sulfate in 10 ml of 10 percent sulfuric acid (H_2SO_4) and dilute to 100 ml. To 25 ml of this solution add 10 ml of 10 percent H_2SO_4 and dilute to 1 liter.

(c) Iron Determination. Pipette 10.0 ml of the specimen solution [see (8a)] into an evaporating dish, add 1 ml of concentrated hydrochloric acid (HCl) and evaporate to dryness. Dissolve in 2 ml of HCl and 10 ml of water and transfer quantitatively to a Nessler tube, add 3ml of a 30 percent ammonium hydroxide solution and dilute to 25 ml. For grade A ammonium perchlorate a control shall be made by adding 3.4 ml of the standard [see (8b)] to a Nessler tube containing the above reagents. For grade B material a control shall be made by adding 4 ml of the standard [see (8b)] to a Nessler tube containing the above reagents. If the specimen tube is darker than the control the specimen does not conform to the maximum iron requirements.

(9) Chromium.

(a) Preparation of Standard. Prepare a standard potassium chromate (K_2CrO_4) solution by dissolving 0.250 gm of K_2CrO_4 in 100 ml of water. Dilute 10 ml of this solution to 1 liter.

(b) Chromium Determination. Pipette 10 ml of the specimen solution [see (9a)] into a 100 ml Nessler tube. Add 3.0 ml of dilute (1.5) H_2SO_4, mix, add 1.0 ml of 0.25 percent diphenyl carbazide in alcohol solution, mix, and dilute to 100 ml. Prepare a control containing

the above reagents and 4.0 ml of the standard K_2CrO_4 solution of (9a). If the color produced by the specimen is darker than that of the control, the specimen does not meet the chromium requirements.

(10) Calcium and Magnesium as Oxides. Transfer approximately 20 gm of the specimen, weighed to the nearest mg, to a 400-ml beaker and dissolve with 50 to 100 ml of water. Acidify with 2 ml of hydrochloric acid, neutralize with ammonium hydroxide, and add a slight excess. Boil for 5 minutes, filter and wash the precipitate with water. Add to the filtrate 5 ml of a concentrated solution of ammonium phosphate, 5 ml of a concentrated solution of ammonium oxalate, and allow to stand overnight. Filter, wash with 2.5 percent ammonium hydroxide, ignite over a blast burner, and weigh to the nearest 0.1 mg in a tared crucible. Calculate the percent calcium oxide plus magnesium pyrophosphate in the sample as follows:

$$\text{Percent calcium oxide plus magnesium pyrophosphate} = \frac{100\ R}{W}$$

where

R = weight of residue, in gm

W = weight of specimen used, in gm

If the material fails to meet the requirements as specified, then the specimen shall be analyzed for calcium and magnesium oxide separately [see (10a) and (10b) below]

(a) Calcium Oxide. Dissolve 5 gm of the specimen, weighed to the nearest mg, in approximately 100 ml of boiling water.

Add 10 ml of concentrated hydrochloric acid and then ammonium hydroxide until slightly ammoniacal. Boil the solution and filter if necessary. Make the solution acid with a 10 percent solution of oxalic acid and add an excess of 10 ml of the acid. Heat the solution to boiling and add 10 ml of a saturated solution of ammonium oxalate with vigorous stirring. Allow the precipitate of calcium oxalate to settle for at least 1 hour, keeping the solution hot by means of a steam bath. Filter the solution through a sintered glass filter and wash the precipitate free of oxalic acid with water at room temperature. Retain the filtrate and washings for the determination of magnesium. Dissolve the precipitate in 10 ml of a 50 percent solution of sulfuric acid and wash the filter thoroughly with hot water. Dilute the filtrate and washings to approximately 100 ml with water, heat to 60° C, and titrate with 0.1 N potassium permanganate to the first discernible pink coloration. Calculate the percent calcium oxide in the sample as follows:

$$\text{Percent calcium as calcium oxide} = \frac{2.804\ VN}{W}$$

where

V = volume of potassium permanganate used, in ml

N = normality of potassium permanganate solution

W = weight of specimen used, in gm

(b) Magnesium Oxide. Dilute the filtrate and washings from the calcium oxalate filtration [see (10a) above] with water to 400 ml. Add 40 ml of a 10 percent solution of ammonium acid phosphate [$(NH_4)\ H_2PO_4$]. Add dropwise, with vigorous stirring, dilute ammonium hydroxide solution until the solution is ammoniacal. Add an excess of

concentrated ammonium hydroxide equivalent to 1/10 the volume of the solution. Allow the precipitate of magnesium pyrophosphate to settle for at least 4 hours, preferably overnight, filter and wash the residue thoroughly with a 1 percent solution of ammonium hydroxide. Ignite the precipitate gently at first and finally at approximately 1000° C to constant weight. Calculate the percent magnesium in the sample as magnesium oxide as follows:

$$\text{Percent magnesium, as MgO} = \frac{36.21\ A}{W}$$

where

A = weight of magnesium pyrophosphate in gm

W = weight of specimen used, in gm

(11) Purity. Transfer approximately 0.5 gm of the specimen weighed to the nearest 0.1 mg, to a platinum crucible containing approximately 5 gm of sodium carbonate and mix carefully to avoid any mechanical loss of the specimen. Fill the crucible with a known weight of sodium carbonate so that a correction can be made for any chlorine impurity in the sodium carbonate. Fuse the sodium carbonate and ammonium perchlorate carefully over a low flame for approximately 30 minutes and then gradually increase the flame to full. Dissolve the fusion in warm water to which a small amount of nitric acid has been added. Neutralize the solution with ammonium hydroxide, make slightly acid with nitric acid, add 20 ml of a 10 percent solution of silver nitrate, and stir vigorously. Heat to boiling and allow to stand overnight in a dark place. Add a few drops of the silver nitrate solution to test for complete precipitation and filter through a tared

filtering crucible. Calculate the weight of the residue as percent of the residue as percent of ammonium perchlorate in the specimen as follows:

$$\text{Percent of ammonium perchlorate} = \frac{81.97A}{W} - (2.2C \quad 1.1D \quad 0.96E)$$

where

A = weight of residue from specimen in gm

C = percent chlorides as ammonium chloride [see (6)]

D = percent chlorate as ammonium chlorate [see (4)]

E = percent ash as sodium perchlorate [see (3)]

W = weight of specimen used, in gm

(12) pH of Water Solution. Add 50 ml of freshly boiled water to 20 gm of specimen. Stir and cool to room temperature (20° to 25°C). Measure pH on any potentiometric meter having a glass electrode.

(13) Particle Size. Assemble the sieves conforming to Specification RR-S-366 beginning with the sieves with largest openings on top and proceeding to the bottom with the sieve on bottom having the smallest openings. Weigh 100 gm of ammonium perchlorate to the nearest 0.1 grams and place into the top of the assembled sieves. Shake on a mechanical shaker geared to produce 300 15 gyrations and 150 10 taps of the striker per minute for 5 minutes. If shaking is done by hand shake for 10 minutes.

(a) Class 1, 2, and 3. Brush the material adhering to the bottom of the top sieve into the next lower sieve, transfer the contents to a sheet of glazed paper, and weigh to the nearest 0.1 gm.

Clean the material from the remaining sieves in the same manner adding each fraction to the preceeding ones. Record the cumulative which is equal to the percentage cumulation retention of the original specimen.

c. JAN-P-217 Potassium Perchlorate

(1) Color of Aqueous Solution. Transfer a weighed portion of the sample to a beaker, add 300 ml of distilled water, warm until solution is complete, and cool to room temperature. By means of a colorimeter determine if the intensity of color of the solution is less than that of a solution of 0.005 gm of pure potassium chromate in 1 liter of distilled water.

(2) Moisture. Transfer a weighed portion of approximately 5 gm of the sample to a tared weighing bottle. Dry the bottle and contents at 105° C for 3 hours, cool in a desiccator, and weigh. Calculate the loss in weight as percentage of moisture in the sample.

(3) Grit. Transfer a weighed portion of approximately 10 gm of the sample to a 250 ml beaker and dissolve in 200 ml of boiling distilled water. Allow any insoluble matter to settle and rub with the smooth, flattened end of a glass rod. Note if any of the insoluble material consists of gritty particles.

(4) Acidity or Alkalinity. Dissolve a weighed portion of approximately 10 gm of the sample in 200 ml of hot distilled water, cool the solution to room temperature, and decant the resulting mixture through a rapid filter paper. Wash the residue several times with cold distilled water, using a total volume of not more than 50 ml. Add 3 drops of phenolphthalein indicator to the filtrate and note if the solution is alkaline as shown

by the development of a pink color. If no pink color develops, add 3 drops of methyl orange indicator and note if the solution is acid as shown by the development of a pink color.

(5) Chlorides. Dissolve a weighed portion of approximately 5 gm of the sample in 100 ml of hot distilled water. Make the solution just acid to methyl red indicator with 5 percent nitric acid solution, and then add 1 ml of a 35 percent nitric acid solution. Filter the solution if necessary. Add 5 ml of a 1 percent silver nitrate solution and boil until any precipitate coagulates. Transfer the precipitate to a tared filtering crucible and wash with a 1 percent nitric acid solution. Dry the crucible and residue in an oven at 135° C for at least 2 hours, cool in a desiccator and weigh. Calculate the increase in weight to percentage of potassium chloride in the sample on a moisture-free basis.

$$\text{Percent potassium chloride} = \frac{52.01\,A}{W}$$

where

A = weight of residue.

W = weight of dry sample

(6) Chlorates. Dissolve a weighed portion of approximately 5 gm of the sample in 100 ml of hot distilled water. Add 10 ml of a 4 percent ferrous ammonium sulfate solution, and boil for 5 minutes. Cool the solution to room temperature and filter if necessary. Make the solution just acid to methyl red indicator with 5 percent nitric acid solution, and then add 1 ml of a 35 percent nitric acid solution. Filter the solution if necessary. Add 5 ml of a 1 percent silver nitrate solution and boil until any

precipitate coagulates. Transfer the precipitate to a tared filtering crucible and wash with a 1 percent nitric acid solution. Dry the crucible and residue in an oven at 135° C for at least 2 hours, cool in a desiccator and weigh. Correct for any chlorides found present. Calculate the increase in weight to percentage of potassium chlorate in the sample on a moisture-free basis, correcting for chlorides and bromates.

$$\text{Percent potassium chlorate} = \frac{85.50\,A}{W} - 1.64B - 1.36C$$

where

A = weight of residue

B = percent potassium chlorides [see (5)]

C = percent potassium bromate [see (8)]

W = weight of dry sample

(7) Hypochlorites. Add a strip of potassium iodide-starch paper to the solution previously tested for acidity. (This paper should be of the same quality as furnished by the Naval Powder Factory, Indian Head, Md., for use in carrying out the standard KI test on pyrocotton, etc.). Consider the immediate appearance of a blue coloration to indicate the presence of hypochlorites.

(8) Bromates. Transfer a weighed portion of approximately 10 gm of the sample to a 500 ml flask provided with a glass stopper. Add 200 ml of freshly boiled and cooled distilled water to dissolve the sample. Add 5 ml of approximately 1:9 hydrochloric acid solution, 5 ml of freshly prepared 10 percent KI and 5 ml of starch indicator solution prepared by making a very thin paste of 4 gm of soluble starch in cooled

distilled water mixed into 2 liters of hot distilled water and boiling for a few minutes. (Keep the starch solution in glass-stoppered bottles in a cool, dark place.) Stopper the flask containing the sample and reagents, set in a dark place for 1 hour and titrate with approximately 0.02 N sodium thiosulfate solution until the blue color disappears. Run a blank on the reagent and calculate the percentage of potassium bromate in the sample.

$$\text{Percentage of potassium bromate} = \frac{2.783(V - v)N}{W}$$

where

V = ml of sodium thiosulfate solution used for sample.

v = ml of sodium thiosulfate solution used for blank.

N = normality of sodium thiosulfate solution.

W = weight of sample.

(9) Sodium Salts.

(a) Magnesium uranyl acetate reagent preparation.

Prepare magnesium uranyl acetate reagent as follows: Prepare solution A by dissolving 90 gm of uranyl acetate, $UO_2(C_2H_3O_2)_2 \cdot 2H_2O$, in 60 ml of glacial acetic acid and sufficient distilled water to make a volume of 1 liter by heating to 70° C, and stirring until solution is complete. Prepare solution B by dissolving 600 gm of magnesium acetate, $Mg(C_2H_3O_2)_2 \cdot 4H_2O$, in 60 ml of glacial acetic acid and sufficient distilled water to make a volume of 1 liter by heating to 70° C and stirring until solution is complete. Mix together solutions A and B while at 70° C, and cool the mixture at 20° C. After allowing the mixture to stand at this temperature for 2 hours or longer, filter it through a dry filter paper into an amber-colored bottle. Store the

bottle containing the solution where it is not exposed to direct sunlight. If a precipitate appears on standing, filter the solution again prior to use.

(b) Alcohol wash liquid preparation. Saturate 95-percent ethyl alcohol at 29° C with dry sodium magnesium uranyl acetate, and filter prior to use.

(c) Procedure. Grind a portion of the sample to fine powder and transfer a weighed portion of approximately 10 gm of the ground material to a beaker. Add 50 ml of distilled water and heat to boiling. Allow the solution to cool to room temperature and decant through a filter catching the filtrate in a small beaker. Rinse the solid residue with two 5 ml portions of distilled water and decant these through the filter, uniting the filtrate and washings. Evaporate the solution to a volume of 5 ml and cool to room temperature. Filter the supernatant liquid into a beaker and wash the solid residue with two 2 ml portions of distilled water, uniting the filtrate and washings. Evaporate the solution to a volume of approximately 5 ml and cool to 20° ±1° C. Add rapidly 100 ml of magnesium uranyl acetate solution which has been held at 20° ±1° C. Partially immerse the vessel containing the mixture in a bath maintained at 20° ±1° C, and stir the mixture vigorously for 1 hour. Filter through a tared filtering crucible, using slight suction, transferring the precipitate to the crucible by means of magnesium uranyl acetate solution. Wash the precipitate in the crucible with 5 ml portions of alcohol wash liquid, allowing the crucible to be sucked dry after each washing. Dry the crucible and contents in an oven at 105° to 110° C for 30 minutes, cool in a desiccator, and weigh. Calculate the weight

of precipitate, sodium magnesium uranyl acetate, $NaMg(UO_2)_3(C_2H_3O_2)_5 \cdot 6\text{-}1/2H_2O$ to percentage of sodium perchlorate in the sample.

$$\text{Percentage of sodium perchlorate} = \frac{8.13\ A}{W}$$

where

A = weight of precipitate

W = weight of sample.

(10) Calcium salts. Dissolve 5 gm of the sample in approximately 100 ml of boiling distilled water. Add 10 ml of concentrated hydrochloric acid to the solution, then ammonium hydroxide until slightly ammoniacal. Boil the solution and filter if necessary. Make the solution acid with a 10-percent solution of oxalic acid and add an excess of 10ml of the acid. Heat the solution to boiling and add 10 ml of a saturated solution of ammonium oxalate with vigorous stirring. Allow the precipitate of calcium oxalate to settle for at least 1 hour, keeping the solution hot by means of a steam bath. Filter the solution and wash the precipitate free of oxalic acid with distilled water at room temperature. Retain the filtrate and washings for the determination of magnesium salts. Dissolve the precipitate in 10 ml of approximately 50-percent sulfuric acid solution and wash the filter thoroughly with hot distilled water. Dilute the filtrate and washings to approximately 100 ml, heat to 60° C, and titrate with 0.1 N potassium permanganate to the first discernible pink coloration. Calculate the percentage of calcium salts in the sample as calcium oxide as follows:

$$\text{Percentage of calcium salts as CaO} = \frac{2.804\ VN}{W}$$

where

V = ml of potassium permanganate used

N = normality of the potassium permanganate solution

W = weight of sample.

(11) Magnesium salts. Dilute the filtrate and washings from the calcium oxalate filtration with distilled water to 400 ml. Add 40 ml of 10 percent ammonium acid phosphate solution. Add dropwise, with vigorous stirring, dilute ammonium hydroxide solution until the mixture is ammoniacal. Add an excess of concentrated ammonium hydroxide equivalent to 1/10 of the volume of the solution. Allow the precipitate of magnesium pyrophosphate to settle for at least 4 hours, preferably over night, filter and wash the residue thoroughly with 1 percent ammonium hydroxide solution. Ignite the precipitate, gently at first and finally at approximately 1000° C to constant weight. Calculate the percentage of magnesium salts in the sample as follows:

$$\text{Percentage of magnesium salts as MgO} = \frac{36.21A}{W}$$

where

A = weight of residue

W = weight of sample.

(12) Purity.

(a) First method. Mix intimately an accurately weighed portion of approximately 0.5 gm of the sample with approximately 2 gm of ammonium chloride in a platinum crucible. Cover the crucible, place in a cold muffle furnace and bring the temperature of the muffle

furnace up to approximately 600° C gradually over a period of 1-1/2 hours. Remove the cover, add 2 gm of ammonium chloride, mix and continue heating in the muffle at approximately 600° C for an additional period of approximately 1 to 1-1/2 hours until complete volatilization of the ammonium chloride is assured. Dissolve the melt in approximately 200 ml of boiling water. Add 4 ml of 35-percent nitric acid and 10 ml of 10 percent silver nitrate solution. Boil the solution until the supernatant liquid is clear, filter through a tared filtering crucible, and wash the precipitate of silver chloride thoroughly with 1 percent nitric acid solution. Ignite the crucible and residue gently or dry in an oven at 135° C for at least 1 hour, cool in a desiccator and weigh. Calculate the increase in weight to percentage of potassium perchlorate in the sample on a moisture-free basis, correcting for chlorides, chlorates and sodium perchlorate.

$$\text{Percent potassium perchlorate} = \frac{96.66A}{W} - 1.86B - 1.13C - 1.13D$$

where

A = weight of precipitate.

B = percent potassium chloride [see (5)].

C = percent potassium chlorate [see (6)].

D = percent of sodium perchlorate [see (9)].

W = weight of the dry sample.

(b) Alternate method. Transfer an accurately weighed portion of approximately 0.5 gm of the sample to a Parr sulfur bomb cup (iron). Add 1 gm of NaOH pellets and approximately 14 gm of sodium

peroxide-sucrose mixture (12 gm of 40-mesh sucrose to 250 gm of sodium peroxide). Assemble and tighten the bomb and place the holder within a shield. Ignite the contents of the bomb by directing the flame of an oxy-gas burner against the bottom of the cup. After the initial ignition continue the heating until the lower half of the cup attains an even cherry-red color. Remove the bomb from the shield allow to stand for approximately 5 minutes and then cool in water. Remove the outer fastenings without disturbing the cap, wash the exterior of the cup and cap with water and discard the washings. Remove the cap, place the cup on its side in an 800 ml beaker, wash the material adhering to the underside of the cap into the beaker with a stream of water from a wash bottle cover with a watch glass and add water until the cup is approximately 3/4 covered. When the material in the cup is dissolved, add 2 gm of sodium peroxide, stir, boil until the peroxides are decomposed and allow to cool. Lift the cup from the solution and rinse thoroughly with a stream of 1:20HNO_3 from a wash bottle. Add 1:1 HNO_3 in small portions allowing sufficient time between additions of the acid for the completion of the reaction in order to avoid a large excess of acid. When the solution is clear, cool and determine the total halogen by the Volhard method. The iron in solution (from the cup) acts as the indicator. Calculate the result on a moisture-free basis to percent potassium perchlorate correcting for chloride, chlorate and sodium perchlorate as follows:

$$\text{Percent potassium perchlorate} = \frac{13.86(AN - BN_1)}{W} - 1.86C - 1.13D - 1.13E$$

where

A = ml of $AgNO_3$ used

B = ml of KCNS used

C = percent chloride as KCl [see par. (5)]

D = percent chlorates as $KClO_3$ [see par. (6)]

E = percent $NaClO_4$ [see par. (9)]

N = normality of $AgNO_3$ used

N_1 = normality of KCNS used

W = weight of dry sample.

(13) Granulation. Place an accurately weighed portion of approximately 100 gm of the sample on the specified nest of sieves properly superimposed and assembled with a bottom pan. Add 2 metal washers weighing not more than 15 gm to the upper sieve to help break up lumps. Cover and shake for 5 minutes by hand or mechanically by means of a shaker geared to produce 300 ± 15 gyrations and 150 ± 10 taps of the striker per minute. Weigh the portions retained or passed by the various sieves and calculate the results to a percentage basis.

2. Industrial Specifications

Specifications which have been developed directly from the military specifications or are based on plant experience are being used by industrial concerns. In particular company specifications on ammonium and potassium perchlorate are used by the following companies:

Aerojet-General Corporation

Astrodyne, Inc.

Atlantic Research Corporation

Thiokol Chemical Corporation

The analytical methods used in these specifications are essentially the same for each company. As an illustration of these procedures the methods used by Aerojet-General Corporation are reproduced in the following sections.

a. Ammonium Perchlorate (Unground, Crystalline) AMS-C66 (Aerojet-General Corporation)[a]

(1) Water insoluble. Heat 15 g NH_4ClO_4 in about 200 cc of distilled water until all salt is dissolved (just below boiling). Filter hot on dried and weighed Gooch crucible. Wash with hot water, dry in oven and reweigh. Difference is insoluble matter.

(2) Ash (Sulfuric Acid Treated). Add 4 or 5 drops concentrated H_2SO_4 to 2 g of NH_4ClO_4 in dried and weighed porcelain crucible. Heat on hot plate to fumes, but do not let mixture ignite. When material has almost completely disappeared, ignite over burner for a few seconds, cool and reweigh crucible. Difference is H_2SO_4 treated ash.

(3) Chlorates as sodium chlorate. Same as paragraph F-4h in JAN-A-192 specification. (See b. 4)[b]

a Reproduced by special permission from Aerojet-General Corporation, Sacramento, California.

b Refers to paragraphs in section B1. 5 of this Appendix.

(4) Chlorides as ammonium chloride. Same as paragraph F-4e in JAN-A-192 specification. (See b. 6)

(5) Sulfates as ammonium sulfates. Dissolve 5 g of NH_4ClO_4 in about 100 cc hot distilled water; add 2 or 3 drops concentrated HCl and 5 cc 10% Ba Cl_2 solution. Let settle on hot plate just below boiling for at least one hour; then filter on dried and weighed Gooch crucible. Wash with hot water and dry to constant weight. Reweigh crucible, difference is weight of (Ba SO_4•$(NH_4)_2SO_4$) = (Ba SO_4 x 0.5661).

(6) Bromates as sodium bromate. Same as paragraph F-4 g in JAN-A-192 specification. (See b. 5)

(7) Non-alkali metals. Dissolve 15 g NH_4 ClO_4 in about 200 cc hot distilled water, made slightly acid with HCl; filter off insolubles. Make filtrate definitely alkaline with Na_2CO_3: let digest and settle, filter while hot on dried and weighed Gooch crucible. Wash with hot water, ignite, and weigh crucible. Difference in weight is oxides of heavy metals.

(8) Moisture.

(a) Surface moisture. A sample of ammonium perchlorate is put in 60/40 benzene-methanol mixture and the surface moisture is determined by adding an excess of Karl Fischer reagent and back titrating automatically with water-methanol solution to an electrometric end point.

(b) Total moisture. A sample of ammonium perchlorate is dissolved in a 60/40 mixture of ethylene glycol-methanol. The total moisture is determined by adding an excess of Karl Fischer reagent and back titrating automatically with water-methanol solution to an electrometric end point.

(9) Reaction to methyl orange. Solution of NH_4ClO_4 in distilled water should be neutral to methyl orange.

(10) Ammonium perchlorate assay. Same as paragraph F-4j in JAN-A-192 specification. (See b.11)

(11) Screen analysis. Screen analyses are determined on 25 g of dry material using Tyler Standard Screens automatically shaken for ten minutes. The following screen meshes are used:

325, 150, 100, 48, 16.

b. Potassium Perchlorate (Unground Crystalline) AMS-C1 (Aerojet-General Corporation)[a]

(1) Organics. Add 10 cc ethyl ether to 10 g $KClO_4$. Stir 3 or 4 times, pour off ether and add a pinch of anhydrous Na_2SO_4 to ether extract. Wash $KClO_4$ with 5 cc ether and add to extract, stir, let settle and filter ether extract into weighed aluminum dish. Distill off ether at room temperature and reweigh dish. Difference is organic material.

(2) Grit. Same as paragraph F-4c in JAN-P-217 specification. (See C.3)[b]

---

a Reproduced by special permission from Aerojet-General Corporation, Sacramento, California.

b Refers to paragraph in Section B1-5 this Appendix.

(3) Odor. Solution of $KClO_4$ in water should be odorless.

(4) Color of solution. Same as paragraph F-4a in JAN-P-217 specification (see c. 1).

(5) Chlorates as potassium chlorate. Same as paragraph F-4f in JAN-P-217 specification (see c. 6).

(6) Chlorides as potassium chloride. Same as paragraph F-4e in JAN-P-217 specification (see c. 5).

(7) Bromates as potassium bromate. Same as paragraph F-4h in JAN-P-217 specification (see c. 8).

(8) Sodium as sodium chloride. Dissolve 10 g $KClO_4$ in 250 cc boiling distilled water. After cooling make to 250 cc in volumetric flask and take sample of supernatant liquid for analysis in flame spectrophotometer.

(9) Calcium and magnesium salts as calcium chloride and magnesium chloride. Same as paragraphs F-4j (see c. 10) and F-4k (see c. 11) in JAN-P-217 specification.

(10) Hypochlorites. Same as paragraph F-4g in JAN-P-217 specification (see c. 7).

(11) Insoluble. Heat 15 g K ClO_4 in about 200 cc of distilled water until all salt is dissolved (just below boiling). Filter hot on dried and weighed Gooch crucible. Wash with hot water, dry in oven and reweigh. Difference is insoluble matter.

(12) Nitrogen compounds. Digest 0.2 g $KClO_4$ in micro-kjeldahl flask with usual Kjeldahl reagents and distill into standard acid. Calculate amount of N.

(13) Moisture. A sample of potassium perchlorate is put in a 60/40 benzenemethanol mixture and the moisture is determined by adding an excess of Karl Fischer reagent and back titrating automatically with methanol solution to a potentiometric end point.

(14) Potassium perchlorate assay. Same as paragraph F-41 in JAN-P-217 specification (see c. 12).

(15) Particle size. A Roller Analyzer is used to determine percentage of particles 74 microns or less. Cuts are made at 0-15 microns, 0-30 microns, and 0-60 microns. Screen analyses are determined on 25 g of dry material using Tyler Standard Screens (80 and 200 mesh) automatically shaken for ten minutes.

c. Sodium Chlorate

Of the chlorates and perchlorates mentioned in this volume, sodium chlorate is consumed in greatest quantity. The principal use of this compound is as a source of chlorine dioxide for bleaching purposes in the pulp and paper industry. Specifications for the material in use were not found to be available. However, absence of oxidizable materials, both inorganic and organic, is necessary for safety's sake, and at least one manufacturer supplies a product of 99.5 percent minimum purity.

BIBLIOGRAPHY

1. Achiwa, Shigeichi, C.A. 44, 9867[h].
2. Amelink, F., C A. 33, 2844[8].
3. Anon., C A. 37, 6588[3].
4. Aznárey, J. Ibarz, and Vinade, J. Virgili, C.A. 46, 2961[d].
5. Azzarello, E., C A. 38, 1367[3].
6. Banerjee, Pares C., C.A. 30, 8072[8].
7. Barnebey, O. L., C.A. 10, 730[9].
8. Belcher, R , and West, T. S., C.A. 46, 852[a] (852[d])
9. Berne, E., C A. 46, 4860[8].
10. Biber, V., and Barskaya, F., C.A. 31, 6580[6].
11. Birckenback, Lother, and Goubeau, Josef, C.A. 26, 1876[8].
12. Bodenheimer, W., and Weiler, H., C.A. 49, 13022[i].
13. Bodenheimer, Wolf, and Weiler, Hannah, C.A. 49, 13835[a, b]
14. Bolliger, Adolf, C.A. 28, 71[2].
15. Boyle, A. J., Hughey, V. V., and Castro, Clyde C., C.A. 38, 3927[3].
16. Brandt, Warren W., and Smith, G. Frederick, C.A. 44, 2406[a]
17. Brunnee, H., and Mellet, R., C.A. 2, 1941[9].
18. Carlson, B., and Gelhaar-Mansbo, J., C.A. 2, 2528[2]
19. Cerny, Pavel, C.A. 49, 13819[h].
20. Charlet, G., C A. 42, 7202[b].
21. Cherryshev, A. S., and Semenova, N. G , C.A. 51, 950[e].

22. Crump, Nathaniel L., and Johnson, Nathaniel C., C. A. 49, 11499[d].

23. Day, Jr., H. O., Gill, J. S., Jones, E. V., and Marshall, William L., C. A. 48, 7479[g].

24. De Bacho, Ferruccio, C. A. 14, 1092[8].

25. Dimitroff, M., C. A. 17, 3303[9].

26. Dobroserdov, D., C. A. 21, 2447[3].

27. Dobroserdov, D., and Erdmann, Y., C. A. 21, 2447[1].

28. Douris, R., and Plessis, M., C. A. 26, 2998[3]

29. Druetzke, Olga, C. A. 26, 308[8].

30. Durand, Jules, C. A. 31, 6270[5].

31. Eagles, Douglas C., C. A. 49, 1482[e].

32. Eger, Chaim, C. A. 49, 13835[c].

33. Ensink, A., and Hofman, J. J, C. A. 29, 7866[4].

34. Erdey, L., C. A. 48, 5714[b].

35. Erdey, Laszlo, C. A. 46, 849[h].

36. Erdey, Laszlo, and Bodor, Endre, C. A 45, 10137[b].

37. Erdey, L., Bodor, E., and Pápay, M., C. A. 50, 7664[i].

38. Farkas, Ladislaus, and Lewin, Menachem, C. A. 41, 6838[d].

39. Fedorova, O. S., C. A. 28, 2297[3].

40. Fedorova, Olga S., C. A. 24, 39[1].

41. Fedorova, O. S., C. A. 22, 1746[6].

42. Fedorova, O. S., C. A. 22, 2723[5].

43. Feigl, F., C A. 33, 5771-5.

44. Feigl, Fritz, and Goldstein, David, C. A. 52, 8829[f].

45. Feigl, F., Spot Tests In Inorganic Analysis, Elsevier Pub Co., New York (1958).

46. Ferney, G. J. W., C. A. 478[7].

47. Flatt, Robert, C A. 24, 4731[4].

48. Foucry, J., C. A. 27, 2650[2].

49. Gajatto, Sante, C. A. 34, 3292[6].

50. Gaukhman, M. S , and Stefanovskii, V. F., C. A. 34, 72038.

51. Glen, Karl, C. A. 28, 1629[4].

52. Goto, Hidehiro, C. A. 33, 1627[4].

53. Greenberg, Alexander L., and Walden, Jr., Geo. H., C. A 34, 7165[3].

54. Groh, P., and Neumeister, A., C. A. 21, 2629[1].

55. Hahn, F. L., C. A. 20, 1967[1].

56. Haight, Jr., G. P , C. A. 47, 5846[c].

57. Hendrixson, W. S., C. A. 17, 3306[2].

58. Hofmann, A., C. A. 47, 7715[a].

59. Höpner, Theodor, C. A. 44, 8652[b]

60. Hovorka, V., and Holzbecher, Z., C. A. 44, 4825[e]

61. Hunt, I. V., C. A. 33, 83[9].

62. Hunt, I. V., C. A. 33, 8836[4].

63. Husken, A., and Gaty, F., C. A. 42, 2207[i].

64. Intonti, R., and Gargiulo, M., C. A. 40, 7071[4].

65. Isibasi, Masayosi, and Havada, Yasuo, C. A. 35, 3191[4].

66. Ishibashi, Kiyoshi. C. A. 50, 16561[f].

67. Ishibashi, Kiyoshi, C. A. 50, 16561[g].

68. Jellinek, K., and Winogradoff, L., C.A. 17, 3303[1].

69. Joan, Sister M., and Reedy, J. H., C.A. 35, 2442[7].

70. Jones, R. A., C.A. 26, 669[6].

71. Junck and Küpper, C.A. 21, 2237[2].

72. Kaneko, Seiji, and Nemoto, Chujiro, C.A. 26, 5272[7].

73. Kikindai, M., C.A. 49, 12081[i].

74. Knecht, E., C.A. 2, 2057[4].

75. Knecht, E., C.A. 4, 2246[7].

76. Kolb, A, C.A. 7, 1687[5].

77. König, Fritz, C.A 16, 881[2].

78. Korenman, I. M, J. Applied Chem. (U.S.S.R.), 9, 157-8 (1936).

79. Koryta, J., and Te ygl, J, C.A. 48, 7493[b].

80. Kubli, H., C.A. 41, 4407[a].

81. Lamb, Arthur B., Marden, John W., C.A. 6, 2585[8].

82. Lenher, Victor, and Losterud, Martin, C.A. 16, 1196[3].

83. Lesnicenko, Konstantin, C.A. 27, 683[1].

84. Mach, F., and Herrmann, R., C A. 23, 4994[2].

85. Mahr, C., and Ohle, Hertha, C.A. 34, 48[7].

86. Marqueyrol, M., C.A. 5, 2606[7].

87. Marvel, C.S., and Du Vigneud, V., C.A. 19, 449[5].

88. Meldrum, Jr., W. B, Clarke, R. A., Kouba, D. L., and Becker, W. W., C.A. 43, 1567[h].

89. Moerk, Frank X., C.A. 7, 1262[g].

90. Monnier, A., C A. 11, 426[9].

91. Nichols, M. L., C. A. 29, 1360[8].

92. Noyes, A. A., and Swift, E. H., A Course of Instruction in the Qualitative Chemical Analysis of Inorganic Substances, The McMillan Co., New York (1942).

93. Odekerken, Jules M., C. A. 45, 67[i].

94. Pamfilov, A., and Jofinow, W., C. A. 18, 3158[1].

95. Paul, Ram Chand, and Singh, Apar, C. A. 50, 9941[c] (9941[d]).

96. Peters, K., and Deutschländer, E., C. A. 22, 3600[9].

97. Philipson, Tore, C. A. 46, 3196[b].

98. Pieraerto, J., C. A. 7, 1460[7].

99. Poch, P., C. A. 17, 2090[9].

100. Pollard, F. H., McOmie, J. F. W., and Elbeih, I. I. M., C. A. 45, 5559[e].

101. Popor, P. G., C. A. 30, 2879[4].

102. Pozzi-Escot, E., C. A. 7, 3094[5].

103. Raikowa-Kowachewa, Theodora P., C A. 25, 893[6].

104. Rosenberg, A., C. A. 27, 44[5].

105. Rosenfels, Richard S , C. A. 33, 1075[4].

106. Rosenthaler, L., C. A. 33, 9195[2].

107. Roy, M. B., C. A. 35, 7879[6].

108. Rupp, E., C. A. 12, 1744[1].

109. Russo, C., and Sensi, G., C. A. 8, 1937[7].

110. Sá, A., C. A. 30, 6672[5].

111. Sacchi, Vittorio, C. A. 23, 1592[5].

112. Samuelson, Olaf, C. A. 40, 2417[2].

113. Samuelson, Olaf, C.A. 40, 5657[9].

114. Saredo, Juan F., C.A. 47, 445[c].

115. Scharrer, K., C A. 21, 715[1].

116. Scharrer, K., C.A. 20, 2129[1].

117. Scheringa, K., C.A. 5, 2791[7].

118. Schmäh, Hans, C.A. 41, 5359[g].

119. Schnell, E., C.A. 48, 6912[i].

120. Schwicker, Alfred, C.A. 31, 2958[5].

121. Scott, W. W., Standard Methods of Chemical Analysis, Vol. I and II, D. Van Nostrand, and Co., Inc., New York (1939).

122. Servigne, Yvette, C.A. 49, 7446[b].

123. Servigne, Yvette, C.A 50, 9224[h].

124. Shead, A. C , and Bailey, Ph. S., C.A. 41, 3016[c].

125. Shraibman, S. S., and Balur, A. V., C.A. 30, 5905[5].

126. Singh, Balwart, and Singh, Sarwan, C.A. 51, 4868[c].

127. Singh, Balwart, Singh, Sarwan, and Singh, Harbans, C.A. 51, 2451[f]

128. Singh, Balwart, and Singh, Surjit, C A. 50, 16532[d].

129. Singh, Balwart, Singh, Surjit, and Singh, Harbans, C.A. 50, 16532[c].

130. Smeets, C., C.A. 29, 2883[5].

131. Smith, G. F , C.A. 19, 1548[7].

132. Smith, G. F., and Ross, J. F., C.A. 19, 1548[8].

133. Someya, Kinchi, C.A. 20, 2470[2].

134. Spitalskii, Fugen, and Jota, S., C.A. 22, 1930[2].

135. Stainier, C., and Grarjean, L., C.A. 50, 7667[1].

136. Stapp, C., and Bucksteeg, Wilhelm, C.A. 32, 7184-5.

137. Sunder, H., C.A. 22, 4407[1].

138. Swift, Ernest, H., and Lee, Thomas S., C.A. 36, 4056[6].

139. Tananaev, N. A., and Voshchinskaya, M. S., C.A. 32, 1607[5].

140. Tananaev, N. A., and Voshchinskaya, M. S., C.A. 32, 4466[8]

141. Taylor, R. L, C.A 9, 2564[6].

142. Tomula, E.S., C.A. 22, 742[2].

143. Tomula, E. S., C.A. 30, 1691[2].

144. Tomula, E. S., and Pelkonen, K., C.A. 28, 3027-9.

145. Treadwell, W. D., C.A. 17, 505[4].

146. Treadwell, F. P., and Hall, William T., Analytical Chemistry, Vol. II, 9th English Ed., 5th Print, John Wiley and Sons, Inc., New York, (1947).

147. Troberg, Bolge, C.A. 27, 682[9].

148. Van Bers, H. C, and Fieldmeyer, J. H., C.A. 26, 1542[6].

149. van der Meulen, J. H., C.A. 25, 3591[5].

150. van der Meulen, J. H., C.A. 25, 4485[2].

151. Vasil'ev, A., and Shtutzer, E., C.A. 26, 1876[7].

152. Vil'yamqvich, E. T., C.A. 37, 2302[3].

153. Virgili, Juan Fages, C.A. 3, 1737[7].

154. Virgili, J. F., C. A. 3, 2102[9].

155. Virgili, J. F., C.A. 3, 2173[2].

156. Virgili, J. F., C.A 4, 159[2].

157. Virgili, Juan Fages, C.A. 4, 1370[5].

158. Vlasyuk, E. I., C.A. 47, 7221[d].

159. Vürtheim, A., C.A. 21, 1607[9].

160. Wagenaar, G. H., C.A. 34, 5785[5].

161. Wagner, E. C., C.A. 18, 2484[1].

162. Wagner, E. C., C.A. 20, 159[5].

163. Weiner, Robert, C.A. 51, 4878[a].

164. Willard, H. H., and Diehl, H., Advanced Quantitative Analysis, D. Van Nostrand, and Co., Inc., New York (1943).

165. Willard, Hobart H., and Perkins, Lowell R., C.A. 48, 2507[a].

166. Willard, H. H., and Thompson, J. J., C.A. 24. 4238[9].

167. Williams, Dwight, C.A. 39, 4812[5,6].

168. Williams, Dwight, and Meeker, C.C., C.A. 39, 4812[9].

169. Williams, J.G., C.A. 13, 3320[3].

170. Yamaguchi, Kazutake, C.A. 48, 3201[a].

171. Yarowski, L, K. and Hynes, W. A., C.A. 33, 1630[5].

172. Yoshida, Yukito, C.A. 32 2866[5].

APPENDIX C

CALCULATION OF PRODUCTION COSTS

CALCULATION OF PRODUCTION COSTS FOR SODIUM CHLORATE

(Results are given in Tables 2-17 and 2-18)

Basis - 18,000 ton/yr

1. Raw Materials

Salt - 1150 lb/ton $NaClO_3$

$$18000 \times \frac{1150}{2000} \times \$20/\text{ton} = \$207,000$$

HCL (100%) - $\frac{27 \text{ lb}}{2000} \times \frac{100}{32} \times \$30/\text{ton} = \$22,800$

$Na_2Cr_2O_7$ - 10 lb/ton $NaClO_3$

$$18000 \times \frac{10 \text{ lb}}{\text{ton}} \times 13¢/\text{lb} = \$23,400$$

2. Utilities

Electricity for cells; 3.3 kw/lb chlorate[15]

$$3.3 \times 36,000,000 \times .3¢/\text{kwhr} = \$357,000$$

Water

500 gpm for 6,000,000 lb/yr plant[15]

$$\frac{36}{6} \times 500 \times 60 \times 24 \times 330 \text{ days on stream/yr} = 1.430 \text{ MM gal}$$

3. Steam

5.5 lb steam/lb chlorate[15]

$$5.5 \times 36,000,000 \frac{\text{lb}}{ClO_3} \times 40¢/1000 \text{ lb steam} = \$79,200$$

4. Aux. Electricity

$$700 \text{ hp} \times \frac{36}{6} \times .746 \times 24 \times 330 \times 0.3¢/\text{kwhr} = \$74,200$$

5. Operating Labor

Cell Room

2 operators/shift

1 - $2.75/hr x 24 x 365 = $24,000

1 - $2.25/hr x 24 x 365 = 19,700

$43,700

Finishing Labor

2 operators/shift

1 - $2.75/hr x 24 x 365 = $24,000

1 - $2.25/hr x 24 x 365 = 19,700

$43,700

Drying and Packaging

1 man/shift

1 - $2.50/hr x 24 x 365 = $21,900

Salt Preparation

2 men/day shift only

2 x 40 x 52 x $2.25/hr = $ 9,400

Total Operating Labor	-	$118,700
Payroll Burden	-	23,800
		$142,500

6. Operating Supervision

Shift Foreman

1 man/shift - $7200 x 3 = $21,600

Operating Superintendent

$750/month x 12 = $ 9,000

Total Supervision	-	$30,600
Payroll Burden	-	6,120
		$36,720

7. Maintenance Labor and Materials

5% of Plant Investment

.05 x $5,600,000 = $280,000

8. Anode Replacement

25¢/lb ClO_3[15]

25¢/lb x 36,000,000 = $90,000

9. Laboratory

Labor

1 - Chief Chemist	-	$ 8,400
2 - Chemists at $6600 each	-	13,200
2 - Technicians at $4200 each	-	8,400
Total Labor	-	$30,000
Payroll Burden	-	6,000
		$36,000
Materials		6,000
		$42,000

10. Management

Plant Manager	$10,000
Account Office Manager	8,400
2 Clerks at $3600	7,200
2 Stenos at $3600	7,200
2 Engineers at $7200	14,400
	$47,200
Payroll Burden	9,440
	$56,640

11. Insurance

1% of Investment
.01 x $5,600,000 = $56,000

12. Property Taxes

1% of Investment
.01 x $5,600,000 = $56,000

13. Depreciation

10% of Plant Investment
.10 x $5,600,000 = $560,000

CALCULATION OF PRODUCTION COSTS FOR SODIUM PERCHLORATE

1. Raw Material

$NaClO_3$ - 95% yield

$\frac{8680}{.95}$ x 2000 x 9¢/lb = $1,645,000

2. Chemicals

Hydrochloric acid assume

= .02¢/lb x 20,000,000 = $4000

Sodium dichromate assume

= .06 x 20,000,000 lb/yr = $12,000

3. Utilities

Electricity - 2 kwhr/lb $NaClO_4$ includes all power (Schumacher)[36]

2 x 20,000,000 lb/yr x .3¢/kwhr = $120,000

Water - assume water requirement the same as chlorate

$\frac{20}{6}$ x 500 = 1670 gpm x 60 x 24 x 330 days = 795 MM gal

795 MM gal x 3.5¢/M gal = $27,800

Steam

5.5 lb steam/lb perchlorate - same as chlorate

5.5 x 20,000,000lb/yr x 40¢/1000lb = $44,000

4. Operating Labor

Cell Room

2 operators/shift

1 x $2.75/hr x 24 x 365 = $24,000

1 x $2.25/hr x 24 x 365 = 19,700

$43,700

Finishing Labor

2 men/shift

1 x $2.75/hr x 24 x 365 = $24,000

1 x $2.25/hr x 24 x 365 = 19,700

$43,700

Drying, Packaging and Salt preparation (operators would divide their time between chlorate and perchlorate)

Total Operating Labor	$ 87,400
Payroll Burden	17,480
	$104,880

5. Operating Supervision

Shift Foreman

1/shift - $7200 x 3 = $21,600

Operating Superintendent - $9000

Total	$30,600
Payroll Burden	6,120
	$36,720

6. Maintenance Labor and Materials

5% of Plant Investment

.05 x $3,600,000 = $180,000

7. Anode Replacement (Material only)
(Labor included in maintenance labor)

0.2 oz Pt loss/ton product

0.2 x 10,000 x $57/oz = $114,000

8. Laboratory

Assume $1000/month or $12,000 expense

9. Management

Use same plant manager for both chlorate and perchlorate plant; also engineers, office manager

Add 2 clerks - $3600 each x 2 =	$7200
Payroll Burden	1440
	$8640

10. Insurance - 1% Plant Investment

.01 x $3,600,000 = $36,000

11. Property Taxes - 1% of Plant Investment

1% x $3,600,000 = $36,000

12. Depreciation - 10% of Plant Investment

10% x $3,600,000 = $360,000

CALCULATION OF PRODUCTION COSTS FOR AMMONIUM PERCHLORATE

1. Raw Materials

Sodium perchlorate: assume 98% yield

9,500 ton/yr x 13.7¢/lb x 2000 = $2,620,000

Ammonia

910 ton/yr x $88/ton = $80,000

HCl

$$2850 \text{ ton/yr} \times \frac{100}{32} \times \$30/\text{ton} = \$266,000$$

2. Utilities

Very little information is available on electrical, steam and water requirements. It has been assumed that 1¢/lb NH_4ClO_4 produced is total utility cost.

3. Operating Labor

Reactor Section - 2 operators/shift

1 x $2.75 x 24 x 365 = $24,100

1 x $2.25 x 24 x 365 = $19,700

Crystallization and Centrifuge - 1 operator/shift

1 x $2.50 x 24 x 365 = $21,800

Drying and Packing - 1 operator/shift

1 x $2.50 x 24 x 365 = $21,800

Total Labor	$ 87,400
Payroll Burden - 20%	17,480
	$104,880

4. Operating Supervision

1 Shift Foreman $600/month $7200 x 3 =	$21,600
1 Operating Superintendent	9,000
	$30,600
Payroll Burden	6,120
	$36,720

5. Maintenance

5% of Investment

.05 x $4,800,000 = $240,000

6. Laboratory

Assume $1000/month x 12 = $12,000

7. Management

Same plant manager, etc.

2 clerks - $3600 x 2 = $7200

20%	1440
	$8640

Plant Superintendent - shown in operating supervision

8. Insurance

1% of Plant Investment

.01 x $4,800,000 = $48,000

9. Property Taxes

1% of Plant Investment

.01 x $4,800,000 = $480,000

10. Depreciation

10% of Plant Investment

.01 x $4,800,000 = $480,000

ILLUSTRATIONS

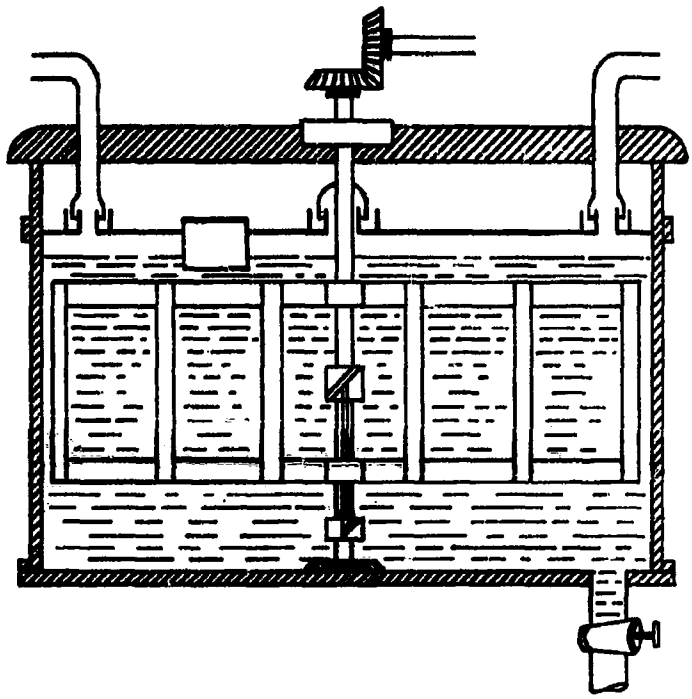


FIGURE 2-1. VAT USED IN MANUFACTURE OF $CaClO_3$

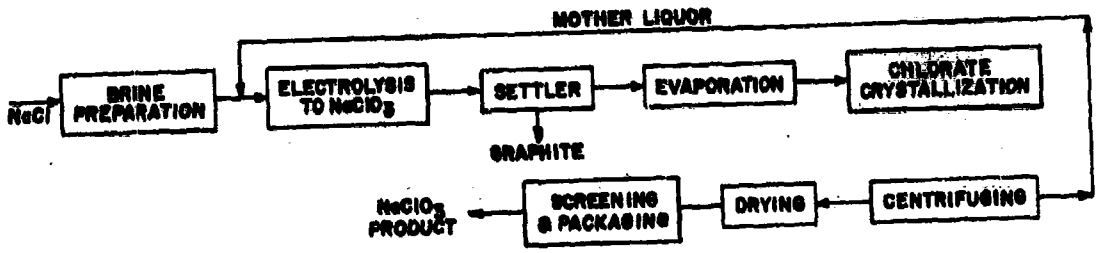
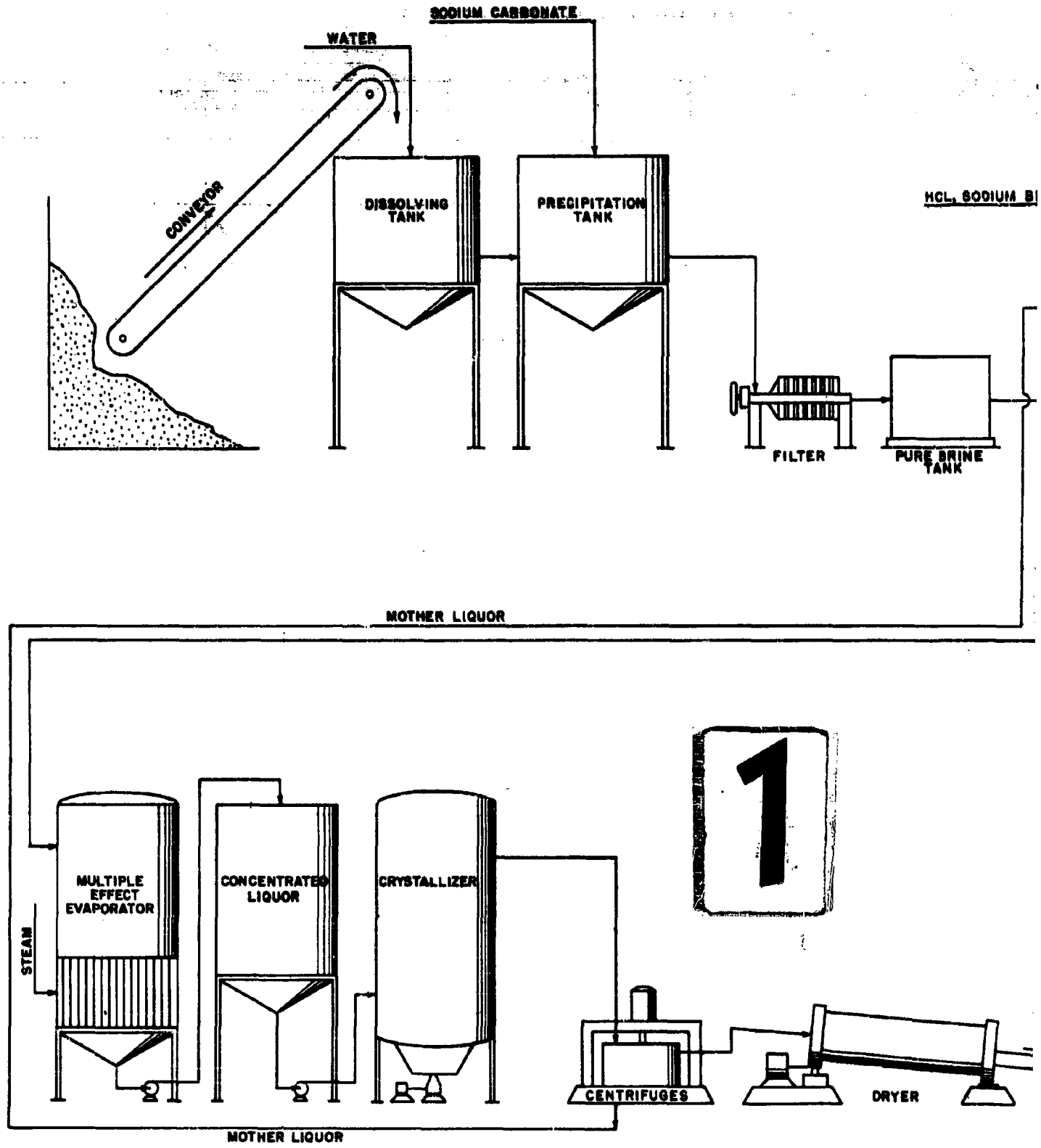
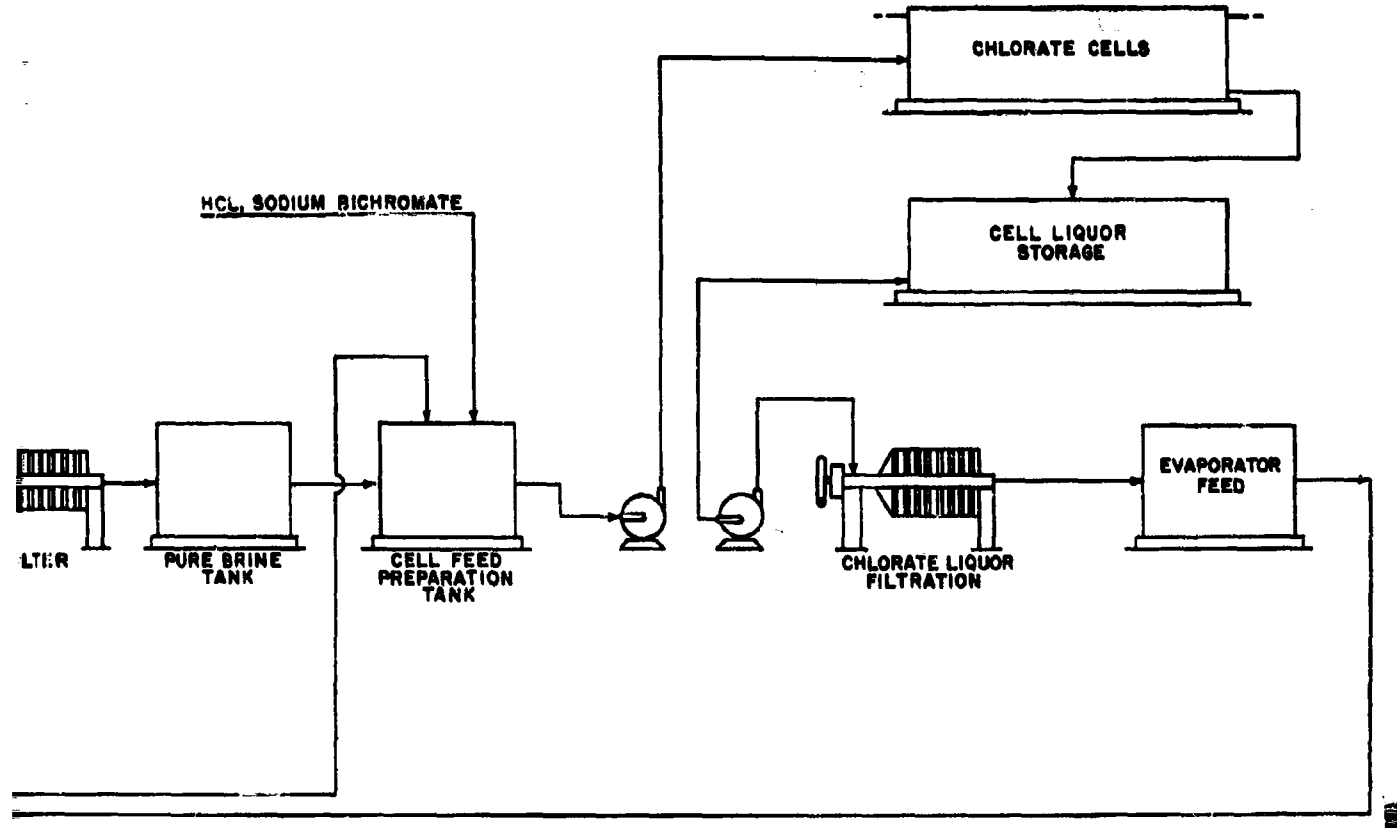


FIGURE 2-2. SCHEMATIC FLOW DIAGRAM OF MANUFACTURE OF $NaClO_3$ BY ELECTROLYSIS METHOD


SODIUM CARBONATE
WATER
CONVEYOR
DISSOLVING TANK
PRECIPITATION TANK
HCL, SODIUM BI
FILTER
PURE BRINE TANK
MOTHER LIQUOR
MULTIPLE EFFECT EVAPORATOR
STEAM
CONCENTRATED LIQUOR
CRYSTALLIZER
1
CENTRIFUGES
DRYER
MOTHER LIQUOR



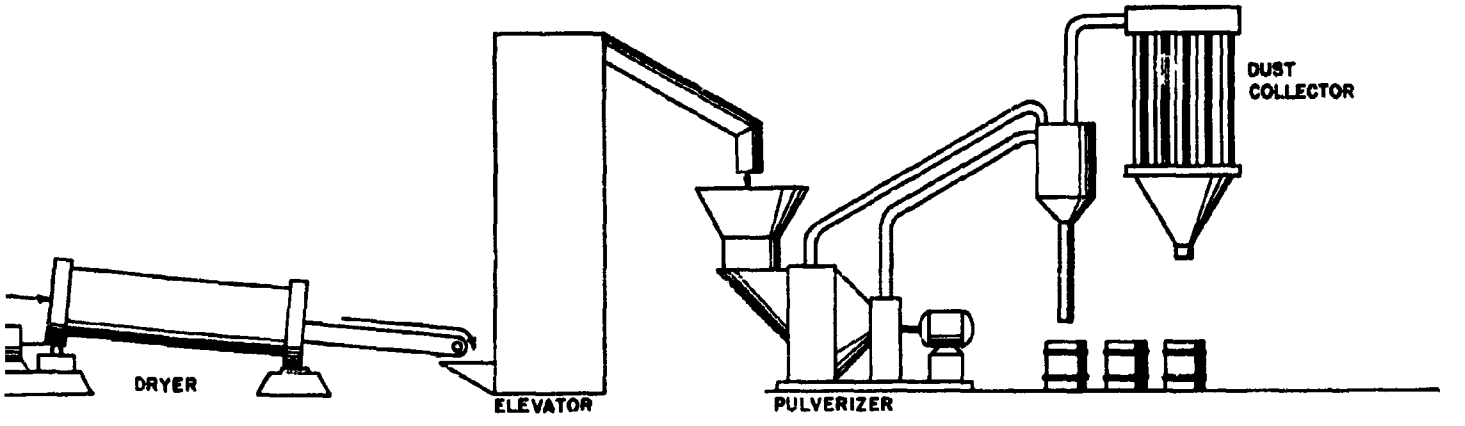


FIGURE 2-3. FLOW SHEET FOR MANUFACTURE OF $NaClO_3$ BY ELECTROLYSIS METHOD (REF. 3)

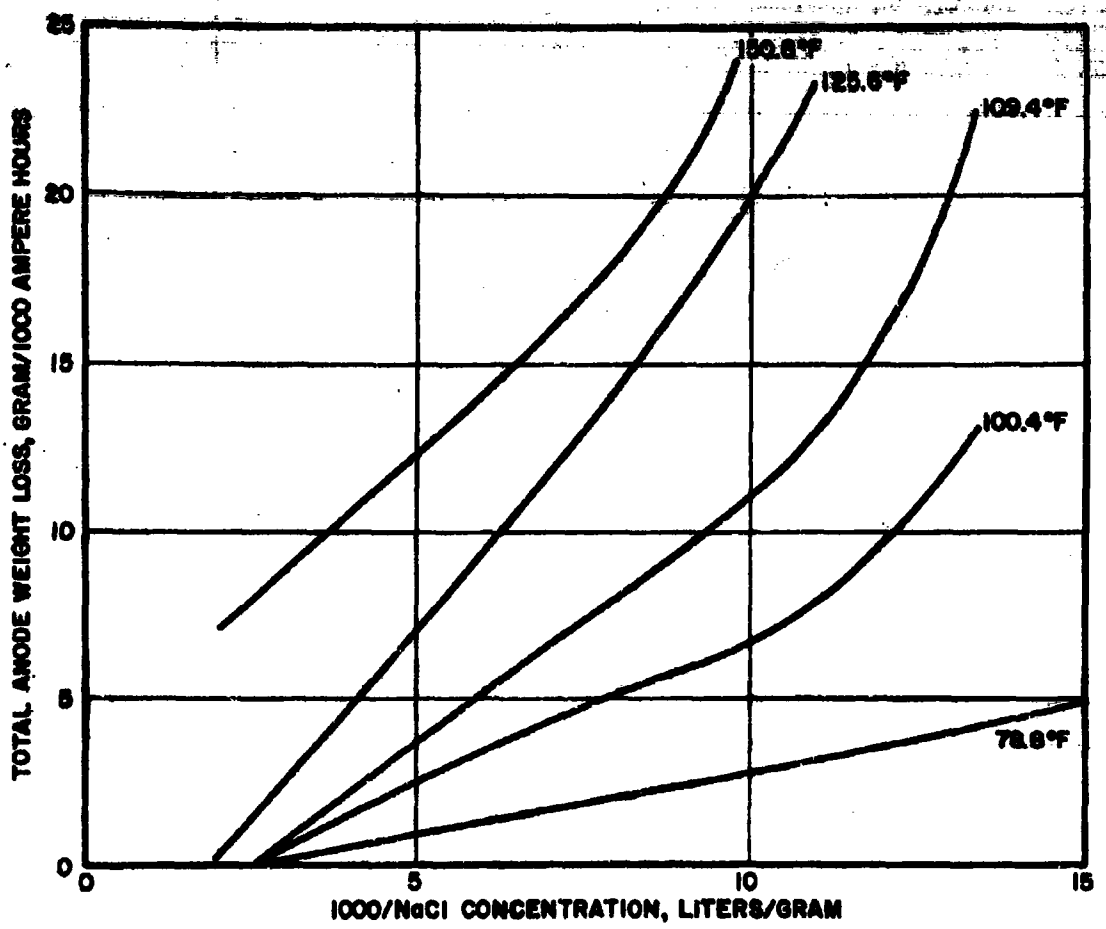


FIGURE 2-4. GRAPHITE ATTACK AS A FUNCTION OF RECIPROCAL OF NaCl CONCENTRATION

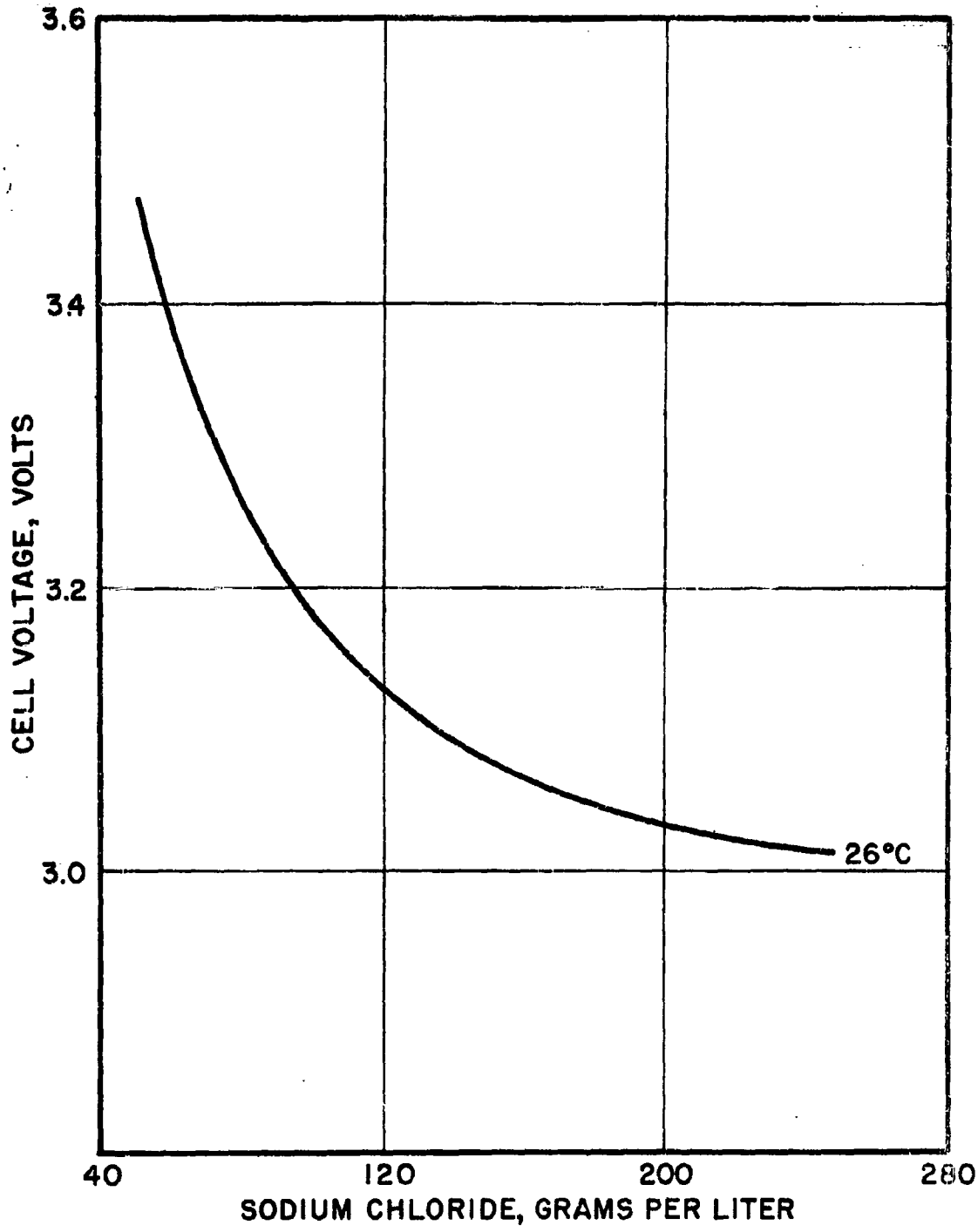


FIGURE 2-5. EFFECT OF NaCl CONCENTRATION ON CELL VOLTAGE (REF. 20)

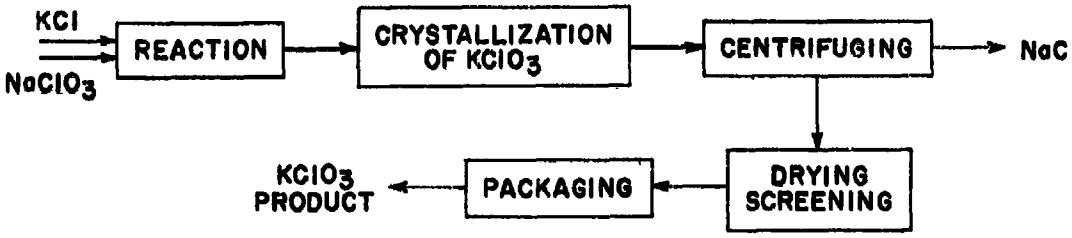
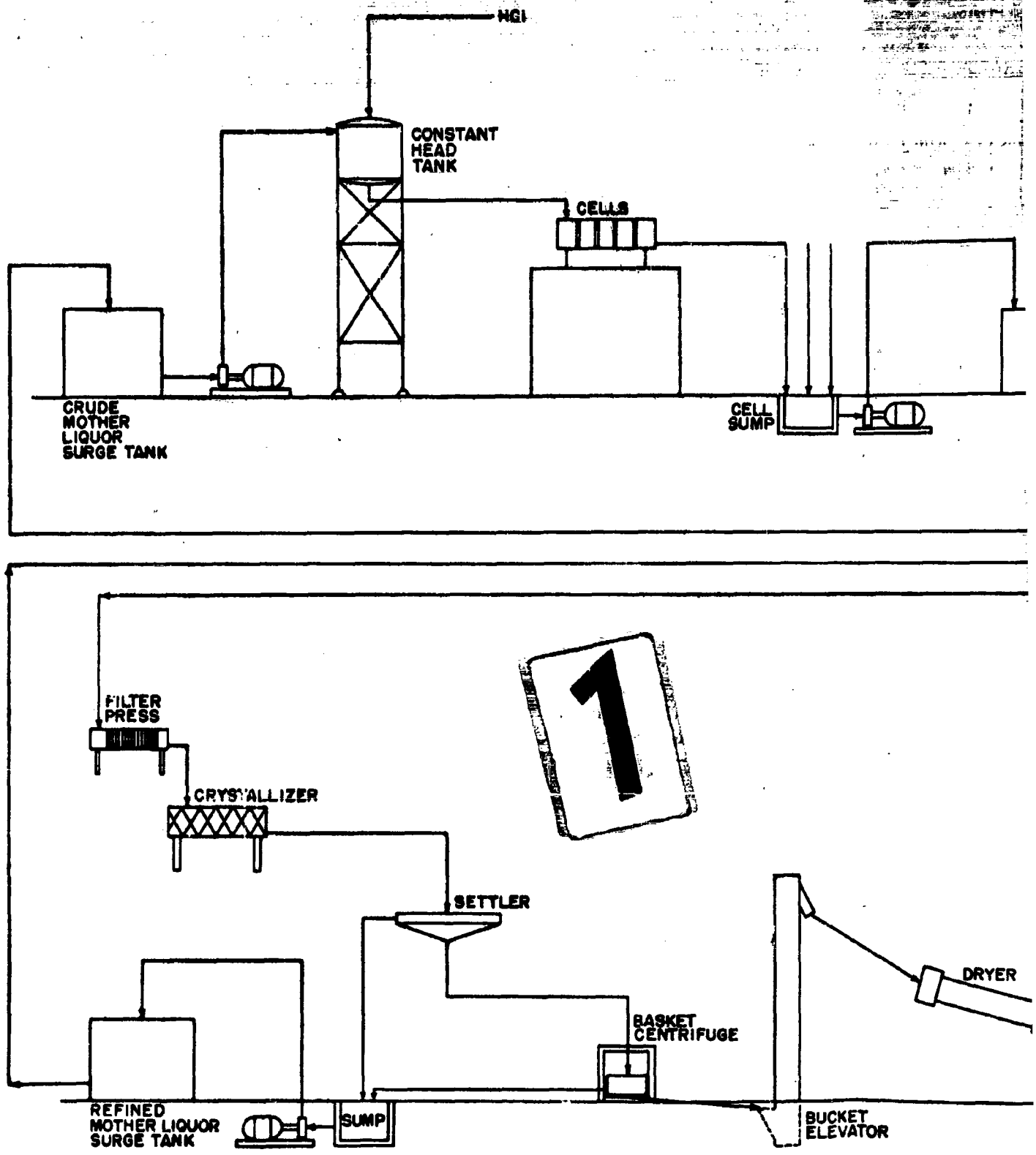
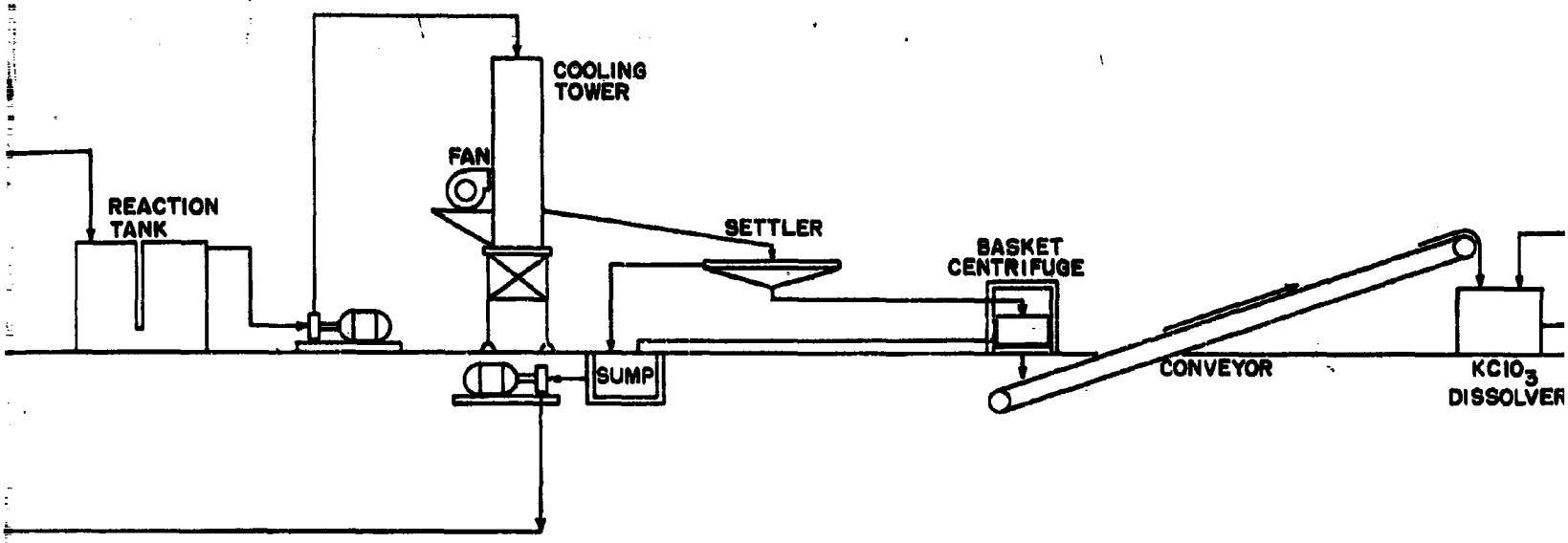
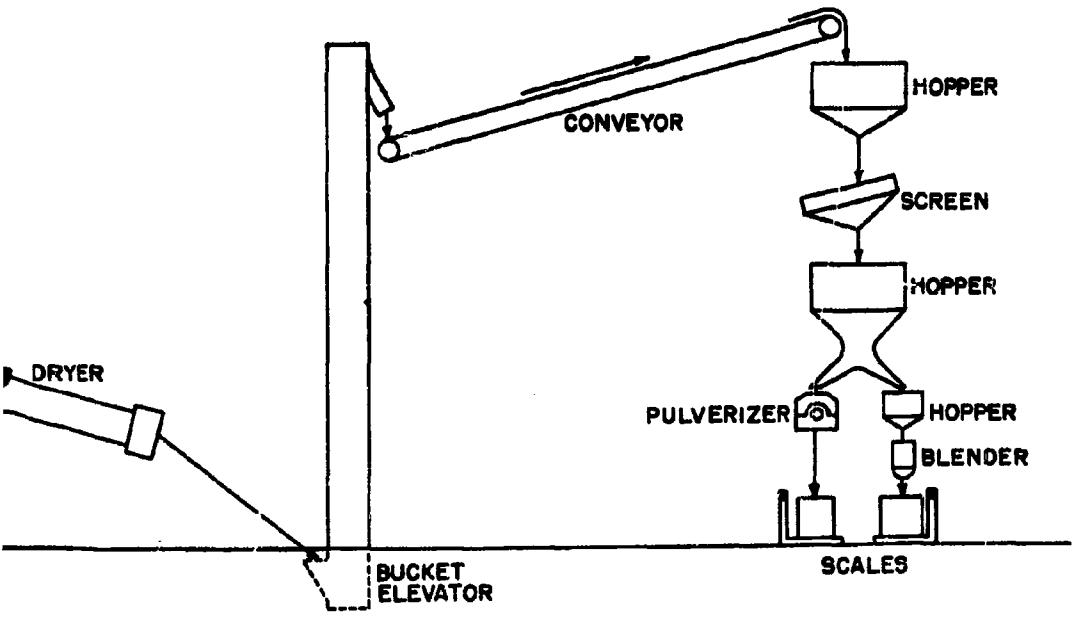


FIGURE 2-6. SCHEMATIC FLOW DIAGRAM FOR THE MANUFACTURE OF $KClO_3$

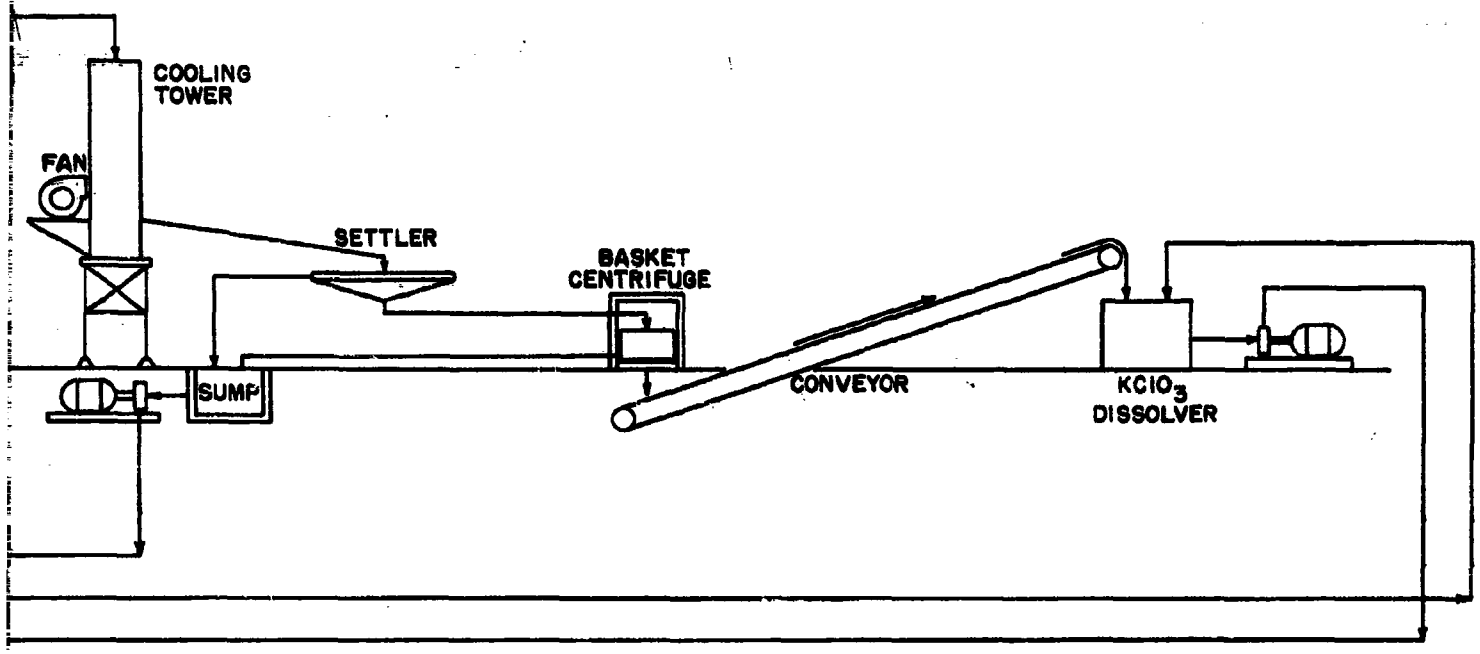

HCl
CONSTANT
HEAD
TANK
CELLS
CRUDE
MOTHER
LIQUOR
SURGE TANK
CELL
SUMP
FILTER
PRESS
CRYSTALLIZER
1
SETTLER
DRYER
BASKET
CENTRIFUGE
REFINED
MOTHER LIQUOR
SURGE TANK
SUMP
BUCKET
ELEVATOR





2

FIGURE 2-7. FLOW SHEET FO
$KClO_3$ (REF.



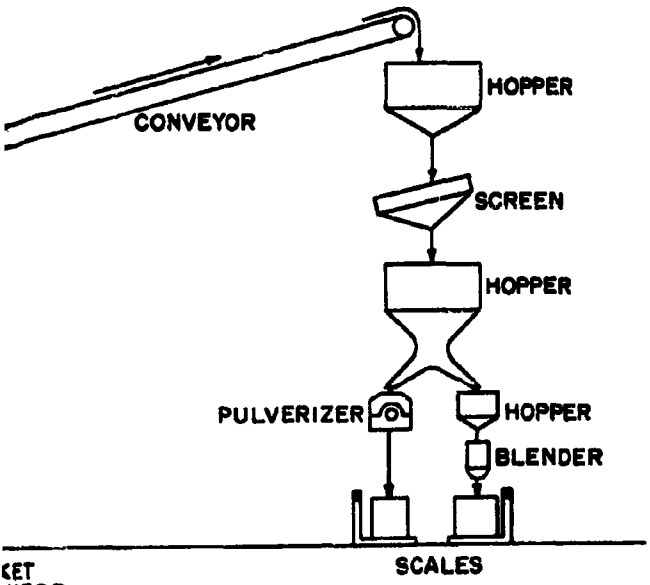


FIGURE 2-7. FLOW SHEET FOR MANUFACTURE OF $KClO_3$ (REF. 19)

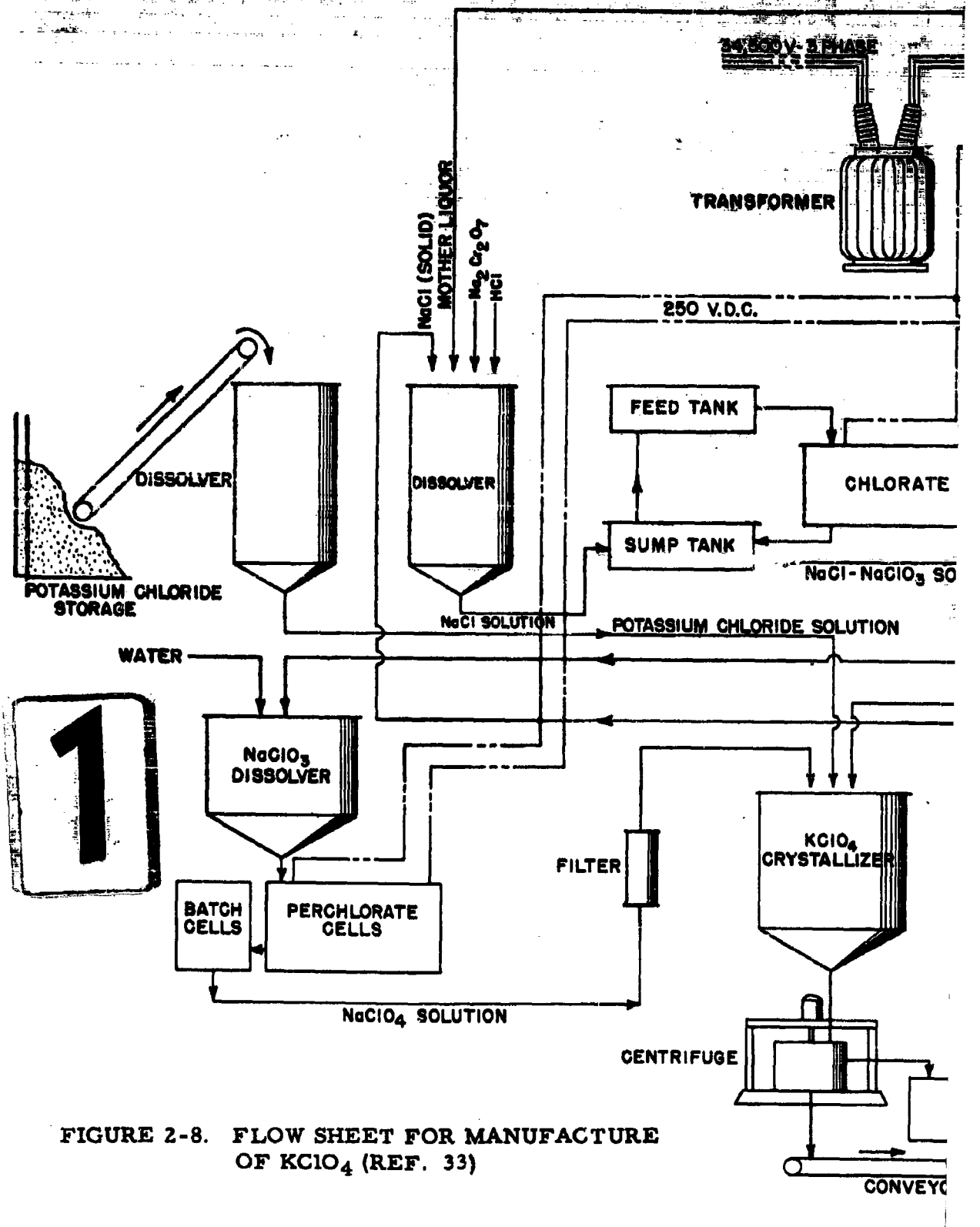
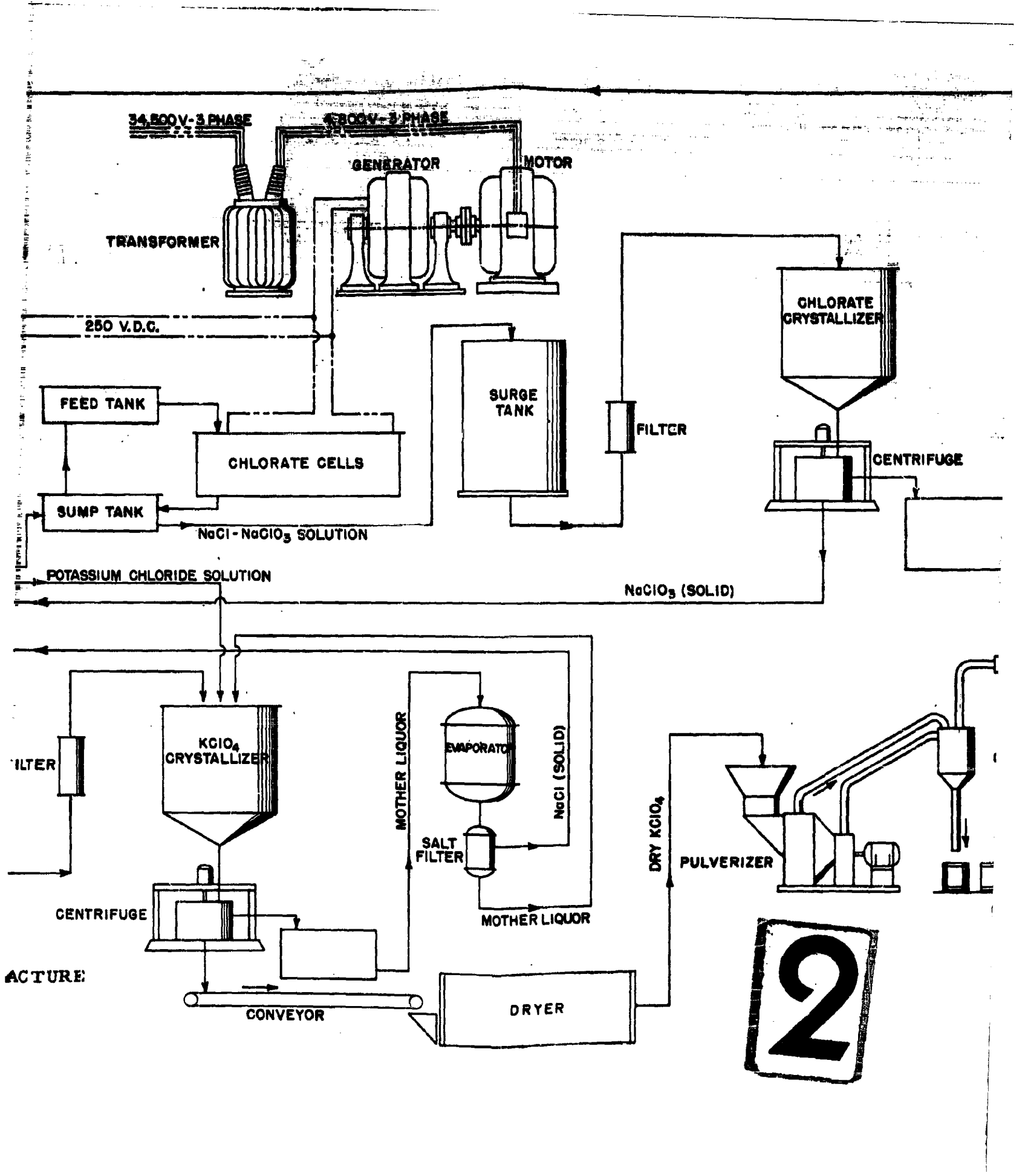
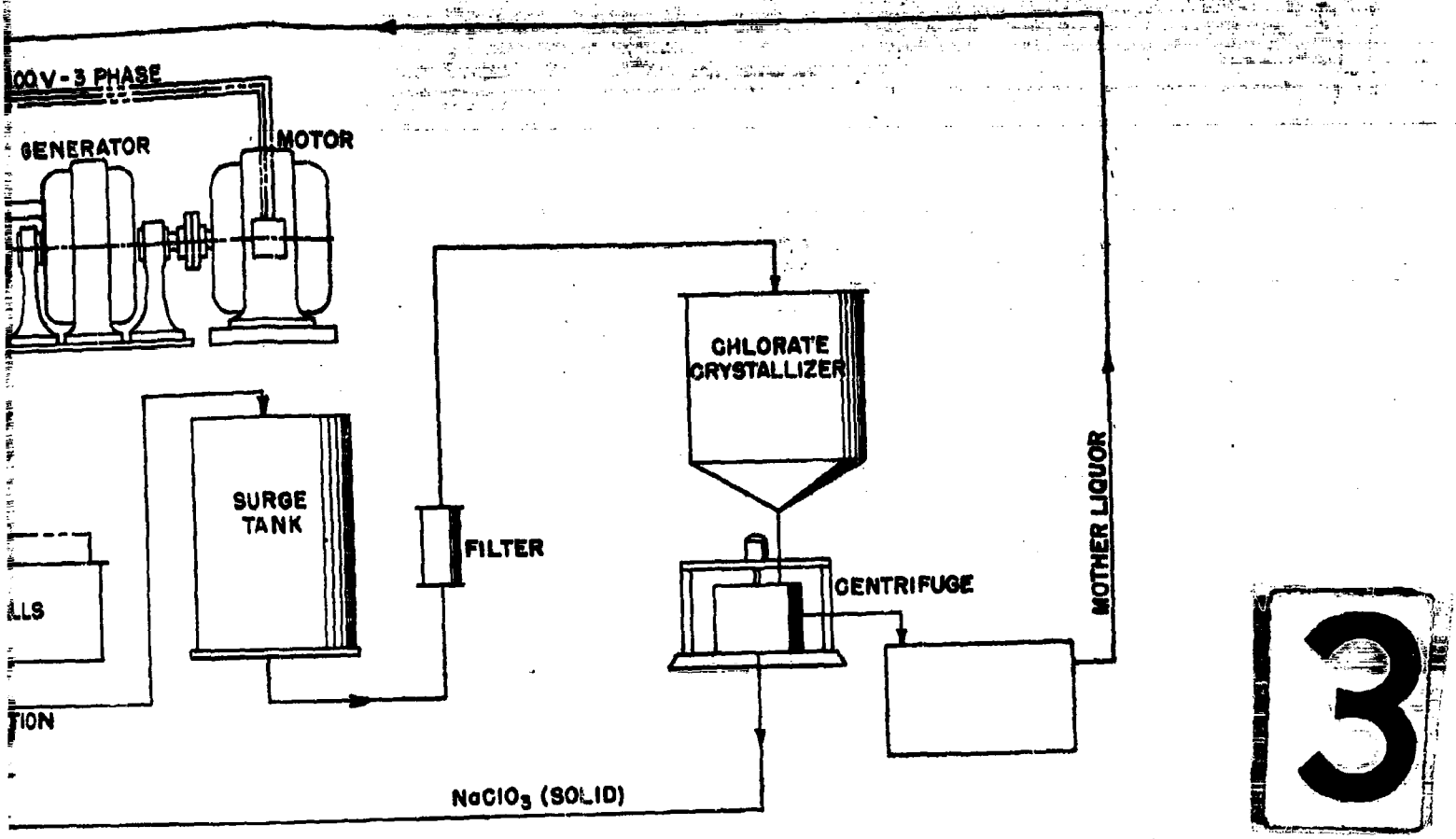
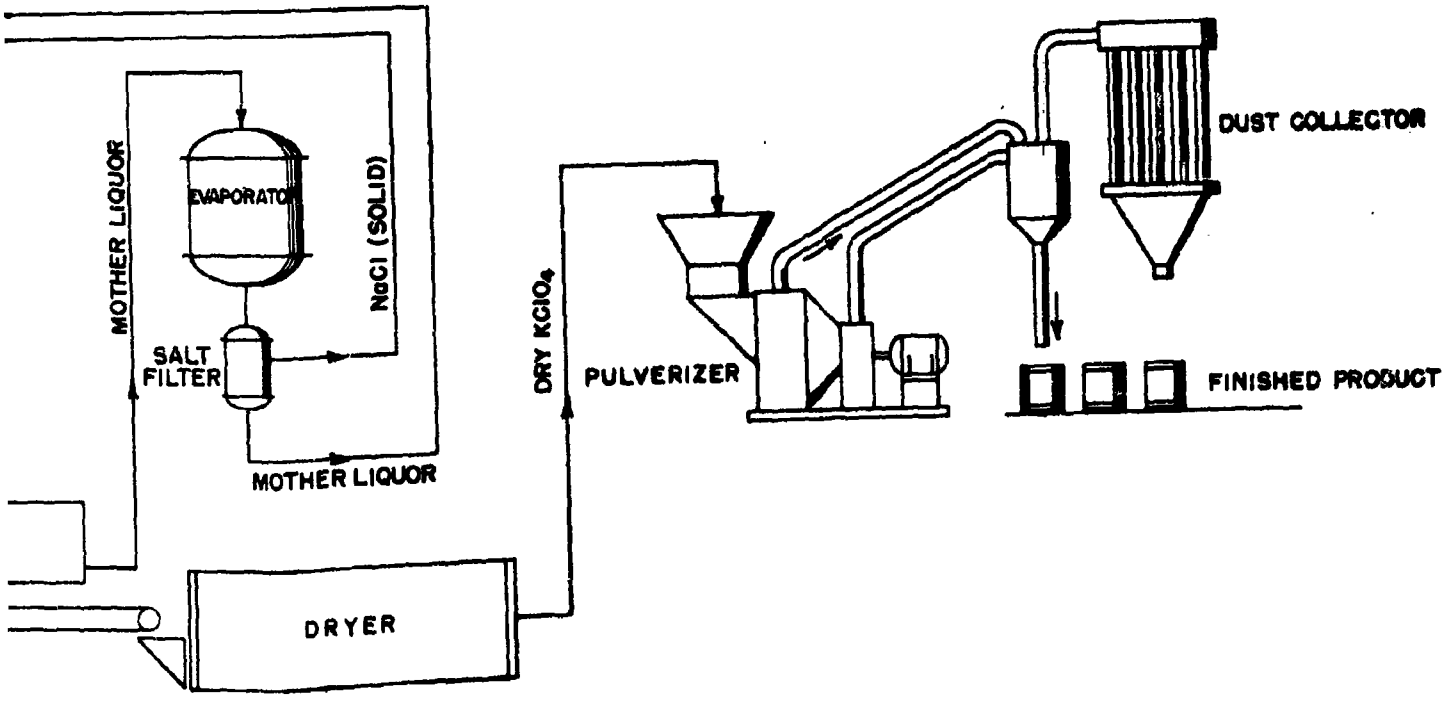


FIGURE 2-8. FLOW SHEET FOR MANUFACTURE OF $KClO_4$ (REF. 33)


34,500 V - 3 PHASE
4,800 V - 3 PHASE
GENERATOR
MOTOR
TRANSFORMER
250 V.D.C.
FEED TANK
CHLORATE CELLS
SUMP TANK
NaCl - NaClO3 SOLUTION
SURGE TANK
FILTER
CHLORATE CRYSTALLIZER
CENTRIFUGE
POTASSIUM CHLORIDE SOLUTION
NaClO3 (SOLID)
ILTER
KClO4 CRYSTALLIZER
MOTHER LIQUOR
EVAPORATOR
NaCl (SOLID)
SALT FILTER
DRY KClO4
PULVERIZER
CENTRIFUGE
MOTHER LIQUOR
ACTURE
CONVEYOR
DRYER
2


00 V - 3 PHASE
GENERATOR
MOTOR
CHLORATE CRYSTALLIZER
SURGE TANK
FILTER
CENTRIFUGE
MOTHER LIQUOR
LLS
TION
NaClO3 (SOLID)

3


MOTHER LIQUOR
EVAPORATO
NaCl (SOLID)
SALT FILTER
MOTHER LIQUOR
DRY KClO4
PULVERIZER
DUST COLLECTOR
FINISHED PRODUCT
DRYER

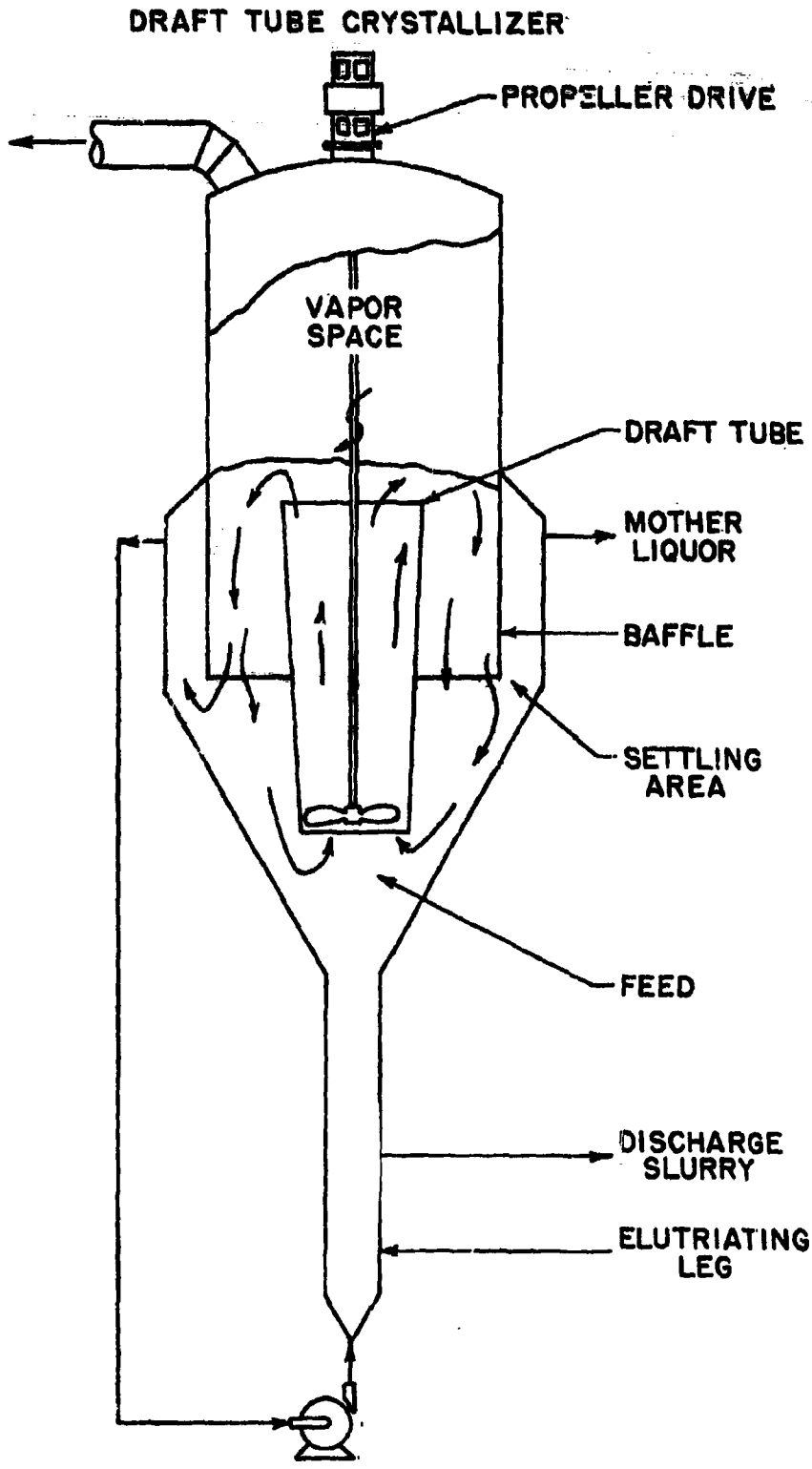


FIGURE 2-16. SECTIONAL VIEW OF A VACUUM-COOLED CRYSTALLIZER (REF: SWENSON EVAPORATOR CO.)

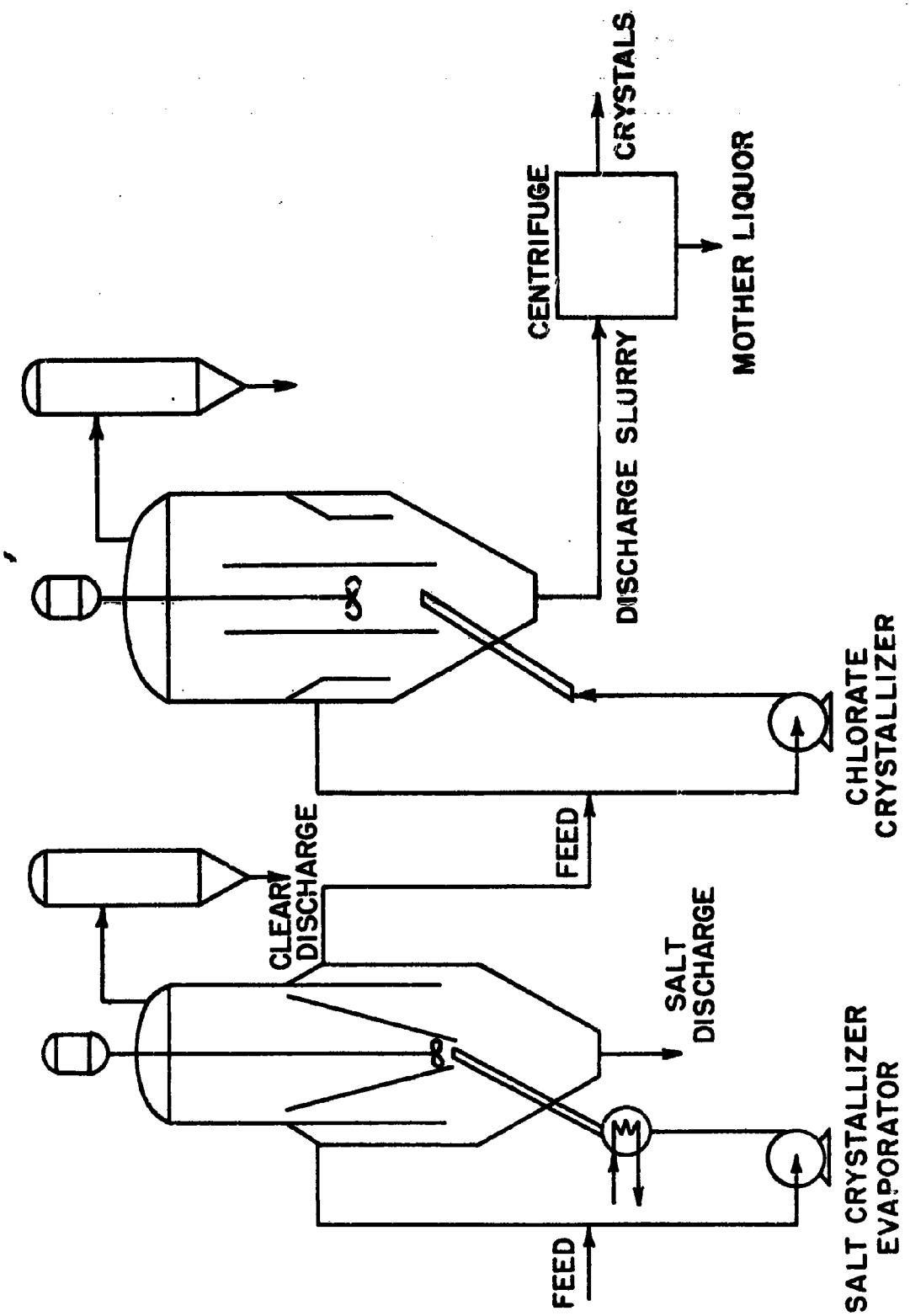


FIGURE 2-15. SCHEMATIC SKETCH OF A VACUUM-COOLED CRYSTALLIZER SYSTEM (REF: SWENSON EVAPORATOR CO.)

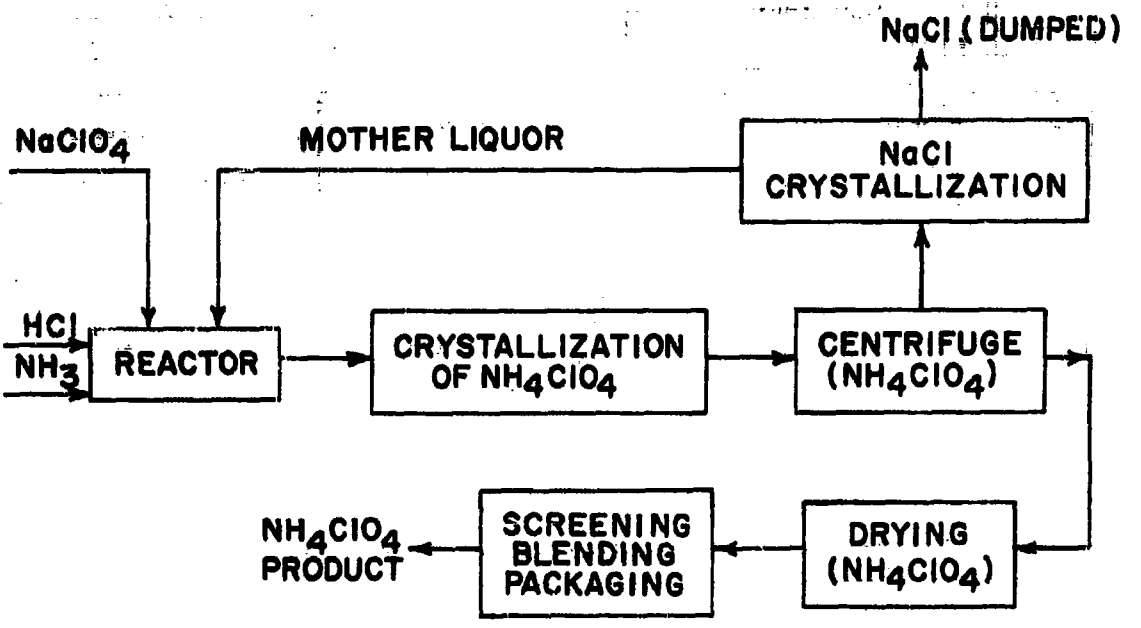


FIGURE 2-9. SCHEMATIC FLOW DIAGRAM FOR THE MANUFACTURE OF AMMONIUM PERCHLORATE

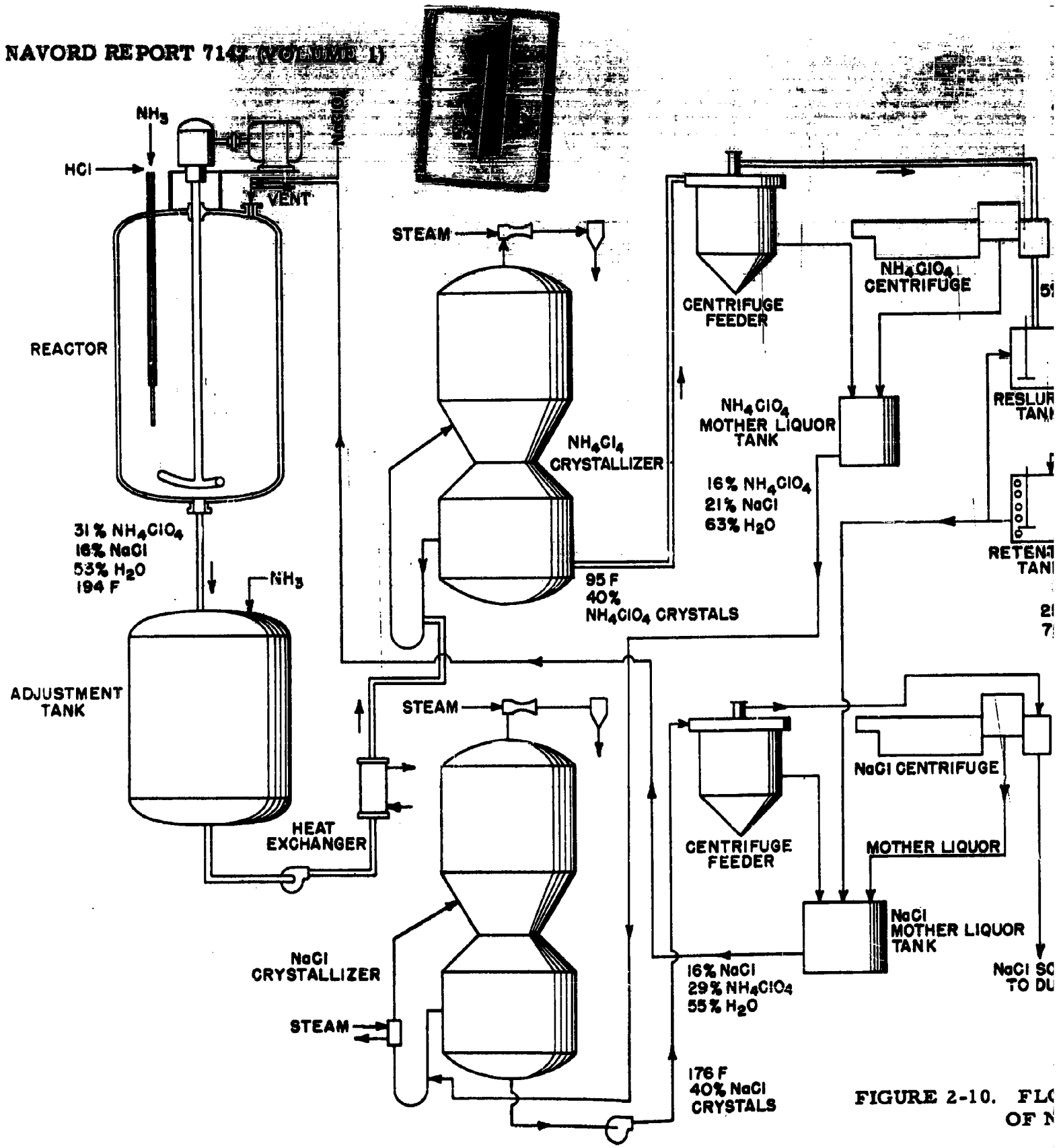


FIGURE 2-10. FL
OF N

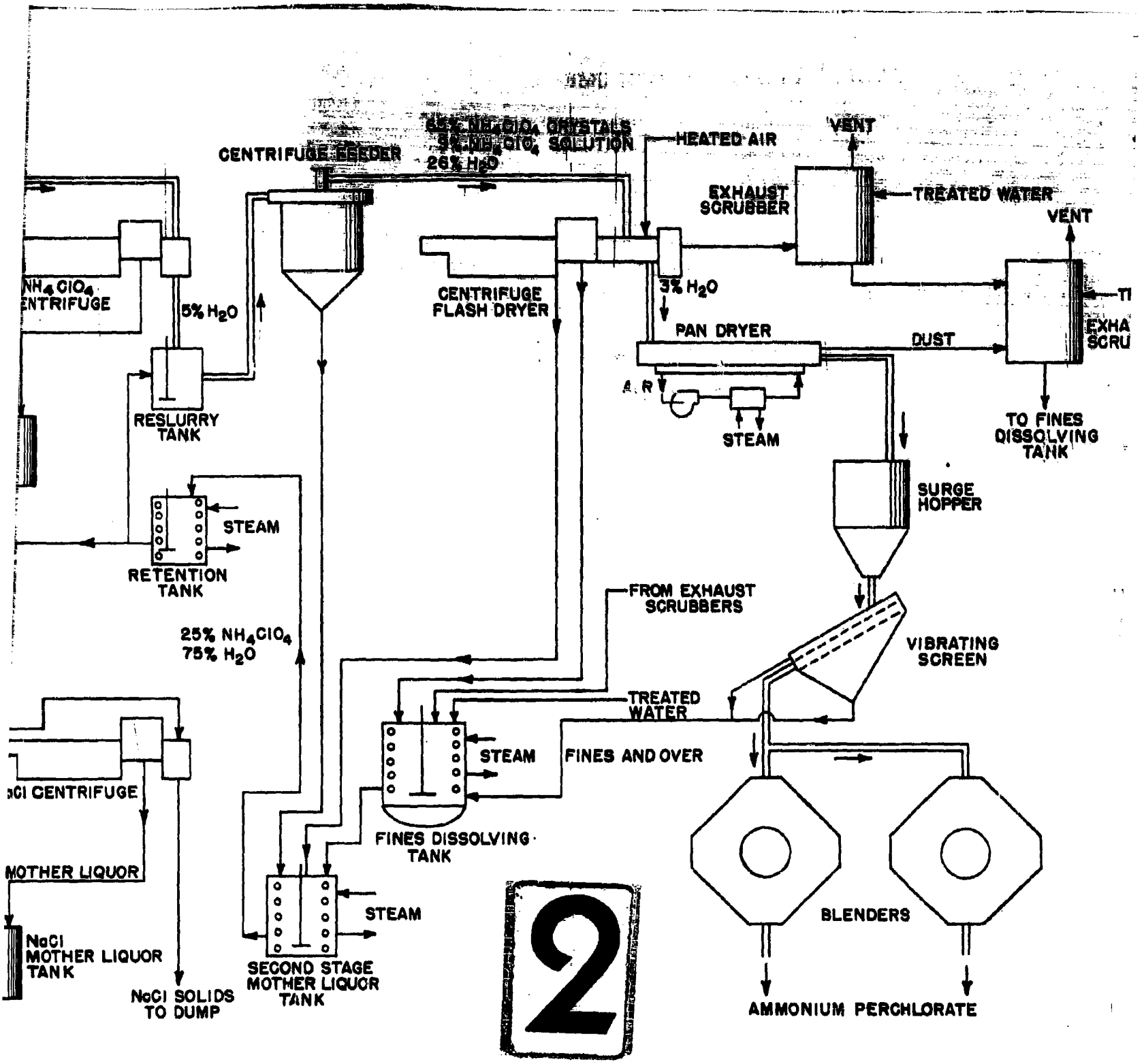
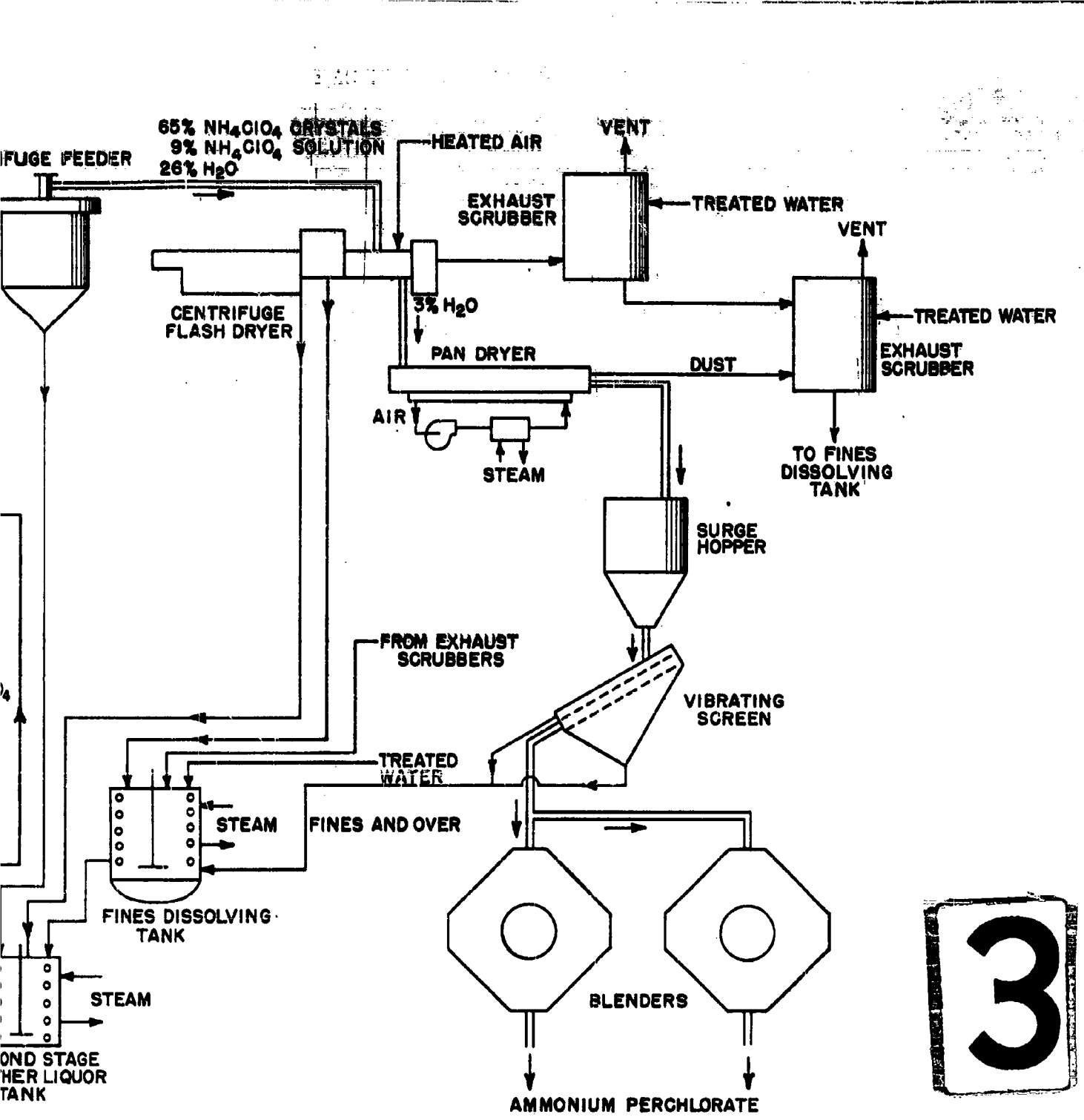


FIGURE 2-10. FLOW SHEET FOR MANUFACTURE OF NH_4ClO_4 (REF. 36)



T FOR MANUFACTURE
(REF. 36)

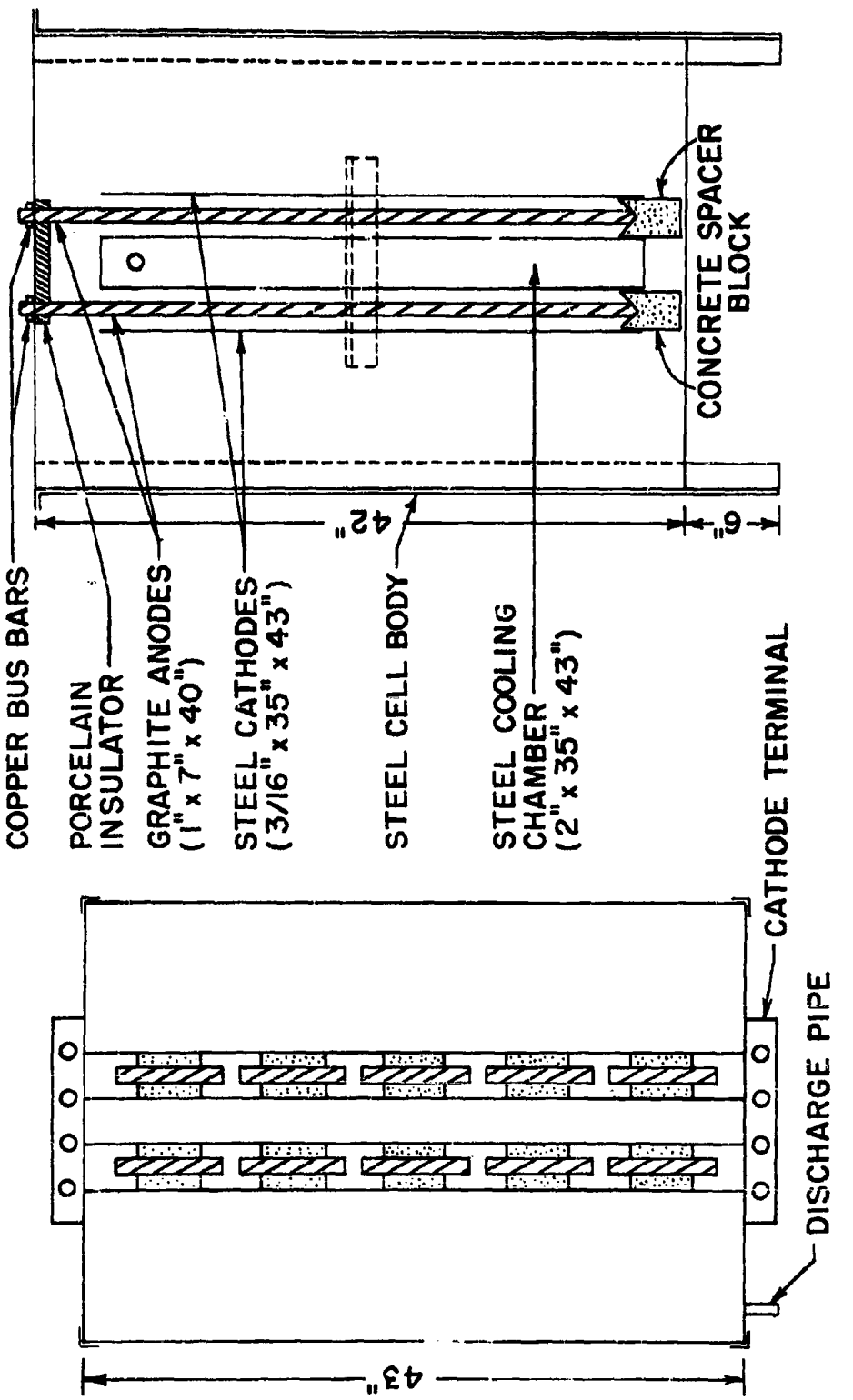


FIGURE 2-11. SECTIONAL VIEWS OF A BATCH-TYPE CHLORATE CELL (REF. 18)

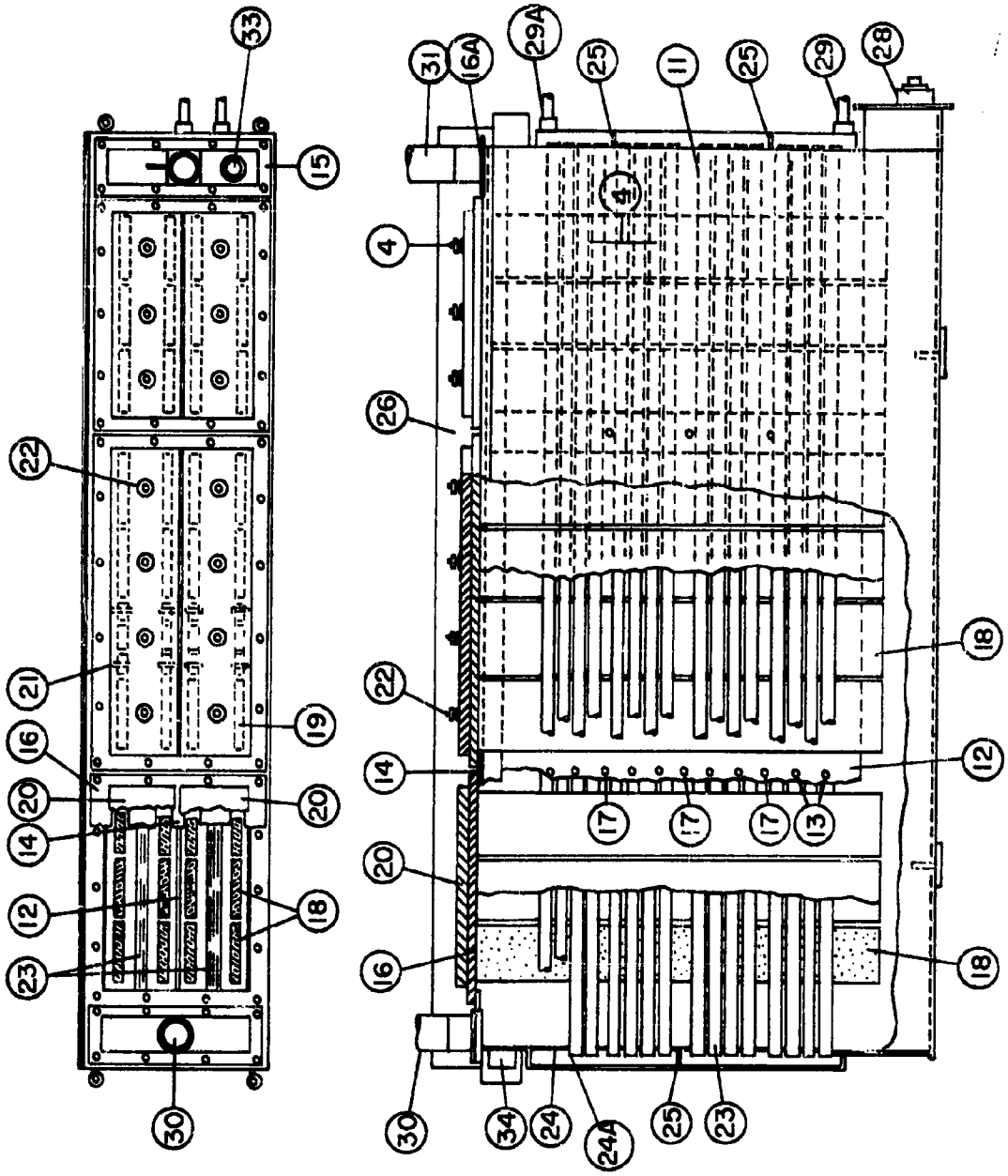


FIGURE 2-12. DESIGN OF A CONTINUOUS CHLORATE CELL (REF. 45)

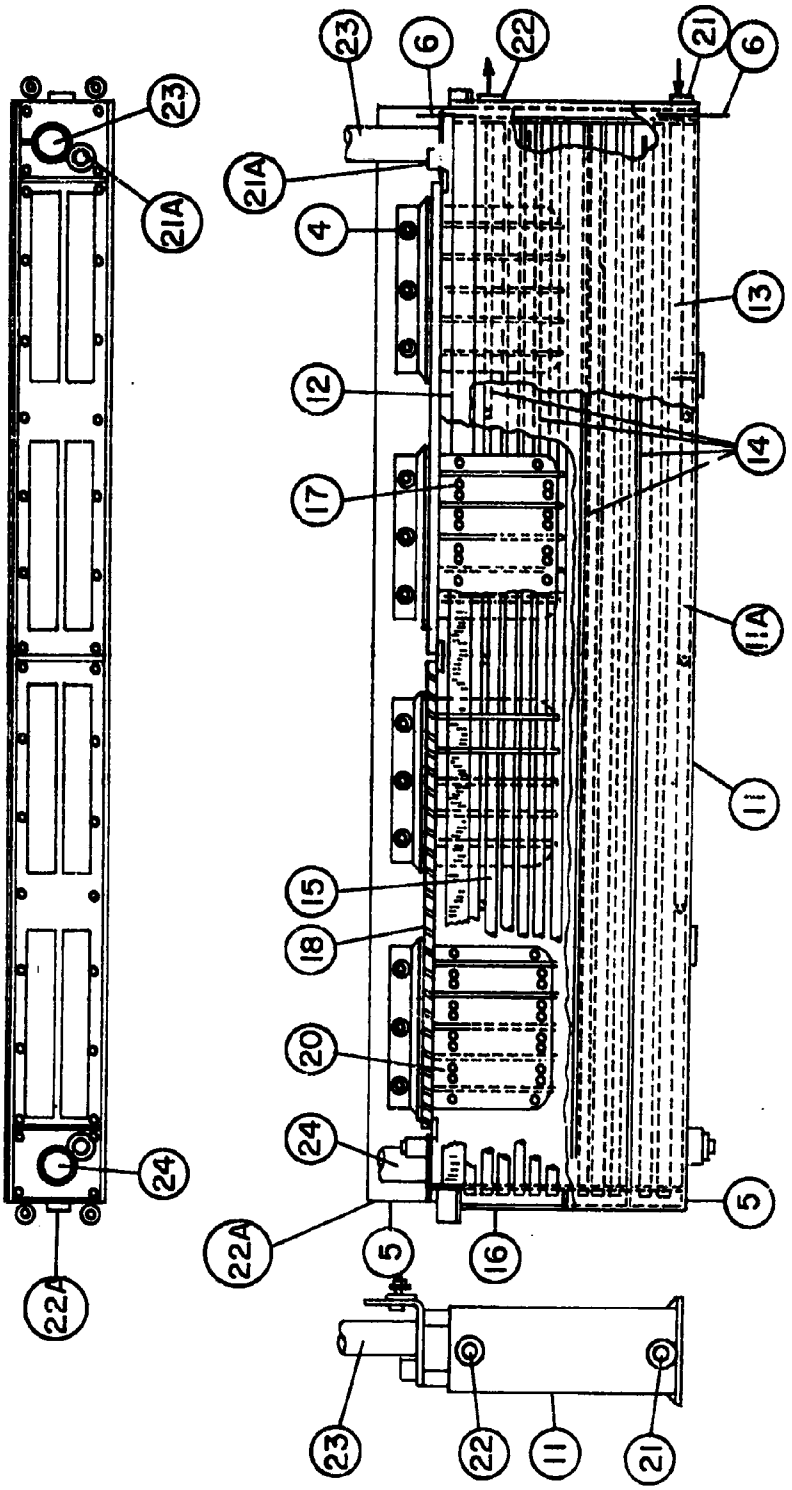


FIGURE 2-13. DESIGN OF A CONTINUOUS PERCHLORATE CELL (REF. 43)

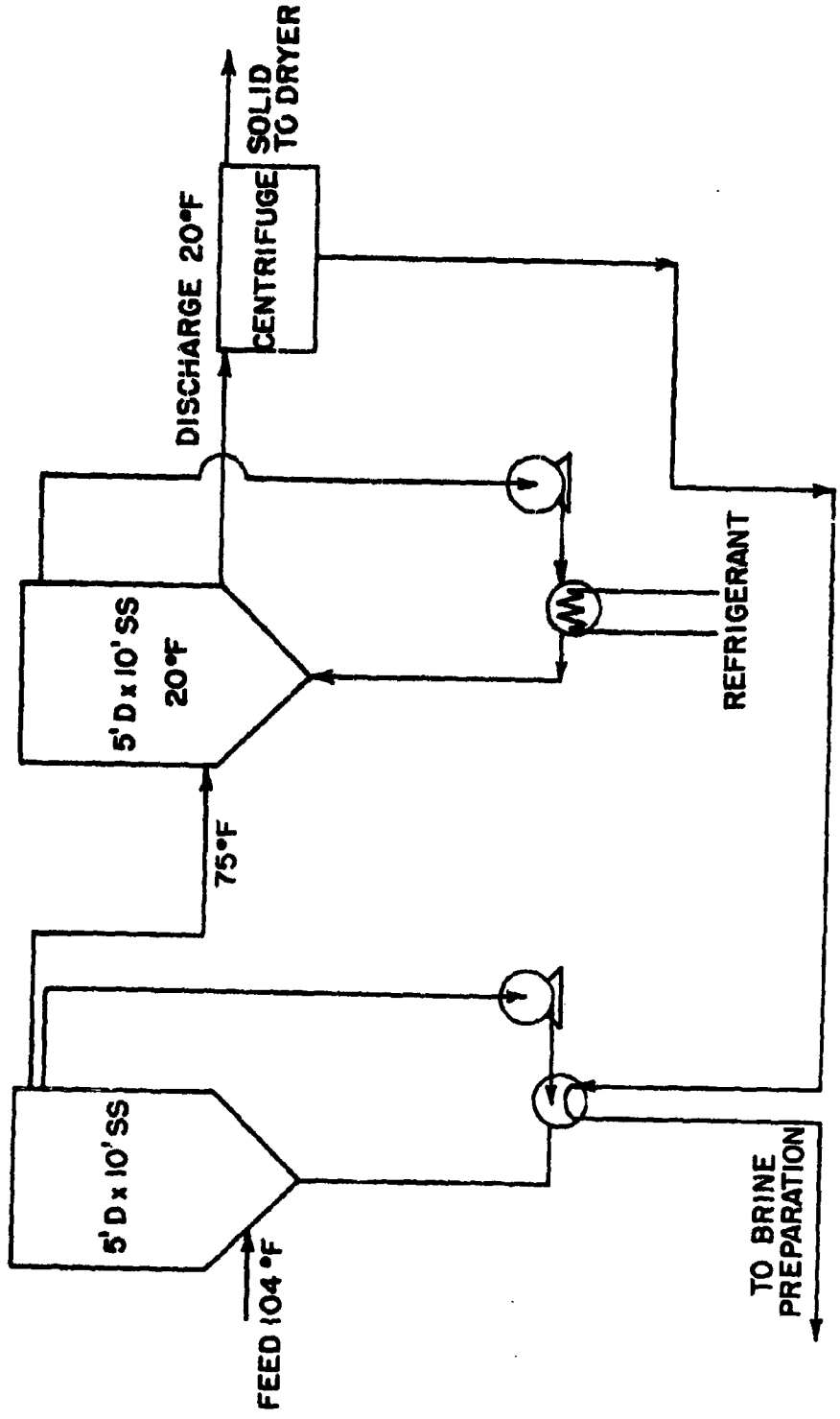


FIGURE 2-14. SCHEMATIC SKETCH OF A SURFACE-COOLED CRYSTALLIZER SYSTEM

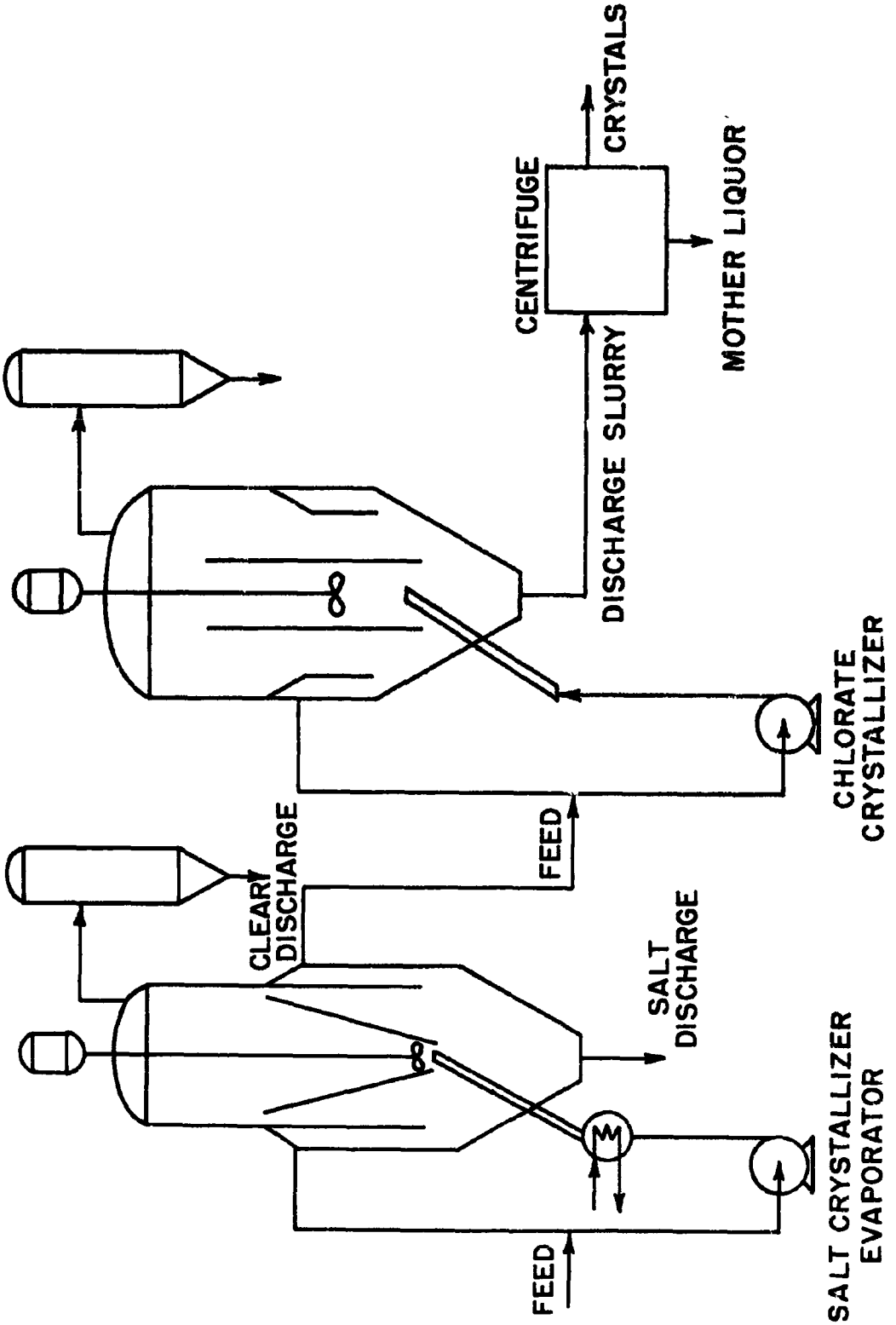


FIGURE 2-15. SCHEMATIC SKETCH OF A VACUUM-COOLED CRYSTALLIZER SYSTEM (REF: SWENSON EVAPORATOR CO.)

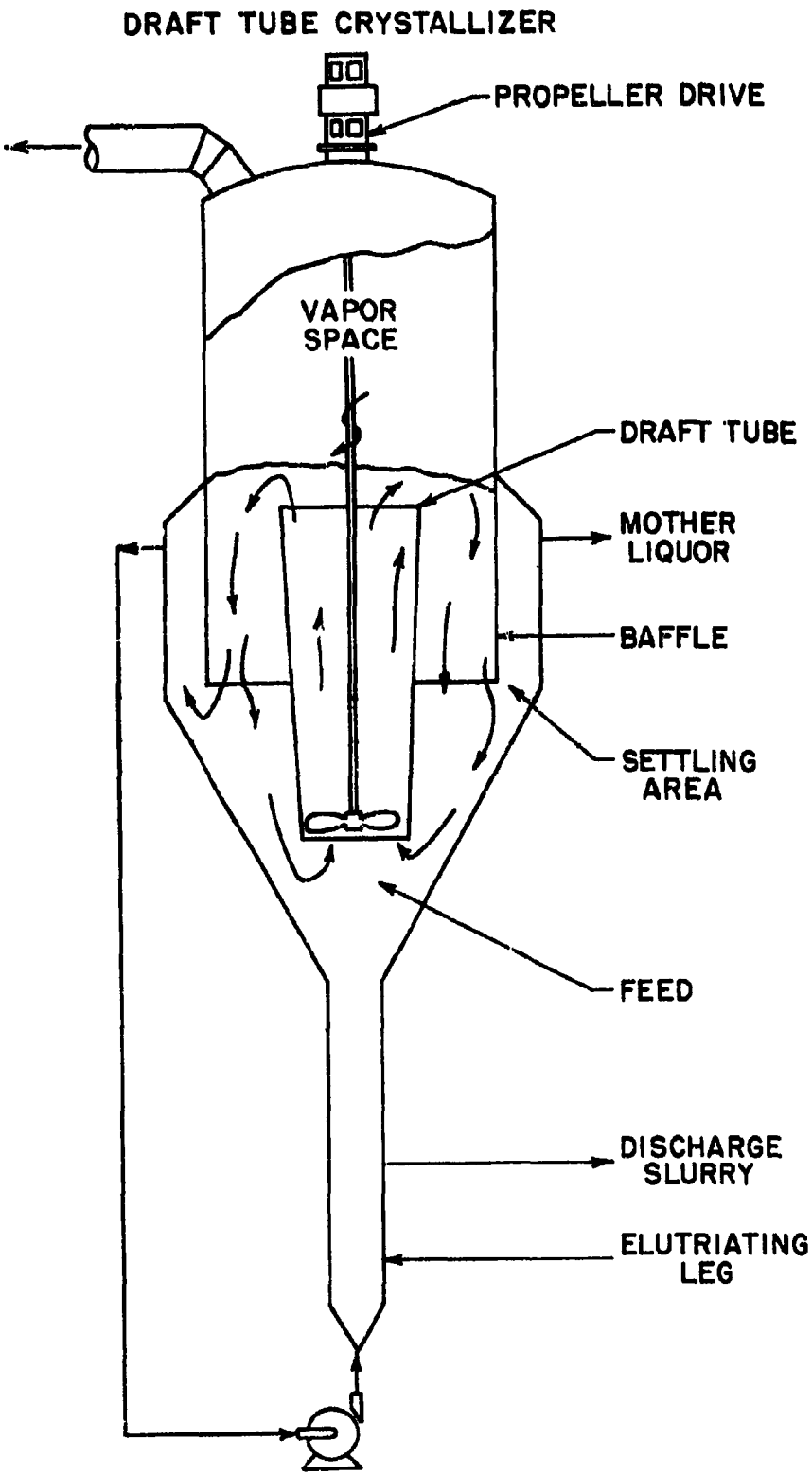
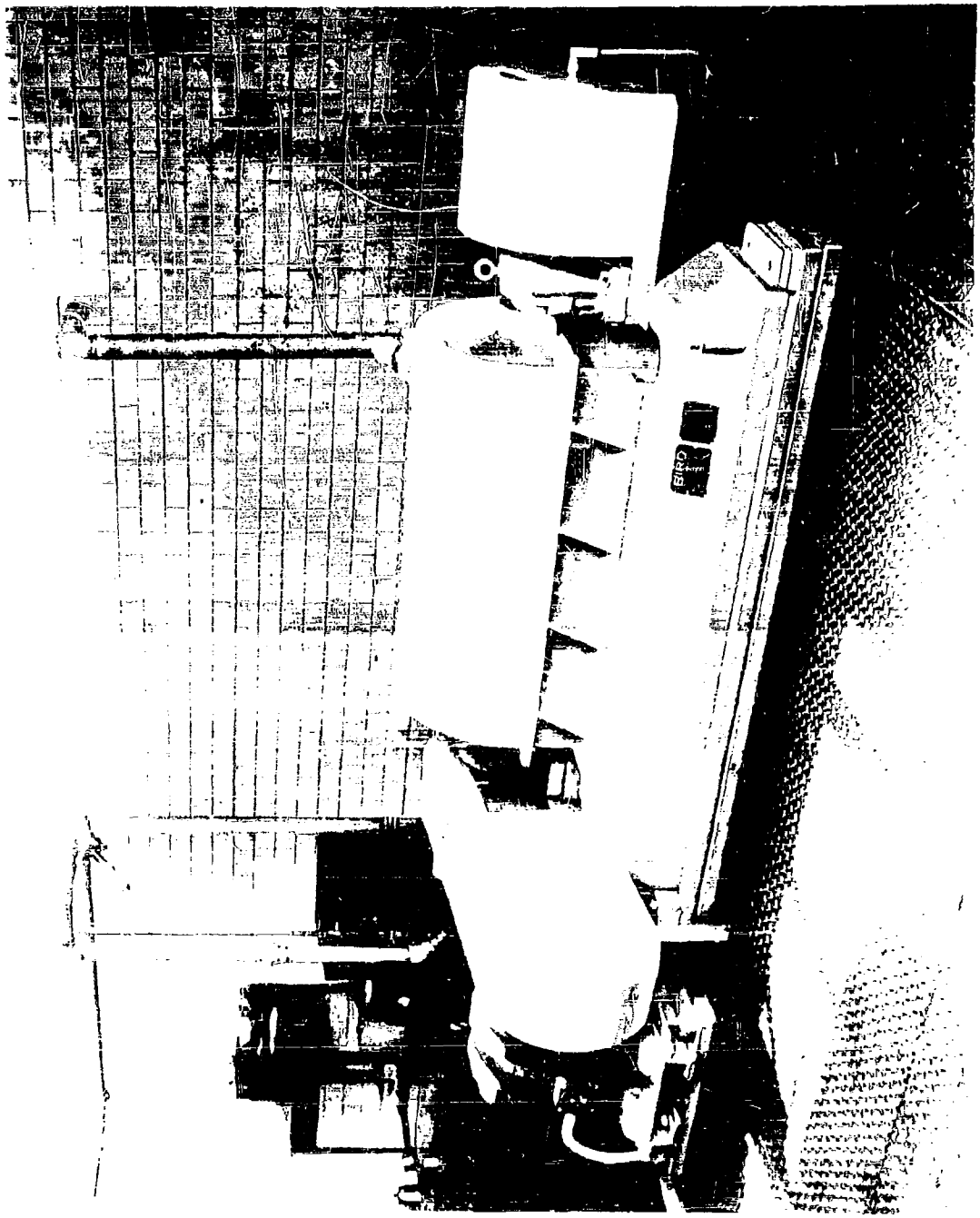


FIGURE 2-16. SECTIONAL VIEW OF A VACUUM-COOLED CRYSTALLIZER (REF: SWENSON EVAPORATOR CO.)



FIGURE 2-17. TYPICAL VACUUM-COOLED CRYSTALLIZER INSTALLATION (REF: SWENSON EVAPORATOR CO.)


BIRD

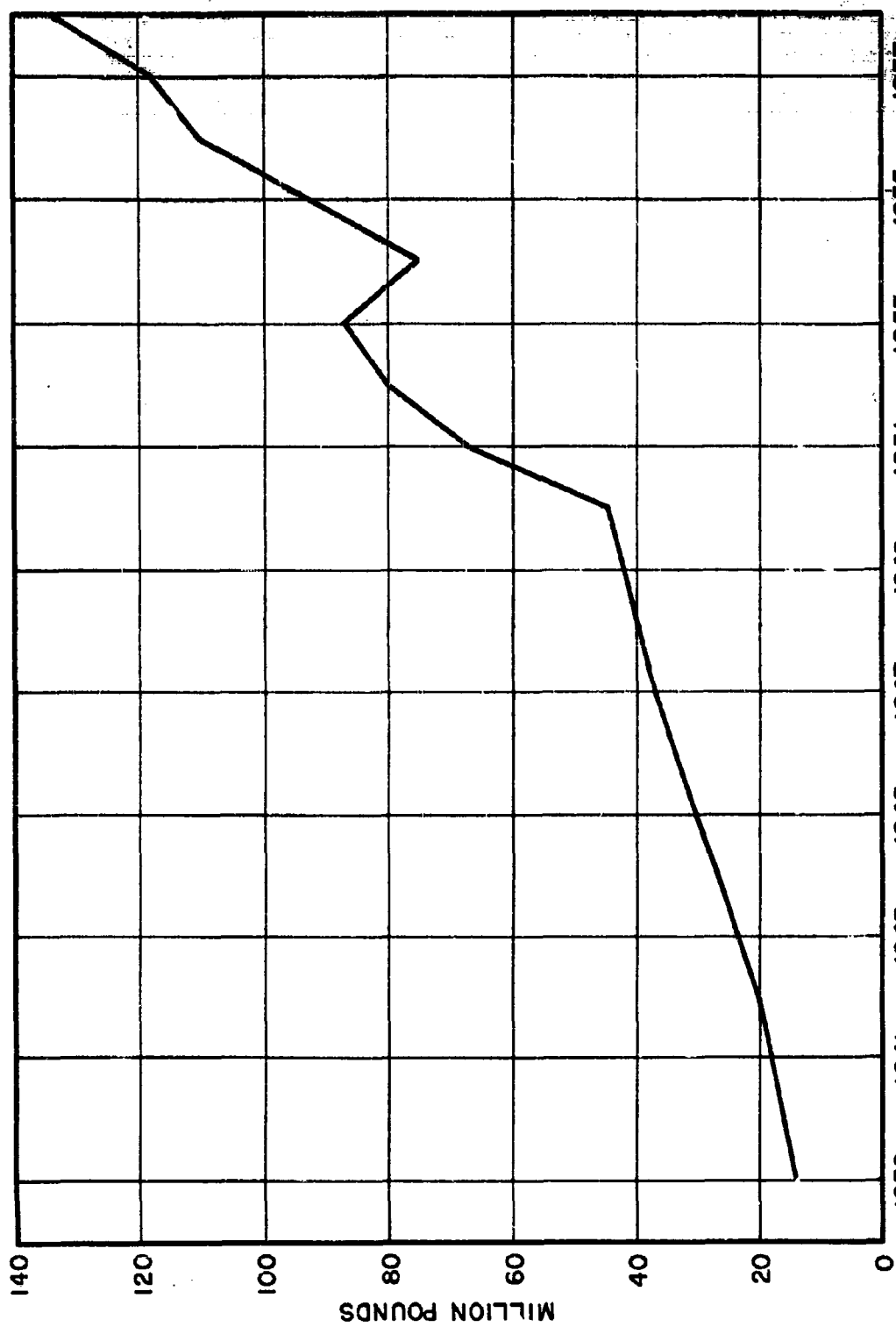


FIGURE 2-19. PRODUCTION OF $NaClO_3$ IN UNITED STATES (1939-1958) (REF. 4, 13)

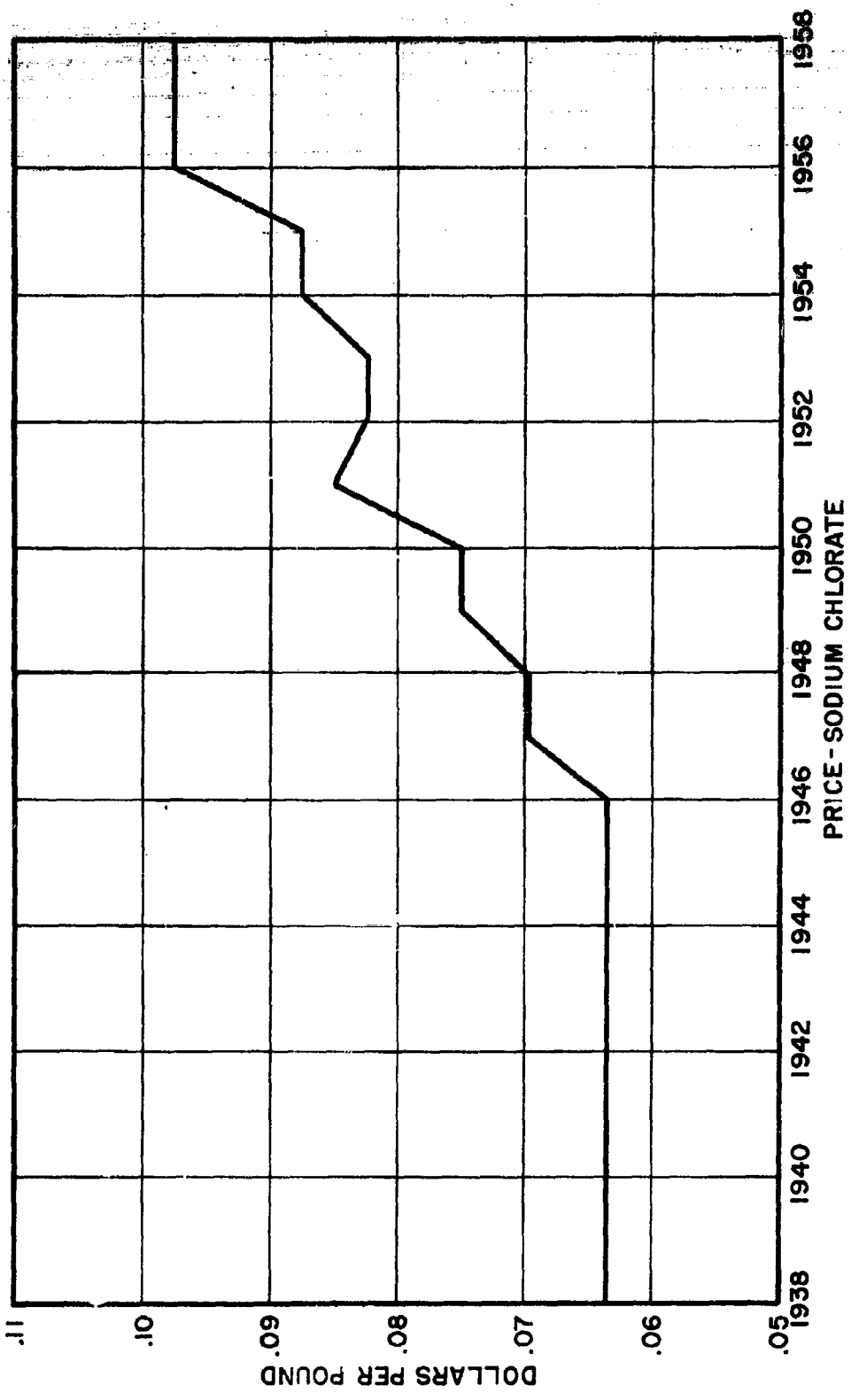


FIGURE 2-20. SELLING PRICE OF $NaClO_3$ IN UNITED STATES (1938-1958) (REF. 4, 13)

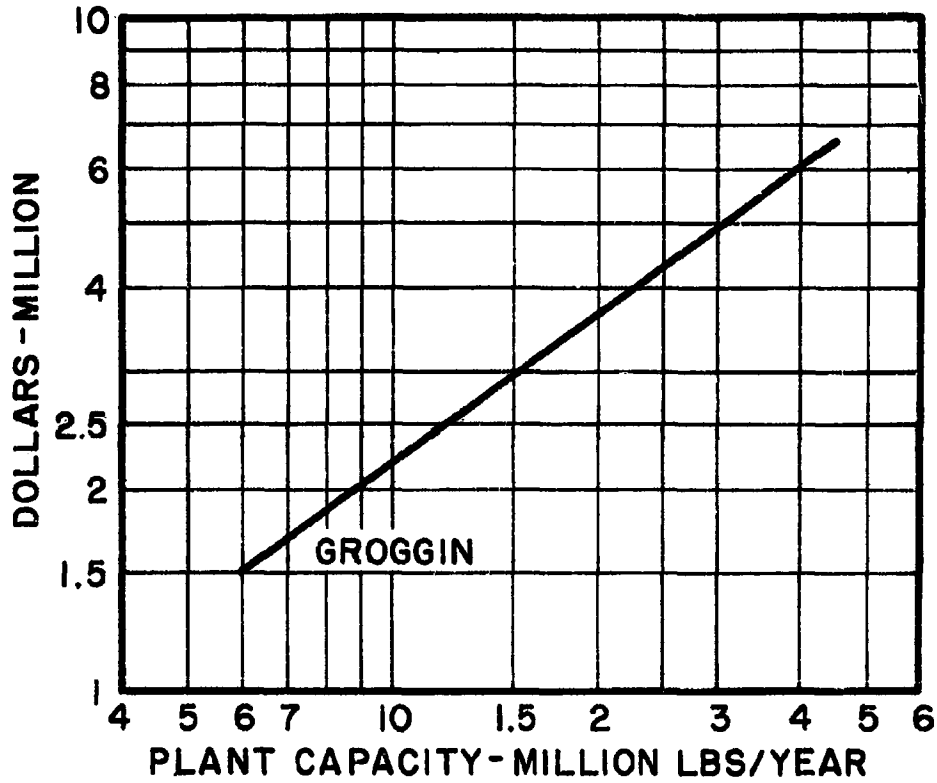


FIGURE 2-21. PLANT INVESTMENT VERSUS CAPACITY FOR $NaClO_3$ PLANTS (REF. 15)

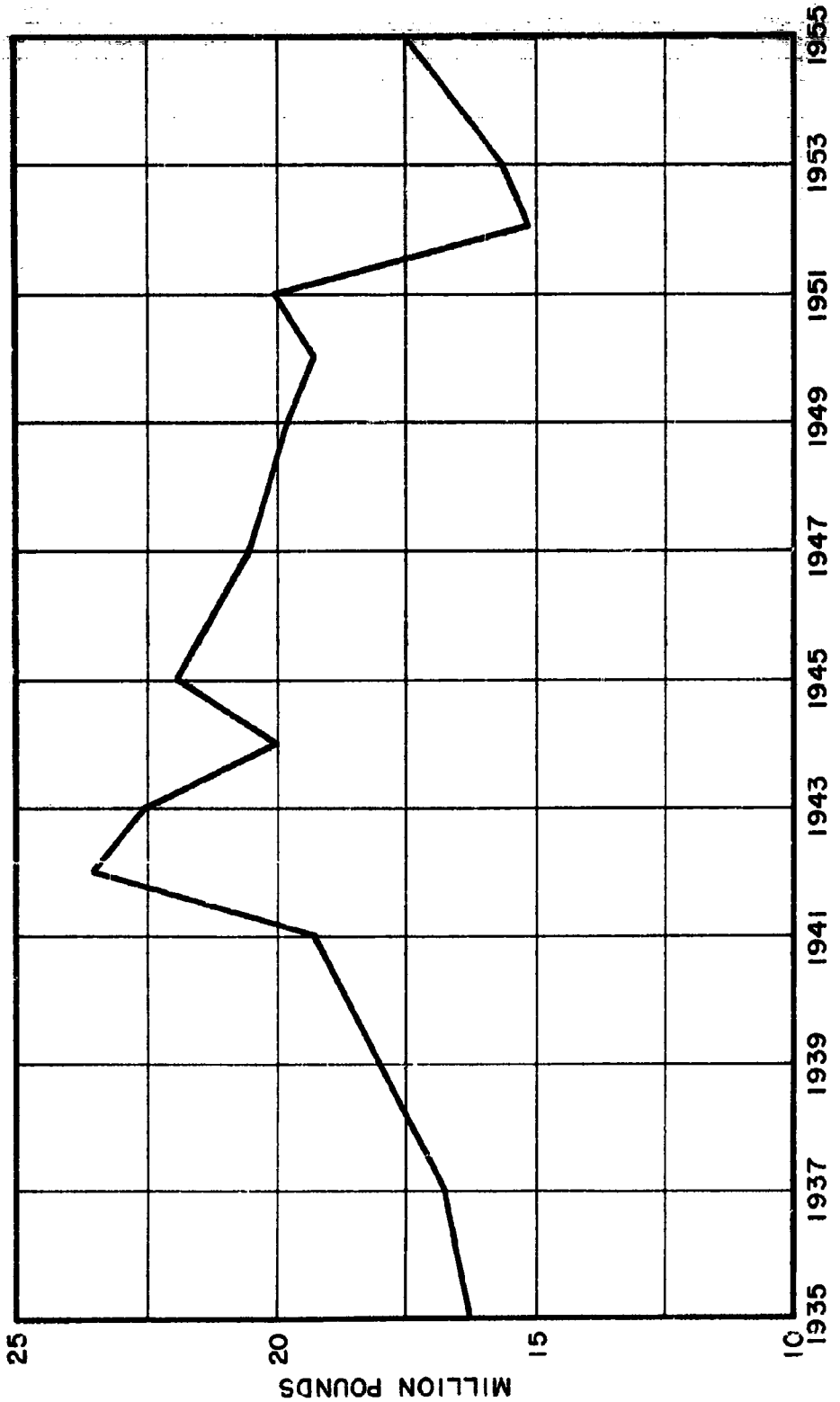


FIGURE 2-22. PRODUCTION OF $KClO_3$ IN UNITED STATES (1935-1955) (REF. 4, 13)

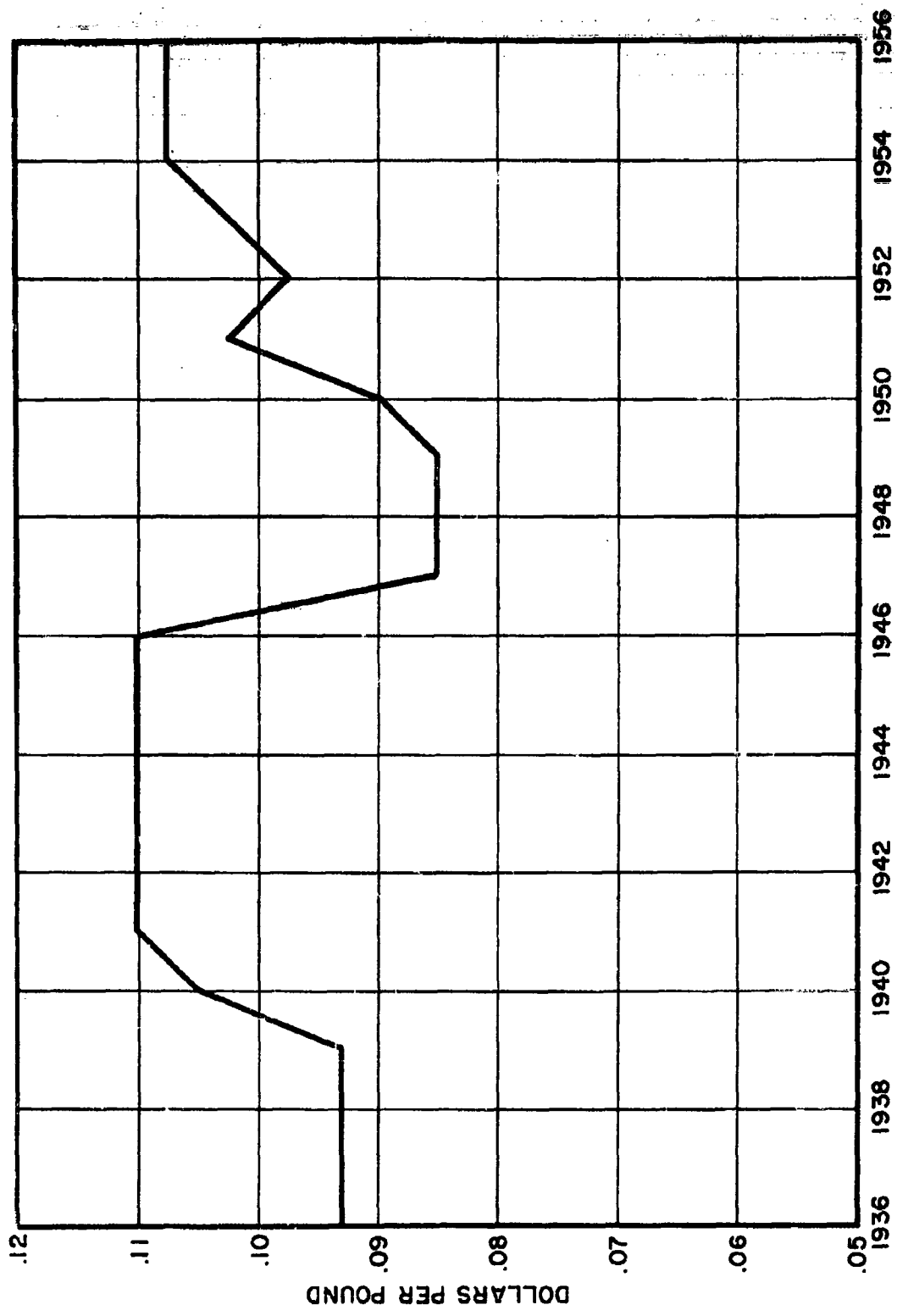


FIGURE 2-23. SELLING PRICE OF $KClO_3$ IN UNITED STATES (1936-1956) (REF. 4, 13)

TABLES

TABLE 1-1. CHLORATE COMPOUNDS

No.	Name	Formula
1.	Aluminum chlorate	$Al(ClO_3)_3$*
2.	Aluminum chlorate	$Al(ClO_3)_3 \cdot 6H_2O$
3.	Ammonium chlorate	NH_4ClO_3
4.	Barium chlorate	$Ba(ClO_3)_2$
5.	Barium chlorate	$Ba(ClO_3)_2 \cdot H_2O$
6.	Calcium chlorate	$Ca(ClO_3)_2$
7.	Calcium chlorate	$Ca(ClO_3)_2 \cdot 2H_2O$
8.	Lithium chlorate	$LiClO_3$
9.	Lithium chlorate	$LiClO_3 \cdot 1/2H_2O$(or $1/3H_2O$)
10.	Lithium chlorate	$LiClO_3 \cdot H_2O$
11.	Lithium chlorate	$LiClO_3 \cdot 3H_2O$
12.	Magnesium chlorate	$Mg(ClO_3)_2$
13.	Magnesium chlorate	$Mg(ClO_3)_2 \cdot 2H_2O$
14.	Magnesium chlorate	$Mg(ClO_3)_2 \cdot 4H_2O$
15.	Magnesium chlorate	$Mg(ClO_3)_2 \cdot 6H_2O$
16.	Potassium chlorate	$KClO_3$
17.	Silver chlorate	$AgClO_3$
18.	Sodium chlorate	$NaClO_3$

*According to Sidgwick (5), this compound is not known in the anhydrous state because upon dehydrating the hexahydrate, ClO_2 is generated, causing an eventual explosion.

TABLE 1-2. PERCHLORATE COMPOUNDS

No.	Name	Formula
1.	Aluminum perchlorate	$Al(ClO_4)_3$
2.	Aluminum perchlorate	$Al(ClO_4)_3 \cdot 6H_2O$
3.	Aluminum perchlorate	$Al(ClO_4)_3 \cdot 9H_2O$
4.	Ammonium perchlorate	NH_4ClO_4
5.	Barium perchlorate	$Ba(ClO_4)_2$
6.	Barium perchlorate	$Ba(ClO_4)_2 \cdot 3H_2O$
7.	Calcium perchlorate	$Ca(ClO_4)_2$
8.	Calcium perchlorate	$Ca(ClO_4)_2 \cdot 4H_2O$
9.	Lithium perchlorate	$LiClO_4$
10.	Lithium perchlorate	$LiClO_4 \cdot 3H_2O$
11.	Magnesium perchlorate	$Mg(ClO_4)_2$
12.	Magnesium perchlorate	$Mg(ClO_4)_2 \cdot 2H_2O$
13.	Magnesium perchlorate	$Mg(ClO_4)_2 \cdot 3H_2O$
14.	Magnesium perchlorate	$Mg(ClO_4)_2 \cdot 4H_2O$
15.	Magnesium perchlorate	$Mg(ClO_4)_2 \cdot 6H_2O$
16.	Potassium perchlorate	$KClO_4$
17.	Silver perchlorate	$AgClO_4$
18.	Silver perchlorate	$AgClO_4 \cdot H_2O$
19.	Sodium perchlorate	$NaClO_4$
20.	Sodium perchlorate	$NaClO_4 \cdot H_2O$

TABLE 2-1. DEFINITION OF ELECTRICAL TERMS*

Term	Definition
Ampere	The practical unit of electrical current. It is the quantity of electrical current which will deposit silver at the rate of 0.0011180 g/sec from a solution of $AgNO_3$ under a given set of conditions.
Coulomb	The practical unit of quantity of electricity. It is the quantity of electricity which is transferred through a given cross-section by one ampere in one second.
Current Density	The current in amperes flowing across any point, divided by the cross-sectional area of the conductor (e.g., amperes per square foot or amperes per square centimeter).
Current Efficiency	The ratio of the theoretical to the actual quantity of current used in an electrochemical process.
Faraday's Laws	(1) The quantity of substance set free at the electrode is directly proportional to the quantity of electricity which passes through a solution. (2) For the same quantity of electricity passed through solutions of various electrolytes, the amounts of each substance liberated at the electrodes are directly proportional to the chemical equivalents of the electrolytes. One chemical equivalent is liberated by 96,500 coulombs. This quantity of electricity is called a Faraday (F).
Ohm	The unit of electrical resistance. It is the resistance under which a potential difference of one volt has a current of one ampere flowing through it.

* Lange, N. A., (ed), Handbook of Chemistry, Handbook Publishers, Inc., and Perry[29], Sandusky, Ohio, 1937.

TABLE 2-1. DEFINITION OF ELECTRICAL TERMS* (Cont'd)

Term	Definition
Volt	The unit of electrochemical force. It is the difference in potential required to make a current of one ampere flow through a resistance of one ohm.

TABLE 2-2. OPERATING CHARACTERISTICS OF A TYPICAL SODIUM CHLORATE CELL[3]

Anode Material	Graphite
Anode Current Density	30 amp/ft^2
Cathode Material	Steel
Cathode Current Density	50 amp/ft^2
Volts per Cell	3.0 - 3.5
Amps per Cell	2500
Current Efficiency	75%
Temperature °F	113
Electrolyte	NaCl

TABLE 2-3. OPERATING CHARACTERISTICS OF A TYPICAL PERCHLORATE CELL[32]

Anode Material	Platinum*
Anode Current Density, amps/ft^2	250
Cathodic Material	Steel
Cathode Current Density, amp/ft^2	140
Volts per Cell	5.5-6.0
Amps per Cell	2500
Average Current Efficiency	90%
Temperature, °F	149
Electrolyte	$NaClO_3$

* Platinum losses amount to about 0.2 oz (troy) per ton of product.

TABLE 2-4. SUMMARY OF DATA ON THE THERMAL DECOMPOSITION OF SODIUM CHLORATE[46]

	$NaClO_3$ Orig. (g)	NaCl Remaining (g)	$NaClO_3$ Remaining (g)	$NaClO_3$ Reacted (g)	$NaClO_4$[a] (Theoretical (g)	$NaClO_4$ Yield (g)	$NaClO_4$[b] Yield, %	Conversion[c] Efficiency, %
1	10.00	.25	8.75	1.25	1.08	0.50	4.32	46.3
2	10.00	.50	7.60	2.40	2.07	1.40	12.10	67.7
3	10.00	1.00	5.20	4.80	4.14	3.25	28.00	78.7
4	10.00	1.2	4.20	5.80	5.00	4.20	36.20	84.1
5	10.00	1.5	2.75	7.25	6.25	5.00	43.20	80.0
6	10.00	2.2	0.75	9.25	7.98	6.00	51.70	75.2
7	10.00	2.6	0.40	9.60	8.27	5.00	36.2	60.4
8	10.00	3.5	0.25	9.75	8.40	4.00	33.5	47.6

a Calculated from the following equation $4NaClO_3 \xrightarrow[x]{106.5} 3NaClO_4 \underset{y}{\overset{122.5}{}} + NaCl$

$y = .75(122.5/106.5)\ x = 0.862x$

b Yield divided by amount theoretically possible if 10 grams reacted (i.e., 8.62g).

c Actual quantity formed divided by theoretical equivalent of $NaClO_3$ reacted.

TABLE 2-5. TYPICAL CHEMICAL ANALYSIS FOR POTASSIUM CHLORATE*

$KClO_4$ (assay)	99.8%
Chloride (as KCl)	.05
Chlorate (as $KClO_3$)	.015
Bromate (as KB_1O_3)	.0014
Hypochlorite (as ClO)	none
Sodium (Na)	.03
Calcium and Magnesium (Ca and Mg)	.007
Moisture	.006
Water insoluble	.01

* Product Bulletin No. EC-3, American Potash and Chemical Corp.

TABLE 2-6. TYPICAL CHEMICAL ANALYSIS FOR AMMONIUM PERCHLORATE[36]

	%
Water Insoluble	0.002
Ash	0.060
Chlorates	0.002
Chlorides	0.021
Sulfates	Trace
Bromates	0.001
Nonalkali metals	0.003
Moisture	0.007
Reaction to Methyl Orange	Neutral
NH_4ClO_4 assay	99.9

TABLE 2-7. TYPICAL CHEMICAL ANALYSIS FOR LITHIUM PERCHLORATE*

$LiClO_4$ (assay)	99.5%
Moisture (loss on heating at 356°F)	0.30
Li_2CO_3	.04
Acid Insoluble	.10 max.
Chloride (Cl)	.10
Iron (Fe)	.005
pH, 1% solution	6.5 to 8.5
Particle size	100% passing 40 mesh 95-99% retained on 100 mesh
Apparent Density	90-92 lb/ft^3

* Product Information Bulletin. DLi-10. American Potash and Chemical Corporation.

TABLE 2-8. DETAILS OF BATCH-TYPE CHLORATE CELL[18]

Dimension, Cell Body	Height 42 in., Length 43 in., Width 30 in.
Capacity	200 gal
Anode	10 graphite bars 1 in. by 7 in. by 40 in.
Life	1 year
Consumption	20 lb/ton $NaClO_3$
Cathode	2 Steel Sheets, 43 in. by 35 in. by 9/10 in.
Voltage	3.1-3.5 volts
Current	1600 amps
Current Density, anodic	50 amp/sq ft
Temperature, avg	95°F
pH	6.8
Production per Cell	2 lb $NaClO_3$/hr
Cell Feed	250 g/l NaCl
Cell Effluent	450-550 g/l $NaClO_3$ 85 g/l NaCl

TABLE 2-9. DETAILS OF BATCH-TYPE PERCHLORATE CELL[18]

Dimensions, Cell Body	Height 33 in., Length 30 in., Width 16 in.
Capacity	50 gal
Anode	4 Pt. Clad Cu Rods, 0.5 ft diameter x 30 in. long
Cathode	4 Steel Tubes, 3 in. diameter x 53 in. long
Voltage	6.2-6.8
Current, amps	500/cell
Current Density, anodic	480 amps/sq ft
Current Efficiency	93-97%
Temperature, avg	113°-131°F
pH	Alkaline, less than 10.5
Production/cell	2 lb/hr
Cell Feed	650-700 g/l $NaClO_3$
Cell Effluent	800 g/l $NaClO_4$
	20 g/l $NaClO_3$

TABLE 2-10. COMPARATIVE DATA ON PERCHLORATE CONVERSION WITH PLATINUM AND LEAD DIOXIDE ANODES[14]

Anode	$NaClO_3$ Conc. Range Over Which Efficiency Was Calculated		Current Efficiency
	Initial g/l	Final g/l	
Pt	602	100	83.2
	293	39.8	82.4
	602	100	87.4
	197.6	3.9	65.4
PbO_2	606	100	75.0
	198	1.8	27.1
	612	100	61.2
	186	49.1	33.9

Note:

Anode current density = 0.3 amp/cm^2

Cell temp. = 77-95°F

Cell potential = 5-6.5 volt

TABLE 2-11. GRANULATION REQUIREMENTS FOR $KClO_3$*

(% Passing Specified Sieves)

Sieve No.	Class 1	Class 2	Class 3	Class 4	Class 5	Class 6	Class 7
50	--	--	--	--	98.0	--	--
60	--	--	99.5	--	--	--	--
80	99.0	--	60.0	--	--	--	99.0
100	--	99.9	--	99.9	85.0	--	--
140	50.0 ± 5.0	--	--	50.0 ± 5.0	--	--	--
200	20 ± 3.0	5.0	--	40.0	55.0 ± 15.0	--	90.0
325	--	--	--	--	--	95.0	60.0

Grade A	Ingredient of primer mixtures
Grade B	Ingredient of pyrotechnic mixtures
Grade C	Ingredient of colored smoke mixtures

* MIL-P-150A

TABLE 2-12. COMPARISON OF VARIOUS CHEMICAL AND PHYSICAL REQUIREMENTS FOR NH_4ClO_4 [26]

(All Requirements "max" Unless Otherwise Noted)

	JAN-A-192		Company A					
	Grade I	Grade II	Type I	Type II	Company B	Company C	Company D	Company E
Water Insoluble	-		0.04	0.25	0.10	0.02	0.05	0.01
Sulfated Ash	-		.70	1.90	.25	.25	.25	.70
Chlorates	0.0035	0.10	.02	.02	.15	.15	.04	.02
Chlorides	.20	.10	.155	.155	.20	.10	.09	.10
Sulfates	-				.20	.20	.05	
Bromates	.003	nil	.004	.04	.04	.003	.01	.004
Chromates	-						.015	
Sodium as $NaClO_4$	.30	.60				.20		
Iron as Fe_2O_3	-		.0036	.0036			.01	.0036
Non-Alkali Metals	-				.04			
Ca/mg	.20	nil				.10		
Moisture	.15	.15	.05	.05	.02	.02	.05	.05
pH	4 at 20°C	4 at 20°C	4.3-5.8	5.0-6.5	-	4.0		4.3-5.8
Acidity	-				Neut. M.O.	Neut. M.O.	Neut. M.O.	
Grit	nil	nil						
Stability at 180°C							Min. 3 hr	
Volatile Matter (2 hr at 180°C)							Max. 0.055	
Color	White	White					White	White
Odor	None	None						
Purity (Min.)	99.0	98.0	98.4	98.3	99.0	99.8	99.0	99.0

TABLE 2-13. COMPARISON OF VARIOUS PARTICLE SIZE REQUIREMENTS FOR NH_4ClO_4[26]

(All Requirements "Min" Unless Otherwise Noted)

		JAN-A-192		Company A					
		Class A	Class B	Type I	Type II	Company B	Company C	Company D	Company E
16 Mesh	On						0.0-tr.		
	Through					100.0			
40 Mesh	On								
	Through	99.9							
48 Mesh	On						Max 10.0		
	Through	98.0	99.8			89.0-97.0			
50 Mesh	On			2.0-15.0	0-15.0				
	Through							93.0	
100 Mesh	On								70.0
	Through					18.0-50.0			
140 Mesh	On								
	Through		Max. 1.0						
150 Mesh	On						85.0		
	Through					2.0-15.0			
200 Mesh	On			91.0-99.0	91.0-99.0				
	Through								
325 Mesh	On						98.0		
	Through					0.0-2.0			

TABLE 2-14. THE CORROSION OF VARIOUS METALS BY NH_4ClO_4[36]*

Metal	Corrosion Rate (mils/yr)
Titanium	0
Durimet 20	0
Hastelloy HB-1	0
Hastelloy HC-3	0
347	0.0856
Hastelloy C	0.130
321	0.168
316	0.242
302	0.312
430	0.467
Duriron	0.565
Inconel	0.690
Nickel	1.38
Monel	2.96
Lead	3.45
Mild Steel (tank type)	4.02
Hastelloy B	5.14
Copper	8.06
Cast Iron	65.0
Aluminum	262.0

* Corrosion tests conducted at 140°F in saturated NH_4ClO_4-NaCl solution.

TABLE 2-15. EFFECT OF OPERATING TEMPERATURE ON PERFORMANCE OF A SODIUM CHLORIDE CRYSTALLIZER(36)

Temperature of NaCl Crystallizer, °C	80				60			50			
Temperature of NH_4ClO_4 Crystallizer, °C	25	30	35	50	25	30	35	25	30	35	50
Recycle (tons/ton NH_4ClO_4)	1.60	1.94	2.43	4.19	2.74	3.59	5.04	4.64	6.94	12.9	15.2
Water Evaporated (tons/ton NH_4ClO_4)	1.50	1.51	1.52	1.56	1.53	1.55	1.59	1.56	1.61	1.74	1.79

TABLE 2-16. ESTIMATED BREAKDOWN OF A TYPICAL $NaClO_3$ PLANT INVESTMENT

Plant Capacity - 18,000 ton/year[a]
Plant Cost - $5,600,000[b]

	Breakdown	
Cells & Cell Building	37%	$2,072,000
Electrical Converter and Building	17%	952,000
Process Building	7%	392,000
Auxiliary Electrical Equipment	5%	280,000
Other Process Equipment	11%	616,000
Adminstration and Lab Building	6%	336,000
Plant Facilities (includes warehouses, water mains, sewers, roads, etc.)	8%	448,000
Tools, Fixtures	4%	224,000
Contingency	5%	280,000
	100%	$5,600,000

a On the basis of Faith et al[37], this size plant would cost approximately $5,500,000.

b Based on Groggin's[27] data upgraded for increased costs.

TABLE 2-17. ESTIMATED COST OF PRODUCTION OF SODIUM CHLORATE

Plant Capacity - 18,000 ton/yr

Production, ton/yr % Capacity Raw Materials	18,000 100 $/yr	¢/lb	12,600 70 $/yr	¢/lb	9,000 50 $/yr	¢/lb
Salt	207,000	.575	145,000	.575	103,500	.575
Hydrochloric Acid	22,800	.063	16,000	.063	11,400	.063
Sodium Dichromate	23,400	.063	16,400	.063	11,700	.063
Utilities						
Electricity	357,000	992	250,000	.992	178,500	.992
Water	50,000	.139	35,000	.139	25,000	.139
Steam	79,200	.220	55,500	.220	39,600	.220
Aux. Electricity	74,200	.206	52,000	.206	27,100	.206
Operating Labor	142,500	.396	142,500	.566	142,500	.792
Operating Supervision	36,720	.102	36,720	.146	36,720	.204
Maintenance: Labor and Material	280,000	.778	280,000	1.111	280,000	1.556
Anode Replacement	90,000	.250	63,000	0.25	45,000	.25
Laboratory	42,000	.117	42,000	0.167	42,000	.233
Management (Inc. Account)	56,640	.158	56,640	0.225	56,640	.315
Insurance	56,000	.156	56,000	0.222	56,000	.311
Property Taxes	56,000	.156	56,000	0.222	56,000	.311
Depreciation	560,000	1.556	560,000	2.222	560,000	3.111
TOTAL	$2,133,460	5.929	$1,862,760	7.389	$1,681,660	9.332

For details of calculations see Appendix C.

TABLE 2-18. ESTIMATED RETURN ON INVESTMENT FOR A SODIUM CHLORATE PLANT

Investment - $5,600,000

10.5¢/lb	100% 18,000 ton/yr $/yr	70% 12,600 ton/yr $/yr	50% 9,000 ton/yr $/yr
Gross Sales	3,780,000	2,645,000	1,890,000
Less:			
Production Costs	2,133,460	1,862,760	1,681,660
Profit before Taxes	1,646,540	782,240	208,340
Federal Taxes	855,000	407,000	108,000
Net Profit after Taxes	791,540	375,240	100,340
Percent Return on Investment	14.2	6.7	1.8
9.75¢/lb			
Gross Sales	3,510,000	2,460,000	1,745,000
Less:			
Production Costs	2,133,460	1,862,000	1,681,660
Profit before Taxes	1,376,540	598,240	63,340
Federal Taxes	715,000	311,000	32,900
Net Profit after Taxes	661,540	287,240	30,440
Percent Return on Investment	11.8	5.2	0.55
9.00¢/lb			
Gross Sales	3,240,000	2,270,000	1,570,000
Less:			
Production Costs	2,133,460	1,862,760	1,681,660
Profit before Taxes	1,106,540	407,240	Loss-111,660
Federal Taxes	575,000	211,000	---
Net Profit after Taxes	531,540	196,240	---
Percent Return on Investment	9.5	3.5	---

For details of calculations see Appendix C.

TABLE 2-19. ESTIMATED COST OF PRODUCTION OF SODIUM PERCHLORATE

Plant Capacity - 10,000 ton/yr
Plant Investment - $3,600,000

% of Capacity	100		70		50	
Raw Materials	$/yr	¢/lb	$/yr	¢/lb	$/yr	¢/lb
Sodium Chlorate	1,645,000	8.22	1,152,000	8.22	822,000	8.22
Chemicals						
Hydrochloric Acid	4,000	0.02	2,800	.02	2,000	.02
Sodium Dichromate	12,000	0.06	8,400	.06	6,000	.06
Utilities						
Electricity	120,000	0.60	84,000	0.60	60,000	0.60
Water	27,800	0.139	19,460	0.139	13,900	0.139
Steam	44,000	0.22	30,800	0.222	22,000	0.222
Operating Labor	104,880	0.524	104,880	0.749	104,880	1.048
Operating Supervision	36,720	0.184	36,720	0.262	36,720	0.368
Maintenance	180,000	0.90	180,000	1.286	180,000	1.80
Anode Replacement	114,000	0.57	79,800	0.57	57,000	0.57
Laboratory	12,000	0.06	12,000	0.086	12,000	0.12
Management and Overhead	8,640	0.043	8,640	0.062	8,640	0.086
Insurance	36,000	.18	36,000	.257	36,000	.36
Property Taxes	36,000	.18	36,000	.257	36,000	.36
Depreciation	360,000	1.80	360,000	2.57	360,000	3.60
TOTAL	$2,741,040	13.70	$2,151,500	15.36	$1,757,140	17.57

For details of calculation see Appendix C.

TABLE 2-20. ESTIMATED COST OF PRODUCTION OF AMMONIUM PERCHLORATE

Plant Capacity - 9,000 ton/yr
Plant Investment - $4,800,000

% Capacity	100		70		50	
Raw Materials	$/yr	¢/lb	$/yr	¢/lb	$/yr	¢/lb
Sodium perchlorate	2,620,000	14.55	1,835,000	14.55	1,310,000	14.55
Ammonia	80,000	0.45	56,000	0.45	40,000	0.45
HCl	266,000	1.48	186,000	1.48	133,000	1.48
Utilities						
Steam, Water, Electricity	180,000	1.0	126,000	1.0	90,000	1.0
Operating Labor	140,880	0.582	104,880	0.832	104,880	1.164
Operating Supervision	36,720	0.204	36,720	0.291	36,720	0.408
Maintenance	240,000	1.333	240,000	1.905	240,000	2.666
Laboratory	12,000	0.067	12,000	0.095	12,000	0.134
Management and Overhead	8,640	0.048	8,640	0.069	8,640	0.096
Insurance	48,000	0.266	48,000	0.381	48,000	0.532
Property Taxes	48,000	0.266	48,000	0.381	48,000	0.532
Depreciation	480,000	2.660	480,000	3,810	480,000	5.320
TOTAL	$4,118,240	22.906	$3,181,240	25.244	$2,551,240	28,332

For details of calculations see Appendix C.

TABLE 2-21. ESTIMATED RETURN ON INVESTMENT OF AN AMMONIUM PERCHLORATE PLANT

Investment - $4 800,000

Selling Price - 34¢/lb	9,000 ton/yr 100%	6,300 ton/yr 70%	4,500 ton/yr 50%
Gross Sales	6,110,000	4,280,000	3,060,000
Less:			
Production Costs	4,118,240	3,181,240	2,551,240
Profit before Taxes	1,991,760	1,098,760	508,760
Federal Taxes	1,038,000	570,000	264,000
Net Profit after Taxes	953,760	528,760	244,760
Percent Return on Investment	19.8	11.0	5.1

For details of calculations see Appendix C.