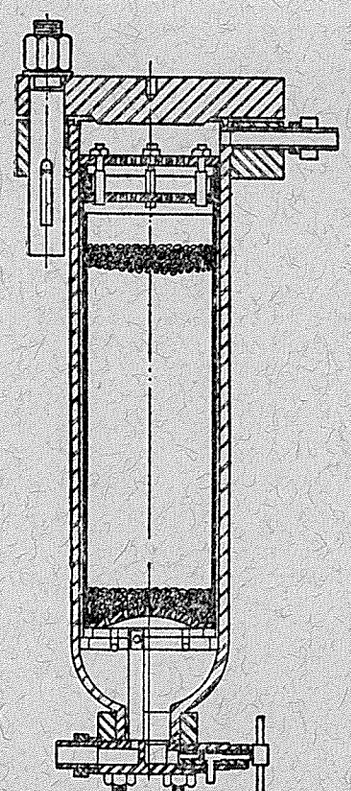
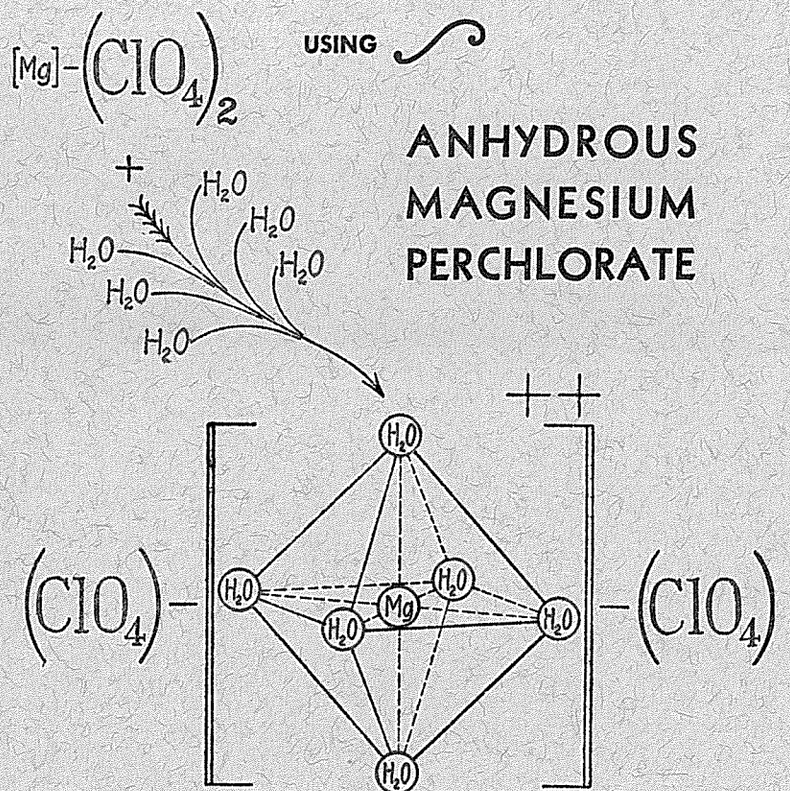


High Pressure Drying Bottle
For Use With
Anhydrous Magnesium Perchlorate

DEHYDRATION STUDIES



+32 700 CALORIES

Published by
THE G. FREDERICK SMITH CHEMICAL CO.
867 McKinley Ave.
COLUMBUS, OHIO

Data Compiled by
G. FREDERICK SMITH, Ph.D.
Professor of Chemistry
Univeristy of Illinois, Urbana

DEHYDRATION STUDIES

USING

ANHYDROUS MAGNESIUM PERCHLORATE

Data Compiled by
G. FREDERICK SMITH, Ph.D.
Professor of Chemistry
University of Illinois, Urbana

Published by
THE G. FREDERICK SMITH CHEMICAL CO.
867 McKinley Ave.
COLUMBUS, OHIO

First printing, 1936.

Second printing, 1943.

Third printing, 1951

Printed in U. S. A. by
Stoneman Press
Columbus, Ohio

CONTENTS

PREFACE

The title of this book was selected for two major reasons. First and foremost, its subject matter deals with the general topic of desiccation. Secondly, because anhydrous magnesium perchlorate, during the past twenty years, has gained preeminence among an increasingly large group of commercially available dehydrating reagents. It is an outstanding representative of the group.

The perchlorate drying agents have gained this widespread recognition and application without the aid of a general attempt to gather together into one descriptive source the widely distributed literature references to their uses and properties. Methods involving the granting of exclusive distributing agencies, has in the past, resulted in what is now believed to be an excessive sale price. At the former price $3 to $4 per pound, the widespread use of the perchlorate driers would not logically be expected. In spite of these facts, the perchlorate drying agents are being sold everywhere throughout the United States and extensively in Canada and England.

Following the general research policy of The G. Fredrick Smith Chemical Company, improvements in the manufacture of the magnesium perchlorate drying agents have been developed. Description of these improvements has been published in the various leading scientific journals. As a result of these advances the time is at hand for the sale of these products at a radical reduction in price.

Finally this booklet is prepared to collect under one cover many facts and experiments on the general topic of dehydration. It therefore takes its place along with previously published booklets provided by this company for general and gratuitous distribution to all users of chemicals, to technologists, scientists, industrial and research chemists and physicists. It is hoped that it will receive the same gratifying recognition given its predecessors "Perchloric Acid," "Periodic Acid," "Cerate Oxidimetry," "Ortho-Phenanthroline," "Cupferron and Neo-Cupferron," "Colorimetry for Chemists," "Electrochemical Analysis with Graded Cathode Potential," and "Applications of Dioximes to Analytical Chemistry," the first three of which are now in their second edition.

G. FREDERICK SMITH,
Department of Chemistry, University of Illinois.

INTRODUCTION

The first preparation of anhydrous magnesium perchlorate was made twelve years before the publication of this booklet.[1] The determination of the vapor pressure of the anhydrous product and its lowest hydrate has demonstrated perfect drying efficiency. Gases dried by its use showed zero vapor pressure. The magnesium perchlorate drying agents have been manufactured and distributed commercially for the past eight years. Since their first introduction in the usual chemical trade channels, reference has been made to their use in a large number of scientific papers appearing in the best chemical journals. Many recent standard text books describe the advantages in their use.[2] Official standard methods of analysis include their use as dehydrating reagents. Apparatus types have been originated and improved, stocked and distributed, which take advantage of new possibilities as a result of the better performance of the magnesium perchlorate driers.[3] Claims made by the manufacturers of these drying agents have been repeatedly substantiated by the results obtained in their use as reported by many scientists in published data. Probably no class or type of dehydrating chemical has been more extensively and exhaustively studied than the perchlorate driers. Since the introduction of the magnesium perchlorate desiccants a number of competitive reagents have appeared on the market.[4] In no single case, it is claimed, can a chemical drying agent be shown to be equal to anhydrous magnesium perchlorate in efficiency, capacity and velocity, combined. Its dehydrating power to produce zero vapor pressure has never been disputed. The capacity under proper conditions provides for a chemical reaction with half its dry weight as moisture which is absorbed. Scientific record of the large scale industrial application of anhydrous magnesium perchlorate in the absolute dehumidification of air has proven, better than any other claims could, its high dehydration speed.[5] In addition to all these simultaneous advantages two other properties are possessed by anhydrous magnesium perchlorate. It does not begin to lose its perfect dehydration efficiency until the temperature 275°F. is reached. Ammonia gas is quantitatively absorbed, up to and including a temperature of 440°F. Approximately 50% of its dry weight can be absorbed as fixed ammonia. Commercial application has been made of this property in the scrubbing of gases to eliminate ammonia.[6] Anhydrous magnesium perchlorate has been frequently used as a catalytic agent in organic chemical syntheses.

The magnesium perchlorate drying agents are regenerative. It is a fact that should be obvious with a moment's thought, that the easier a chemically reacting, or physically absorbent dehydrating agent can be regenerated, the less efficient it must be as a desiccant. This fact is overlooked in many cases. A drying agent in one statement often is praised for its drying efficiency and this contradicted by claims for easy regeneration. Closely linked with the possibility of regeneration is the temperature coefficient of loss in dehydrating efficiency. The lower the temperature of regeneration the lower the dehydrating efficiency must be at that temperature. The spent magnesium perchlorate drying agents are only regenerated with special apparatus and under carefully controlled conditions. A final temperature of 400-480°F. is necessary for complete regeneration. A high vacuum must be employed to realize a satisfactory time rate of dehydration. Recrystallization of the completely spent magnesium perchlorate driers is required if a finished product granular in structure is to be obtained. The perfection of equipment and procedure for its use in the regeneration of the spent perchlorate driers, has been provided by the manufacturers of these products and is described in the subsequent pages of this booklet. Apparatus is included for regeneration on the hundred pound as well as on the one pound basis. Service by the manufacturers for the regeneration of suitable amounts of spent magnesium perchlorate driers is offered to large scale consumers. This service has been repeatedly used by consumers at a very material saving in drier costs. Apparatus for use in the large scale regeneration of the perchlorate driers can be supplied to the consumer by suitable arrangement with its designers. The magnesium perchlorate ammines obtained from the anhydrous salt in its use as an ammonia scrubber in

[1] Willard and Smith, "The Preparation and Properties of Magnesium Perchlorate and Its Use as a Drying Agent." *J. Am. Chem. Soc.* 44, 2255 (1922).

[2] Lundell, Hoffman and Bright, "Chemical Analysis of Iron and Steel," John Wiley and Sons, Inc., New York, (1931). Numerous references to the use of the magnesium perchlorate driers appear in this book and many other recent standard texts and reference works.

[3] Smith, "Magnesium Perchlorate Trihydrate, Its Use as Drying Agent for Steel and Organic Combustion Analysis" *Ind. Eng. Chem.*, 16, 20 (1924).

W. D. Turner, U. S. Patent 1,877,151 "An Improved Absorption Tube for Combustion analysis." *Ind. Eng. Chem. Anal. Ed.*, 3, 63 (1931).

Other references could be included such as the Miller Absorption Bulb, A. H. Thomas Catalogue, 1931 Ed., No. 3854.

[4] Examples are anhydrous alumina, (Al_2O_3) barium oxide (BaO) and calcium sulfate hemihydrate $CaSO_4 \cdot \frac{1}{2} H_2O$.

[5] Smith. "The Improved Dehydration of Air for Use in the Manufacture of High Pressure Tank Oxygen Using Anhydrous Magnesium Perchlorate." *J. Soc. Chem. Ind.*, 53, 357 (1934).

gas purification can be regenerated also.[6] In this case a higher temperature and a lower pressure must be employed for efficient results. In any case, may it be repeated, the more efficient the drying agent the more difficult is its regeneration.

It is the purpose of this booklet to aid in a material way in the clarification of points at issue, to gather together comparative data including all types of dehydrating agents and to summarize the published scientific data related to the subject as a general problem. This problem is solved in small part only through the survey of the present literature. It is fortunate that dehyrating reagents are obtainable commercially of a considerable range of efficiencies and capacities. Differences in chemical and physical classification make for a wider distribution in conditions and extents of application. It is believed that the perchlorate drying agents are without a superior in combined advantages which make for versatility, economy and efficiency. In our discussion to follow it is hoped that this fact will be but one of many valuable ideas to be obtained from this booklet.

[6] Berliner and Burke, *Chem. Met. Eng.*, 37, 751 (1930).

SECTION 1

TYPES OF DEHYDRATING AGENTS CLASSIFIED

1. **Regenerative and Non-Regenerative.** These two main distinctions between all dehydrating reagents and systems involve their adaptation to regeneration to their original drying efficiency after complete or partial absorption of moisture. Some dehydrating agents cannot be regenerated by any practical procedure. Still other types could be restored after use in a satisfactory manner but are not regenerated since the cost of the process is much out of proportion to the original cost of the product. A third type of drying process involves a group of liquid gas scrubbing systems which permit continuous regeneration by the process of gradual withdrawal of spent liquors which are replaced continuously by a fresh supply of the parent substance. The cascade or counter-current flow principles are employed in examples of this type.

2. **Chemically Reacting and Physical Absorption Desiccants.** There are two general mechanisms through the action of which water vapor in a system is removed by the use of drying agents. The water vapor may be fixed as a result of chemical reaction with the drying agent. A new chemical unit is formed involving the interaction of primary chemical valences or, as in most cases, involving coordinate valence relationships. The water vapor may be fixed as a result of physical surface absorption. The latter might be termed contact, or capillary absorbents. The former group is the more common among commercially available products but the latter type is represented by a number of examples. Some drying agents combine the principles of chemical reaction and physical absorption.

3. **Coordination Reagents and Primary Valence Reactants.** Drying agents representing the largest of all groups absorb water through the formation of new chemical species. They are classified best under the Werner system of coordination types. Coordination numbers are commonly 2, 4 and 6 though the values 1, 3 and 5 are not uncommon. The water molecules are attached to the parent substance by secondary valence bonds which are in general less intense in combining power as the number involved increases. The capacity of the drying agents of this type to absorb water is proportional to the number of coordinate valences which come into play. The coordinate types of desiccants vary in drying efficiency (i.e. intensity). The variation is from those poor in

comparison to the primary valence reactants, to a single known illustration having coordinate valence strength equal to the perfect efficiency of the primary valence type. This example is that of anhydrous magnesium perchlorate. The primary valence type of desiccant is represented by the example of phosphorus pentoxide, (P_2O_5). Its reaction with water vapor results in the formation of meta phosphoric acid as a first product of reaction (HPO_3), then ortho-phosphoric acid, (H_3PO_4). A second type of drying agent involving absorption through reaction of primary valence bonds is metallic sodium or potassium. In such cases the dehydration reaction results in the simultaneous formation of hydrogen. The primary valence type of dehydrating reagents as a group shows the greatest number of perfect drying efficiencies. As a class however they are not regenerative desiccants and while exceedingly fast dehydrators, have low capacity. In addition the physical and chemical properties of the product formed are often undesirable.

A classification of commercial drying agents has been made by J. H. Bower [7] which is somewhat different from that outlined above. To the list of drying agents classified at the Bureau of Standards there will be included in this discussion data based upon the use of concentrated sulfuric acid and its solutions in water studied extensively by Wilson [8] and data also from a paper by Wilson and Fuwa [9], concerning other drying agent phenomena particularly of absorption driers.

According to the classification by Bower [7] there are five subdivisions.

Drying agents with efficiencies defined by the chemical and physical reactions of the following types:

Class 1. $A\ (H_2O)\ y\ (solid) + xH_2O = A\ (H_2O)\ x + y\ (solid)$

Class 2. $A\ (solid) + H_2O =$ saturated solution

Class 3. $A\ (liquid) + H_2O =$ solution

Class 4. Adsorption drying agents

Class 5. $M + (H_2O)\ x = M\ (OH)\ x + x/2h_2$ ($M =$ metal)

Drying agents illustrating the five classes listed by Bower are the following:

Class 1. Calcium Chloride Monohydrate

$$CaCl_2 \cdot H_2O + H_2O = CaCl_2 \cdot 2H_2O$$

[7] Bower, "Comparative Efficiencies of Various Dehydrating Agents Used for Drying Gases (A Survey of Commercial Drying Agents)." *Bur. of Stands., J. Res.*, 12, 241 (1934).

[8] Wilson, "Humidity Control by Means of Sulfuric Acid Solutions With Critical Compilation of Vapor Pressure Data." *Ind. Eng. Chem.*, 13, 326 (1921).

[9] Wilson and Fuwa, "Humidity Equilibria of Various Common Substances." *J. Ind. Eng. Chem.*, 14, 913 (1922).

Class 2. Common salt

Class 3. Sulfuric Acid

Class 4. Silica Gel

Class 5. Metals and metal alloys such as sodium or sodium amalgan.

As is common practice, Bower subdivides the study of drying agents into three branches (a) drying power (intensity), (b) drying capacity and (c) speed of drying (velocity of dehydration). Fourth and fifth important studies are (d) the determination of the temperature range of dehydration at maximum intensity and (e) conditions best suited to regeneration.

CHEMICAL AND PHYSICAL DEHYDRATION REACTIONS AS REVERSIBLE EQUILIBRIA

The classification of drying agents as studied by Bower was planned and executed

"to compare the efficiencies of the various agents when used to dry a gas stream by a commonly used laboratory procedure, the results reported should be understood to pertain to approximately equilibrium conditions. No attempt has been made to determine the ultimate drying power. Where this latter information is available in the literature it has been reduced to the same units and is inserted in the table for comparison.* No study has been made of the capacity of the materials or limiting rates of air flow."

Since the chemical or physical reaction of a drying agent is reversible as represented in the following reaction:

$$Mg(ClO_4)_2 + 6H_2O \leftrightarrows [Mg\ (H_2O)_6]\ (ClO_4)_2 + 32708 \text{ calories}$$

it would be instructive to examine into the conditions affecting the equilibrium. The following points will then be evident.

1. The capacity for absorbing moisture is measured by the proportion of water reacting to the amount of drying agent involved.

2. The drying intensity is proportional to the heat evolved by the reaction of absorption.

3. The energy required in regeneration is equal to the heat evolved in the reaction as indicated from left to right above.

The absolute value of the dehydrating efficiency is defined if the vapor pressure of the spent reaction compound (hexaquo-magnesium perchlorate) is known at a series of temperatures. This value does not enter into the balanced equilibrium. The reaction of dehydration may

*Table 1 in the subsequent data.

proceed stepwise and the same three characteristics are involved in each step. Thus the reaction above has two intermediate steps as follows:

$$Mg(ClO_4)_2 + 2H_2O \leftrightarrows [Mg(H_2O)_2]\ (ClO_4)_2 + 13{,}509 \text{ calories}$$
$$Mg(ClO_4)_2 + 4H_2O \leftrightarrows [Mg(H_2O)_4]\ (ClO_4)_2 + 21{,}593 \text{ calories}$$

The calories evolved in the successive additions of two molecules of water diminish with each step to form the next higher coordination compound. Thus:

$$Mg(ClO_4)_2 \rightarrow [Mg(H_2O)_2]\ (ClO_4)_2 \qquad (13{,}509 \text{ calories})$$
$$[Mg(H_2O_2]\ ClO_4)_2 \rightarrow [Mg(H_2O)_4]\ (ClO_4)_2 \qquad (11{,}215 \text{ calories})$$
$$[Mg(H_2O_4]\ ClO_4)_2 \rightarrow [Mg(H_2O)_6]\ (ClO_4)_2 \qquad (7{,}984 \text{ calories})$$

The dehydration efficiency is greatest for the formation of the first coordinate water addition. This is shown by the release of the largest number of calories. The second and third pair of coordination valences are successively satisfied by pairs of water molecules accompanied by the release of progressively smaller numbers of calories. The vapor pressure of the lowest hydrate formed, $[Mg(H_2O)_2]\ (ClO_4)_2$, is found to be zero up to a temperature of 275°F. Since the next higher hydrate, $[Mg(H_2O)_4]\ ClO_4)_2$, is formed with the release of a lesser number of calories the drying efficiency to this stage would be expected to be less and the vapor pressure of the intermediate hydrate to be higher at a given temperature. Following an extension of the same reasoning the third step involves the lowest drying efficiency and the hexahydrated salt has the highest vapor pressure at a given temperature. These facts are substantiated by experiment.

Following the same process of reasoning the combining power of the six coordinate valences must differ from the first two, to the last two. The molecular configuration of one magnesium atom surrounded by six molecules of water must involve a closer packing of the first two waters with relation to the magnesium atom than is the case with the second pair of water molecules. Likewise the third pair of water molecules are least closely bound to the magnesium atom.* This concept is thought to be accurate since as will be shown later the X-Ray powder diffraction patterns of anhydrous magnesium perchlorate and the di, tetra and hexaquo addition compounds are all separate and distinct patterns.

The maximum dehydrating capacity for drying agents of this type is not always attained at maximum efficiency. For the most important

* By this process of reasoning the molecular model shown on the cover page of this booklet is not exact. The water molecules are all placed equi-distant from the magnesium atom.

gas conditioning processes, however, the maximum drying efficiency accompanies maximum capacity since a tower drying column is always emyloyed. The moist gases enter at one end and the gas is emitted while last in contact with the anhydrous desiccant at the exit end. If the drying agent is sufficiently fast in its action it may be spent to within a small distance from the exit end. This is the case in the use of anhydrous magnesium perchlorate as will be shown in subsequent data. For use in

TABLE 1

COMPARATIVE EFFICIENCY OF VARIOUS DRYING AGENTS. RESULTS BY BOWER BUREAU OF STANDARDS, JOURNAL OF RESEARCH, VOL. 12, PAGE 246

Material	*Volume of air per hr. per ml. desiccant ml.*	*Total Vol. of air per ml. of desiccant liters*	*Residual water vapor per liter of air mg.*	*Values from published data mg/liter*
$CuSo_4$ (anhy.)	36 to 50	0.45 to 0.7	2.8(2.7 to 2.9)	1.7 at 30°C
$CaCl_2$ (gran.)	66 to 165	6.1 to 24.2	1.5 (1.4 to 1.6)	
$CaCl_2$ (tech. anhy.)	115 to 150	4.0 to 5.8	1.25 (1.23-1.27)	
$ZnCl_2$ (Sticks)	120 to 335	0.8 to 2.1	0.98 (0.94-1.02)	0.95 at 30°C
$Ba(ClO_4)_2$ (anhy.)	26 to 36	2.3 to 3.7	0.82 (0.76-0.88)	0.33 at 27°C*
NaOH (sticks)	75 to 170	2.3 to 8.9	0.80 (0.78-0.83)	0.16 at 25°C*
$CaCl_2$ (anhy.)	75 to 240	1.2 to 7.8	0.36 (0.29-0.38)	0.36 at 25°C
$Mg(ClO_4)_2 \cdot 3H_2O$	65 to 160	4.0 to 7.2	0.031 (0.028-0.033)	
Silica gel	65 to 135	6.5 to 7.7	0.03 (0.02-0.04)	
KOH (sticks)	55 to 65	3.2 to 7.2	0.014(0.010-0.017)	0.002 at 25°C*
Al_2O_3	65 to 135	6.5 to 7.7	0.005 (0.004-0.009)	0.003 at 25°C
$CaSo_4$ (anhy.)	75 to 150	1.2 to 18.5	0.005 (0.004-0.006)	0.005 at 25°C
CaO	60 to 90	7.6 to 10.1	0.003 (0.003-0.004)	0.2 to 0.3 at 25°C
$Mg(ClO_4)_2$(anhy.)	95 to 130	6.4 to 13.2	0.002 (0.002-0.003)	
BaO	64 to 66	10.6 to 25.0	0.00065 (0.0006-0.0008)	Less than 0.003 at "ordinary" temp.

*In all cases marked by an asterisk the failure in agreement between the data of columns 5 and 4 is probably due to the rapid change in vapor pressure of the hydrate formed in each case with increase in temperature. The data from other sources substantiate this claim. (This note and the asterisks in the table are by the author of this booklet.)

vacuum desiccators it is well to provide sufficient desiccant to insure absorption to partial dissipation only.

The study of the dehydrating efficiency of a given desiccant should be made to include approaching the equilibrium in both directions. As studied by Bower [7] the equilibrium was approached in one direction only. Moist air was dried to give supposed completion with determination of the residual moisture using phopshorus pentoxide. If the spent drying agent is then exposed to a continued flow of gas of the same water content it should be regenerated to its original state. Failure to prove the second equilibrium disproves the first as an accurate determination. In accordance with the data shown below taken from the paper by Bower anhydrous magnesium perchlorate has a barely perceptible vapor pressure. At the same time it has been proven that the first hydrate of mag-

nesium perchlorate cannot be dehydrated to the anhydrous salt by use of a gas stream dried using P_2O_5 at any temperature less than 135°C. as compared to 30°C. the temperature employed by Bower. The experimental work substantiating these claims will be given later. The data according to Bower [7] is contained in Table 1.

"The results reported should be understood to pertain to approximately equilibrium conditions."

No attempt was made to determine the residual moisture corresponding to equilibrium conditions. The data of Table 1 are extremely valuable by way of comparison. The too liberal claims to drying efficiency made on the part of investigators in the case of several drying agents are definitely discredited. In most cases the agreement is good and in some cases the conditions were not sufficiently comparable.

The method employed by Bower in obtaining the data of Table 1 was in accordance with his description as follows:

Properly conditioned air was aspirated through a train of U-tubes containing the desiccating materials to be studied. These materials were arranged in the order of their drying powers with the final tube or tubes containing material such as phosphorus pentoxide. The total gain in weight in all tubes following any one tube, therefore, represented the residual water escaping that tube.

In detail, the whole apparatus consisted of a constant-temperature cabinet containing a wet gas meter followed by a drying tower charged with two layers of "dehydrite" enclosing a layer of "ascarite" (NaOH-asbestos mixture). From the drying tower, connection was made to a 200 mm. U-tube containing $Ba(OH)_2 \cdot 8H_2O$ crystals to supply a suitable amount of water.* This tube was followed by the 100 mm U-tubes containing the various desiccants. All connections beginning with the drying tower and up to the final U-tube were ground joints. A lubricant of negligible vapor pressure was used on these joints and all connections were coated with a layer of wax (rosin and beeswax).

The outlet of the final tube was connected, by means of heavy-walled rubber tubing passing through the end of the cabinet, to a guard tube containing phosphorus pentoxide and this in turn was connected to a flask containing concentrated sulphuric acid, and, through this to a mercury manometer and a filter pump.

Constant temperature was maintained by the use of two 100-watt bulbs, a bimetallic thermoregulator†, an electric fan and a storage battery. The temperature in the cabinet was maintained at 30.5° ± 0.5 C. so as to be able to operate during the summer months. Runs were made only during the day, all stopcocks being closed at night. The rate of air flow varied from 1 to 5 liters per hour in most experiments. The internal pressure of the system was determined in each case. However, corrections for differences in the volumes of air entering and leaving the system were found to be negligible.

* The average equilibrium pressure at 30.5° was found to be about 11.3 mm.

† Later a mercury thermoregulator was used.

MATERIALS USED

Except as otherwise noted the materials studied were commercial products in the form in which they were marketed as drying agents. In most cases they are identified below only by information taken from the label of the container. In some instances, however, a partial analysis was made and the results are indicated. Before use, certain of the drying agents were first subjected to a dehydrating treatment corresponding to that normally employed in preparing them for use or in regenerating them. Such treatments are indicated in each instance.

"Anhydrous Copper Sulphate" was the "C.P." powder. Analysis gave 92.5 per cent if $CuSO_4$. The tube of copper sulphate was heated to 250°C. for 2 hours while passing through it air dried by phosphorus pentoxide. "Calcium Chloride (Granular)" was labeled "anhydrous (dried) granular for drying tubes," and was of 8-mesh fineness. The analysis showed the average composition to correspond approximately to $CaCl_2 \cdot H_2O$. "Calcium Chloride (Technical Anhydrous)" was found by analysis to have an average composition corresponding to the formula $CaCl_2 \cdot \frac{1}{4} H_2O$. "Zinc Chloride (Sticks) was the "C.P." material. Analysis showed 97.9 per cent of $ZnCl_2$. "Barium Perchlorate (Anhydrous)" or "Desicchlora" was a commercial product and was in the form of irregularly shaped lumps varying in size. "Sodium Hydroxide (Sticks)" was the "C.P." material. The analysis showed 97.1 per cent of NaOH and 0.6 per cent of Na_2CO_3. It was crushed to a coarse powder for use. "Calcium Chloride (Anhydrous)" was the granular calcium chloride previously described, which had been heated to 250 to 275°C. in the U-tube, while passing through it air dried by phosphorus pentoxide. The dry air was followed by dry carbon dioxide to neutralize any basic compounds present. "Magnesium Perchlorate Trihydrate" or "Dehydrite" was a commercial product and was in a coarsely granular form. "Silica Gel" was a granular commercial product passing a No. 60 and retained on a No. 200 sieve. Analysis showed 11.3 per cent of water and 0.4 per cent of impurities (iron, etc.). It was prepared for use by heating in the U-tube at 110 to 130°C., in vacuo, for 5 hours. "Potassium Hydroxide" was the U.S.P. material in stick form. Analysis showed 81.9 per cent of KOH and 1.3 per cent of K_2CO_3. It was crushed to a coarse powder for use. "Aluminum Trioxide" was a commercial product known as "Hydralo." It was similar in form to granular calcium chloride. Analysis showed it to be mainly Al_2O_3 with about 11 per cent of water. The U-tube containing the "hydralo" was heated in a bath at 150 to 180°C. for 6 hours while passing through it air dried by phosphorus pentoxide. "Calcium Sulphate, Anhydrous (Soluble Anhydrite)" was prepared from dihydrate $CaSO_4 \cdot 2H_2O$, which was obtained through the courtesy of James R. Withrow. It was in granular form of 1/10 to 1/20-inch (No. 7 to No. 15 sieve) fineness. The U-tube containing the dihydrate was heated to 220 to 230°C. for 2 hours while passing through it air dried by phosphorus pentoxide. The loss in weight indicated that practically all water had been removed. "Calcium Oxide" was the C.P. reagent in powdered form. It was heated to redness (600 to 650°C.) for 4 hours and cooled in a desiccator over barium oxide before use. "Magnesium Perchlorate (Anhydrous)," or "Anhydrone" was a commercial product in the form of small lumps of varying size. It was obtained through the courtesy of G. F. Smith. "Barium Oxide" was a specially prepared product obtained through the coöperation of H. S. Booth. It was in a uniform granular form of 1/10 to 1/20-inch (No. 7 to No. 15 sieve) fineness.

The order in which the air dried was asperated through the drying tubes in the experiments by Bower was that of increasing drying efficiency. For example:

$Ba(OH)_2 \cdot 8H_2O$ - - - $[Mg(H_2O)_3](ClO_4)_2$ - - - $CaSO_4$ - - - $Mg(ClO_4)_2$ - - - P_2O_5

Nineteen combinations similar in principle of arrangement and 56 tests were made in all, from 2 to 6 duplicate determinations in the case of each drying agent studied. The graphical representation of the data of Table 1 shows the various dehydrating efficiencies to fall into four groups of drying agents in accordance with the following scheme. The data upon which this classification is based was taken from the experiments by Bower.[7]

Group 1 (0.00065 to 0.005 milligrams of H_2O per liter of air at 30.5°C.). The most efficient reagent is named first, the second most efficient next, etc.

Barium Oxide
Anhydrous Magnesium Perchlorate
Calcium Oxide
Calcium Sulfate (Anhydrous)

Group 2 (0.01 to 0.02 milligrams of H_2O per liter of air dried at 30.5°C.).

Potassium Hydroxide (Sticks)

Group 3 (0.02 to 0.03 milligrams of H_2O per liter of air dried at 30.5°C.)

Silica Gel
Magnesium Perchlorate Trihydrate

Group 4 (0.1 to 0.3 milligrams of H_2O per liter of air dried at 30.5°C.).

Calcium Chloride (Dehydrated)
Sodium Hydroxide (Sticks)
Barium Perchlorate (Anhydrous)
Zinc Chloride (Sticks)
Calcium Chloride (Technical Anhydrous)
Calcium Chloride (Granular)
Copper Sulfate (Anhydrous)

The comparison in the several efficiencies of the groups from 1 to 4 shows that the only real dehydrating agents are to be found in the first three groups. It is evident from the data that, potassium hydroxide being the cheapest of all the agents classified, and being next in drying

efficiency to the reagents of Group 1 should be used as a preferred foredrier or preliminary gas conditioning agent to be followed by one of the finishing driers listed in Group 1. The drying agents of Group 4 should in view of these contentions be classified only as dehumidifiers and not dehydrating agents. The choice of dehydrating agent selected from Group 1 should logically be made in accordance with a number of specific limitations. These considerations are the following:

(a) Cost of reagent in dollars per pound of moisture absorbed at maximum efficiency.

(b) Cost of regeneration per pound of moisture absorbed at maximum efficiency.

(c) Speed of dehydration.

(d) Chemical adaptability.

(e) Simplicity of apparatus installation and maintenance.

Drying agents are selected often without reference to drying capacity at maximum efficiency. Anhydrous magnesium perchlorate at $1.50 per pound is obviously more economical than anhydrous calcium sulfate at 50 cents per pound if it will absorb (which is a low estimation) four times as much moisture as anhydrous calcium sulfate, and do so more efficiently. If the two drying agents in the same comparison are now regenerated, the cost of regeneration in the case of calcium sulfate would have to be multiplied at least by four to compare with the cost of one regeneration using magnesium perchlorate.

With these points in mind it becomes obvious that the best scheme in practice, consists in the use of a preliminary drier such as walnut size fused caustic potash or a liquid scrubber such as concentrated sulfuric acid followed by the use of the most efficient dehydrating agent having the highest absorption capacity and the greatest speed as finishing drier.* By this scheme the moisture is absorbed 95-98% by the cheap drying agent and 2-5% by the more costly finishing drier. Since this finishing drier has high capacity costs for regeneration are a minimum. Speed in drying action is of importance in many ways in the interests of economy. One only, need be mentioned. The quantity of drying agent required for a given operation is at a minimum and the overhead in stock investment low.

THE INFLUENCES OF TEMPERATURE UPON DRYING EFFICIENCY

In completing this section it is proper to call attention to probably the most important property to be fulfilled by a dehydrating reagent.

* The use of concentrated sulfuric acid for this purpose will be discussed subsequently.

If its dehydrating efficiency is retained at its maximum at a high temperature, its field of application is much extended. If this high temperature drying efficiency is accompanied by a high capacity the value of the drier is further enhanced. And if this high capacity and high temperature drying efficiency is then possible in the case of a regenerative dehydrating agent, an ideal situation is encountered. By application of these selective principles to the dehydrating agents of Group 1, the number can be narrowed down to two possibilities namely, barium oxide and anhydrous magnesium perchlorate. Both reagents according to the data of Bower[7] have the highest drying efficiency. Barium oxide is claimed by Booth and McIntyre[10] to retain its drying efficiency at a red heat. This claim is based upon the failure of its addition compound with water $Ba(OH)_2$ to dissociate to liberate water at a red heat. Anhydrous magnesium perchlorate forms in its first coordination hydrate $[Mg(H_2O)_2]ClO_4)_2$, which does not dissociate to liberate water until a a temperature of 275°F. is attained. Barium oxide has a calculated capacity of 11.7%. (Its higher hydrate $Ba(OH)_2 \cdot 8H_2O$ is valueless as a drier.) Anhydrous magnesium perchlorate has a calculated drying capacity to form its first coordination hydrate of 16.1%. (Its higher coordination hydrates are still efficient dehydrating agents.) Barium oxide is not a regenerative drier. Anhydrous magnesium perchlorate is a regenerative drier. By this comparison Group 1 dehydrating agents narrow down to the selection of the preferred use of anhydrous magnesium perchlorate.

Barium oxide might be suggested as a fore-drier to substitute for potassium hydroxide since both reagents have practically the same drying capacity and are obtainable at a comparable price and since both are non-regenerative. Unfortunately barium oxide has physical properties which make its choice over potassium hydroxide undesirable. The spent barium oxide swells materially when working under pressure in retarding or preventing gas flow. The reverse is true using the perchlorate driers. A shrinkage of up to 20 per cent takes effect. Conditioning air is most economically acquired by working under pressure. This topic will be reserved for later discussion. Finally spent potassium hydroxide forms a liquid that can be drained off preventing clogging of drying towers even when working under extremely high pressure. For these reasons barium oxide should only be used as a finishing drier.

According to the data of Bower[7] equilibrium drying efficiencies in his classification were not attempted. The comparison in absolute drying efficiency cannot be made fairly from Bower's data. The results are strictly satisfactory as a comparison in the performance of commercially available dehydrating agents. As such the data are extremely valuable.

[10] Booth and McIntyre, "Barium Oxide as a Desiccant." *Ind. Eng. Chem. Anal. Ed.*, 2, 12 (1930).

The claim is now made that neither phosphorus pentoxide nor barium oxide is capable of drying efficiency greater than that of anhydrous magnesium perchlorate. A closed system at any pressure from the lowest to ordinary pressure and above, and at any temperature less than 275°F., into which is placed barium oxide or phosphorus pentoxide, in any amount, together with a weighed quantity of the first coordination compound of magnesium perchlorate, $[Mg(H_2O)_2]\ (ClO_4)_2$, will not cause the least dehydration of the hydrated perchlorate. This is a determination of drying efficiency for the equilibrium in reverse compared to that studied by Bower. Therefore, had equilibrium been attained by Bower the dehydrating efficiency for anhydrous magnesium perchlorate would have been equal to that of P_2O_5. By the work of Morley[11] one liter of gas dried by P_2O_5 leaves less than 0.000025 milligrams of water. According to Bower barium oxide leaves 0.000065 milligrams and anhydrous magnesium perchlorate leaves 0.002 milligrams per liter. If the latter figure is an approximately correct one why then are barium oxide and phosphorus pentoxide incapable of dehydrating the first coordinate hydrate of magnesium perchlorate at any temperature to anhydrous magnesium perchlorate? The value given for anhydrous magnesium perchlorate must be excessive.

Phosphorus pentoxide is the standard by the use of which the efficiency of all dehydrating agents is standardized. Some speculation is appropriate in planning experimentation to determine whether gases dried using P_2O_5 are absolutely moisture free. An attempt in this direction could be made by drying large volumes of helium gas using P_2O_5 followed by chilling the dried gases to a temperature just above its freezing point —271°C. Failure to remove water vapor at this temperature would prove the dew point of the gas to be so near absolute zero that its dehydration could be considered complete. The use of anhydrous magnesium perchlorate to completely dry air for use in the manufacture of liquid air[5] has carried this type of experiment down to temperatures of liquid air without any signs of the dew point having been reached.

The classified reference list to literature topics on the subject of dehydrating reagents given in the preceding table which is fairly com-

[11] Morley, "Note on the Amount of Moisture Remaining in a Gas After Drying With Phosphorus Pentoxide." *J. Am. Chem. Soc.*, 26, 1171 (1904).

This Text Ref. No.	Authorship	Journal, Vol. p. (year)	Title
		1. THE PERCHLORATE DEHYDRATING AGENTS	
1	Willard and Smith	J. Am. Chem. Soc. 44, 2255 (1922)	"The Preparation and Properties of Magnesium Perchlorate and Its Use as a Drying Agent"
3	Smith, Brown and Ross	Ind. Eng. Chem. 16, 20 (1924)	"Magnesium Perchlorate Trihydrate, Its Use as Drying Agent for Steel and Organic Combustion Analysis"
5	Smith	J. Soc. Chem. Ind. 53, 357 (1934)	"The Improved Dehydration of Air for Use in the Manufacture of High Pressure Tank Oxygen Using Anhydrous Magnesium Perchlorate"
12	Lehner and Taylor	Ind. Eng. Chem. Anal. Ed. 2, 58 (1930)	"Anhydrous Magnesium Perchlorate as a Drying Agent"
13	Smith, Rees and Hardy	J. Am. Chem. Soc. 54, 3513 (1930)	"New Hydrates of Magnesium Perchlorate. Their Structural Relation to Known Forms of the Hydrated Perchloric Acids and Properties as Intensive Dehydrating Reagents"
14	Smith	Ind. Eng. Chem. 19, 411 (1927)	"Anhydrous Barium Perchlorate and Mixed Alkaline Earth Metal Perchlorates as Dehydrating Reagents"
15	Moles	Chem. Abs. 27, 1555 (1933)	"Comparative Study of Some Dehydrating Agents"
16	Moles	*Ibid.* 27, 2394 (1933)	"The Hydrates of Magnesium Perchlorate"
17	Yoe, McGahey and Smith	Ind. Eng. Chem. 20, 656 (1928)	"Pumice Impregnated With Anhydrous Magnesium Perchlorate as a Drying Agent"
		2. SILICA GEL AS DEHYDRATING REAGENT	
18	McGavack and Patrick	J. Am. Chem. Soc. 42, 946 (1920)	"The Adsorption of Sulfur Dioxide by the Gel of Silicic Acid"
19	Miller	Chem. Met. Eng. 23, 1155 (1920)	"Adsorption by Silica Gel" 1
20	Miller	*Ibid.* 23, 1219 (1920)	"Adsorption by Silica Gel" 2
21	Elder and Brandies	J. Phys. Chem. 35, 3022 (1931)	"The Adsorption of Water and Ethyl Acetate Vapors by Silica Gel"

This Text Ref. No.	Authorship	Journal, Vol. p. (year)	Title
		3. ALUMINA ($Al_2O_3 X H_2O$)	
22	Johnson	J. Am. Chem. Soc. 34, 911 (1912)	"Alumina as Drying Agent"
23	Barnitt, Derr and Scripture	Ind. Eng. Chem. Anal. Ed. 2, 355 (1930)	"Alumina in a New Form as a Laboratory Desiccant"
24	Marden and Elliott	Ind. Eng. Chem. 7, 320 (1915)	"A Comparison of the Relative Drying Powers of Sulfuric Acid, Calcium Chloride and Aluminum Trioxide When Used in Ordinary Scheibler Desiccating Jars"
		4. CALCIUM SULFATE	
25	Hammond and Withrow	Ind. Eng. Chem. 25, 653 (1933)	"Soluble Anhydrite as a Desiccating Agent 1"
26	Hammond and Withrow	*Ibid.* 25, 1112 (1933)	"Soluble Anhydrite as a Desiccating Agent 2 Drying of Organic Liquids"
		5. BARIUM OXIDE	
27	Smith	Ind. Eng. Chem. Anal. Ed. 2, 12, (1930)	"Rapid Dehydration of Alcohol Using Barium Oxide and Metallic Calcium"
28	Booth and McIntyre	*Ibid.* 2, 12 (1930)	"Barium Oxide as a Desiccant"
		6. MISCELLANEOUS DEHYDRATING AGENTS INCLUDING CALCIUM CHLORIDE	
29	Baxter and Warren	J. Am. Chem. Soc. 33, 340 (1911)	"The Efficiency of $CaCl_2$, $ZnBr_2$ and $ZnCl_2$ as Drying Agents"
30	Baxter and Starkweather	*Ibid.* 38, 2038 (1916)	"The Efficiency of $CaCl_2$ NaOH and KOH as Drying Agents"
31	Dover and Marden	*Ibid.* 39, 1609 (1917)	"Comparisons of the Efficiencies of Some Common Desiccants" $CuSo_4$, $ZnBr_2$, $ZnCl_2$, $CaCl_2$ 95% H_2SO_4, $CaBr_2$, CaO, NaOH, MgO, $Al_2O_3 \cdot XH_2O$, KOH and P_2O_5.
32	McPherson	J. Am. Chem. Soc. 39, 1319 (1917)	"Granular Calcium Chloride as a Drying Agent"

plete appropriately concludes the material of the chapter on "Types of Drying Agents Classified."

RESUME

CLASSIFICATION OF DEHYDRATING REAGENTS

A. General Classification

1. Regenerative and Non-Regenerative
2. Chemical Absorption and Physical Adsorption
3. Coordinate convalence absorption and Primary valence absorption

B. Specific Classification. The Bower Classification [7]

1. Anhydrous or partially dehydrated solid salts which absorb water to give solid reaction products
2. A solid which absorbs water to give a saturated solution
3. A liquid which absorbs water to give a solution of low vapor pressure
4. Adsorption drying agents which hold water by capillary phenomena
5. Metals and alloys absorbing water through its decomposition to form hydrogen

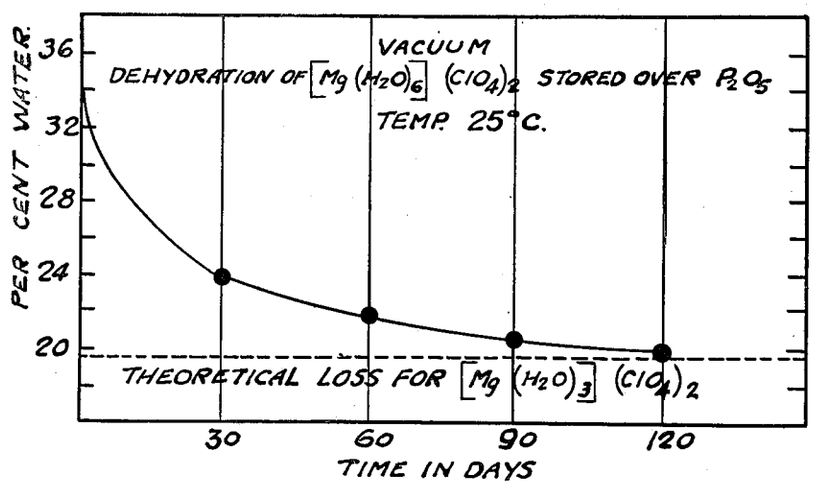
C. Group Characteristics of Dehydrating Reagents. Points of Comparison

1. Drying Power (intensity or efficiency)
2. Drying Capacity
3. Drying Speed (velocity of dehydration)
4. Temperature range of drying at maximum efficiency
5. Conditions under which regeneration is most efficient

SECTION 2

HYDRATES AND AMMINES OF MAGNESIUM PERCHLORATE

Hydrated Magnesium Perchlorate was first prepared in 1831 by Serullas.[33] The hexahydrate was prepared and studied by Weinland and Ensgraber.[34] The vapor pressure of this hydrate is so low that its preparation was studied after drying with P_2O_5 before analysis. $[Mg(H_2O)_6](ClO_4)_2$ was identified following this treatment.



The first study of the preparation of anhydrous magnesium perchlorate was made by Willard and Smith.[1] The further study of the hydrates of magnesium perchlorate was made by Smith, Rees and Hardy.[13] The magnesium perchlorate ammines were prepared by Line [35] and by Smith and Koch.[36] The latter also studied the perchlorate ammines of calcium, barium and strontium. The formulae of these products together

[33] Serullas, "Oxychlorates." *Ann. Chim. Phys.*, 46, 2, 297 (1831).

[34] Weinland and Ensgraber, "Perchlorates of Aluminum, Chromium and Magnesium," *Z. anorg. Chem.* 84, 368 (1914).

[35] Line, "Ammines of Magnesium Perchlorate," Diss. Columbia University (1928).

[36] Koch, "The Preparation and Properties of the Alkaline Earth Metal Perchlorate Ammines," Diss. University of Illinois (1933).

TABLE 2

A Summary of the Various Perchloric Acids, Magnesium Perchlorate Hydrates and Ammines, Their Properties, Water and Ammonia Compositions and Vapor Pressures

	Perchloric acid hydrate	Liter-ature Ref.	Magnesium Salt Werner Formation	Total H_2O %	Liter-ature Ref.	Vapor Pressure	Perchlorate Ammine Werner Formulation	Liter-ature Ref.	Total NH_3 %	Vapor Pressure
1.	$HClO_4$ (m.p. app.—112°) anhydrous perchloric acid	37	$Mg(ClO_4)_2$ anhydrous magnesium perchlorate	0.00	1	.....				
2.	OH_3ClO_4 (m.p. 49.90°) oxonium perchlorate	13	$Mg(H_2O)_2(ClO_4)_2$ diaquo-magnesium perchlorate	24.24	13	0 at 135°C	$Mg(NH_3)_2(ClO_4)_2$ diammino-magnesium perchlorate	35	13.23	0mm at 227°C
3.	$O_2H_5ClO_4$ (m.p.—17.8°) dioxonium perchlorate monohydrate	13	$Mg(H_2O)_4(ClO_4)_2$ Tetraquo-magnesium perchlorate	14.28	13	10mm at 50°S				
4.	$OH_3ClO_4 \cdot H_2O$ (m.p.—19°) oxonium perchlorate monohydrate	13								
5.	$O_2H_5ClO_4$ H_2O (m.p.—29.8°) $O_2H_5ClO_4$	37								
6.	$O_3H_7ClO_4$ (m.p.—37°) Trioxonium perchlorate	37	$Mg(H_2O)_6(ClO_4)_2$ hexaquo-magnesium perchlorate	32.62	34	0mm at 0°C	$Mg(NH_3)_6(ClO_4)_2$ hexammino-magnesium perchlorate	36	31.40	60mm at 253°C
7.	$O_2H_5ClO_4 \cdot H_2O$ (m.p.—43.2°) dioxonium perchlorate monohydrate	37								
8.	$O_3H_7ClO_4$ H_2O $O_3H_7ClO_4$	37								

[37] Van Wyk. Z. anorg. Chem. 48 (1906)

with their analogy to the hydrated perchloric acids and data of importance relating to them is shown in Table 2.

The preparation of triaquo-magnesium perchlorate by vacuum desiccation in contact with phosphorus pentoxide is shown in the data of Figure 1.

Further data on the vapor pressure relationships and dehydration of hexaquo-magnesium perchlorate is shown in Table 3.

TABLE 3

Dehydration of Hexaquo-Magnesium Perchlorate at Various Temperatures (Pressure, 10.15 Mm.)

Sample weights $[Mg(H_2O)_6](ClO_4)_2$ from 2.5 to 3.75 g.

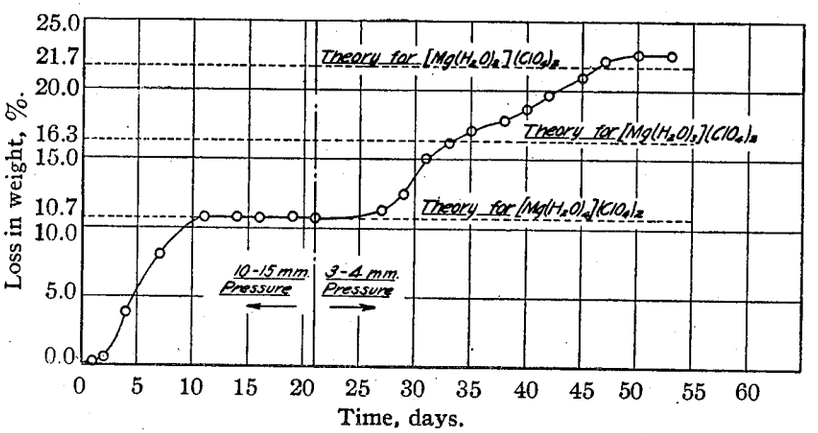
Temp., °C.	Percentage loss in weight — Time in days: 1	2	3	4	5	14	21	Mg. salt hydrate formed	Theoretical loss, %
50*	0.20	0.50	.....	3.79	.....	10.79	10.70	$[Mg(H_2O)_4](ClO_4)_2$	10.81
75	13.57	20.96	21.60	.....	.....	.....	.....	$[Mg(H_2O)_2](ClO_4)_2$	21.62
100	21.66	21.66	.....	.....	.....	.....	.....	$[Mg(H_2O)_2](ClO_4)_2$	21.62
125	21.66	21.69	.....	.....	.....	.....	.....	$[Mg(H_2O)_2](ClO_4)_2$	21.62
150	20.98	.....	28.49	.....	31.89	.....	.....	$Mg(ClO_4)_2$	32.42

*When the pressure was reduced to a value of 3-4 mm. after 29 additional days this sample was dissociated to form diaquo-magnesium perchlorate (loss found, 22.60%).

The data of Table 3 are plotted in Figure 2.

Figure 2

Vacuum dehydration of $[Mg(H_2O)_6](ClO_4)_2$, no desiccant, pressure 10-15 and 3-4 mm.



* Moles[16] published data in which he disclaims the existence of $[Mg(H_2O)_3](ClO_4)_2$. He fails to note in his publication the prior publication of the data of Smith, Rees and Hardy[13] on the subject. The hydrate in question is the least well defined of all but the data of Figures 1 and 2 prove its existence.

The data of Figure 2 shows the successive dehydrations given in the following order:

$$Mg(H_2O)_6(ClO_4)_2 - - - Mg(H_2O)_4(ClO_4)_2 - - - Mg(H_2O)_3(ClO_4)_2 - - - Mg(H_2O)_2(ClO_4)_2$$

The stability of the triaquo derivative * is seen to be less marked than the remaining forms as indicated by the slight break in the curve at the point corresponding to this composition. The preparation of diaquo-magnesium and anhydrous magnesium perchlorate on the large scale for commercial use has been described by Smith and Rees [40] and the data reprinted in this booklet on pages 33-42.

Further data on the dehydration of hexaquo-magnesium perchlorate are contained in the data of Table 4.

TABLE 4

DEHYDRATION OF HEXAQUO-MAGNESIUM PERCHLORATE IN CONTACT WITH VARIOUS DEHYDRATING REAGENTS AT 125-175°

Desiccant	*Temp., °C.*	*Percentage loss in weight* — *Time in hours*				*Fraction of water removed*
		12	*16*	*20*	*24*	*%*
Silica gel	125	.....	.....	1.81	2.57	7.9
"Hydralo"	150	9.06	9.27	.....	.....	28.6
"Hydralo"	175	10.71	10.38	.....	.....	32.0
P_2O_5	150	13.85	14.83	.....	.....	45.74
Anhydrone	150	21.01	.....	.....	21.66	66.81

For the experiments of Table 4, a vacuum metal desiccator was used which is described in this booklet, pages 28-32. It is to be noted that anhydrous magnesium perchlorate (Anhydrone) alone was capable of dehydrating the hexaquo-magnesium perchlorate down to the diaquo-salt at 150°C. Silica gel is practically without drying efficiency at 125°C. and the vapor pressure of aluminum oxide (Hydralo) is too great to account for the dehydration of the magnesium salt below the tetraquo derivative. The use of P_2O_5 above 150°C. is not practicable since the vapor pressure of metaphosphoric acid (HPO_3) is appreciable and the material dried is therefore contaminated by it. The use of barium oxide is preferred in this case.

Heat of Hydration of Various Forms of Hydrated Magnesium Perchlorate. To show the increase in stability of magnesium perchlorate having various degrees of its coördination valences satisfied, the experimental determination of the heats of hydration and solution of the various forms was undertaken. For this purpose the glass reaction vessel shown in Figure 3 was employed. The two partition cell of 150-200 cc. capacity is divided by use of the ring seal into a portion A, to contain the water used, separated from the reaction chamber B, which contains the particular form of magnesium perchlorate being examined, by the delivery tube C,

which extends compartment B into C. The connection between B and C is made by perforating the thin bulb D using the glass plunger indicated. The method used in charging the sample into the reaction vessel consisted in preparing the particular hydrate of magnesium perchlorate to be used in a reaction tube terminating in a narrow neck which could be inserted within the reaction vessel through tube E. A weighed portion of hexaquo-magnesium perchlorate was dehydrated under the proper conditions to prepare the salt hydrate in question. The dehydration was carried out until, by noting that the loss in weight was the theoretical amount, the reaction was complete. Finally the narrow neck of the sample preparation tube was inserted within E and the apparatus turned upside down to deliver the sample to the calorimeter tube. This was then sealed off under vacuum at the point shown. Excess of water was then added at A and the glass plunger inserted, provided with a small rubber bulb at its upper extremity to provide manual circulation of the solution formed after the partition between sections A and B was broken.

The calorimeter tube (Figure 3) was provided with two copper bands around sections A and B having copper fins soldered to them bent at such an angle as to give circulation to the water of the calorimeter when a vertical movement of the calorimeter reaction chamber was employed. The calorimeter tube was a large cylindrical Dewar flask inserted within a still larger cylindrical Dewar flask and the latter placed in a can from which it was separated by infusorial earth and the outside of the can encased in felt. The calorimeter tube was mounted in a support which was provided with a mechanism to impart a vertical movement with an amplitude of 5 cm. The plunging mechanism was operated by use of a motor and pulley and the speed was 30-40 vertical displacements per minute. A weighed portion of water was placed in the inside Dewar flask and a Beckmann thermometer within the same flask. The movement of the calorimeter tube with its stirring mechanism attached stirred the bath water and when the condition of temperature equilibrium of the whole system was obtained the partition between the water chamber A (of the reaction vessel) and the reaction chamber B was broken by a gentle downward thrust on the plunger, the time noted, and the temperature rise plotted. The results of the various determinations are given in Table 5.

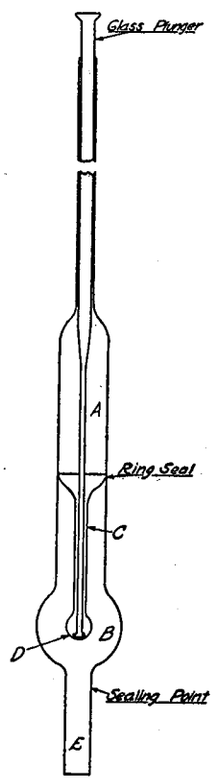


FIGURE 3

From an examination of Table 5 it is noted that heat of hydration of anhydrous magnesium perchlorate (Anhydrone) is practically the same as the heat of reaction between the ordinary amorphous form of phosphorus pentoxide and water (33,000 calories per gram mole). Since the heat of reaction evolved in the saturation of the coördinate covalences of the magnesium ion of magnesium perchlorate is approximately equal to the heat of solution of phosphorus pentoxide in water, which is a covalence reaction phenomenon, the equality between these two dehydrating agents (An-

hydrone and phosphorus pentoxide) in drying intensity would be predicted and has been established. The heat of reaction involved in the saturation of the first two coördination covalences of the magnesium ion is much greater than that for the saturation of the second pair and the saturation of the last pair results in still less heat evolved. The increase in heat evolved upon hydration of the successively lower forms would be predicted from the increase in temperature required to show a measurable vapor pressure for the same forms. Thus, tetraquo-magnesium perchlorate shows its first appreciable vapor pressure at 50°. The diaquo form shows its first appreciable vapor pressure at 135°. If the heat of hydration of the former is taken as 8000 calories per gram mole, the heat of hydration of the

TABLE 5

HEAT OF SOLUTION OF ANHYDROUS MAGNESIUM PERCHLORATE AND ITS HYDRATES

Calorimeter water used in each case, 830 g.

Material	*Dehydration analysis Loss in weight in %*		*Sample g.*	*Rise in temp. ° C.*	*Molecular heat of solution, calories*	*$Mg(ClO_4)_2$ heat of hydration, calories per gram mole*
	Calcd.	*Found*				
$[Mg(H_2O)_6]\ (ClO_4)_2$	.....	.....	7.4560	—0.02	—738	.....
			7.8013	— .025	—881	.....
					Av. —809	
$[Mg(H_2O)_4]\ (ClO_4)_2$	10.86	10.3	9.2558	+0.29	7678	8487
			9.5981	+ .28	7149	7958
			8.0483	+ .22	6698	7507
						Av. 7984
$[Mg(H_2O)_2](ClO_4)_2$	21.73	21.77	6.0588	+0.52	18466	19275
			7.0998	+ .60	18182	18991
			7.3193	+ .63	18521	19330
						Av. 19199
$Mg(ClO_4)_2$	32.60	32.70	7.3531	+1.24	31247	32056
			7.9880	+1.355	31430	32239
			7.6863	+1.37	33021	33830
						Av. 32708

latter would be estimated at 21,500 calories as compared with the value found of 19,200 calories. Conversely, if the heat of hydration of the anhydrous form is 33,000 calories, it would not be expected that the diaquo form would show an appreciable vapor pressure under 200°, which is found to be experimentally justified.

It is to be noted that since the temperature of dehydration of diaquo-magnesium perchlorate must be greater than 135°, anhydrous magnesium perchlorate is a perfect drying agent up to this temperature. The use of the latter drying agent at temperatures between 50 and 135° therefore prevents the formation of higher hydrates than the diaquo form and facilitates regeneration of the spent desiccant.

X-Ray Powder Diffraction Patterns of Hydrated Magnesium Perchlorates. For this study a polychromatic molybdenum radiation produced by a standard out-

fit together with a Hull Quadrant Cassette with a filter of zirconium dioxide was employed. The method of charging the capillary tubes with the samples in question was a problem because of their extreme deliquescence. The process employed was as follows:

A piece of 15-mm. Pyrex tubing about 7 or 10 cm. in length was drawn out on one end to a capillary of about 6.3 cm. length and a half to 1 mm. bore. A sample of magnesium perchlorate hexahydrate, which had been thoroughly ground, together with five or six $\frac{3}{16}$-inch steel ball bearings, was placed in the large part of the tube. The large end of the tube was then drawn down in the flame and a long piece of 6-mm. glass tubing sealed on. The whole thing was then placed in an electric oven at the desired temperature with the long glass tube extending out through the top of the oven. This tube was connected to a vacuum pump with a weighed anhydrone tube in the line. By regulating the temperature of the oven the desired dehydration of the hexahydrated material could be brought about and this could be followed by the increased weight of the drying tube. When the theoretical loss for the production of the desired hydrate had occurred, the system was removed from the oven rolled and shaken in order to effect grinding, and the capillary packed by tapping the material gently down into it. When this was completed the capillary was fused off near the large tube. Later a sample was removed from the large tube and analyzed. This gave a double check on the constitution of the material in the capillary tube.

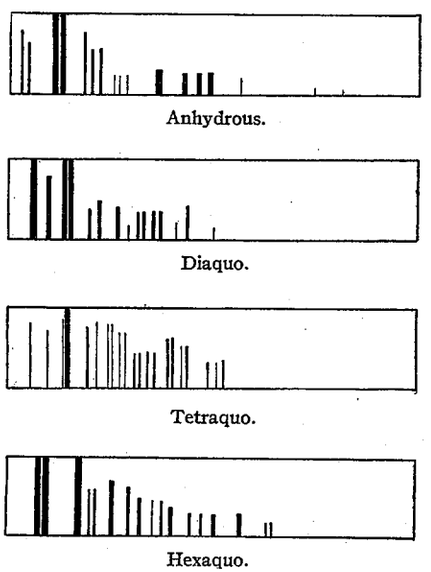


FIGURE 4

The results from the X-Ray powder diffraction photographs are shown by reference to Figure 4. It will be seen from an examination of the results from the various samples that separate and distinct patterns are shown for each form and the deviation is least pronounced in the comparison of the hexaquo and tetraquo forms. The X-Ray examination of the various hydrates of magnesium perchlorate cannot be extended to include Laue diffraction patterns until a process is developed for the preparation of individual crystals of the various types for examination. This problem is complicated by the fact that the lower hydrates cannot be prepared in aqueous solution by ordinary processes because of the high temperatures required. The X-Ray powder patterns indicate the existence of the various forms associated with marked distinction in structural relationships.

Assistance on the part of Professor G. L. Clark in the X-Ray studies is gratefully acknowledged.

SECTION 3

THE COMMERCIAL PREPARATION AND REGENERATION OF THE MAGNESIUM PERCHLORATE DEHYDRATING AGENTS. DESICCATOR DATA.

The requirements in the successful large scale regeneration of the magnesium perchlorate dehydrating reagents include a portion of the manufacturing methods used in their preparation. For this reason, facts concerning the commercial preparation which logically should have made up the earlier pages of this booklet, were reserved until this time. Space does not permit more than a brief outline of methods of preparation with emphasis on points in preparation which are more important in relation to regeneration.

The preparation of hexaquo-magnesium perchlorate follows one of the following methods:

(a) **Solution of Magnesium Carbonate in 70% Perchloric Acid.** The technical grade 68-70% perchloric acid is added to an excess of magnesium carbonate in a 100 gallon acid proof stoneware vat which has been treated with enough water to provide solvent for the finished product. The mass is efficiently stirred during the addition of the acid to allow the escape of carbon dioxide. A slight excess of magnesium carbonate is allowed to remain at the completion of the process which causes the precipitation of iron from the acid added. The insoluble matter is then filtered using a filter press and the clear, almost saturated solution of 100 gallons volume, is concentrated in the same vat using monel metal steam coils until the solution has a temperature of 126°C. Additional solution is added to keep up the volume. Finally the well insulated vat is covered and allowed to cool slowly to ordinary temperatures or below during 24-48 hours. By this process as a result of poly-synthetic twinning large crystal aggregate of plates from 6 to 12 mm. in large dimension and 1 to 2 mm. in thickness are obtained. The crystals are separated from the mother liquor by use of an efficient basket centrifuge and the mother liquor returned to the concentration bath for a second recovery.

Spent magnesium perchlorate drying agents, when a large enough supply has accumulated, are dissolved in water, a little magnesium carbonate added, the solution boiled, filtered and the formation of suitably sized crystals of the hexaquo-salt reformed by the method just described.

Small batch regeneration is not advised for the type of granulation in the case of the finished product is not satisfactory.

(b) **The Method of Smith and Hardy.**[39] A mixture in theoretical proportions of magnesium carbonate and ammonium perchlorate are ground six hours in an Abbe ball mill. The mixed ingredients are then placed in an efficient vacuum tray drier and heated in a high vacuum to 250°C. for 12 hours. The reactions involved are numerous and complicated and their summation is represented in the following equation:

$$MgCO_3 + 2NH_4ClO_4 \text{ at } 250°C. = Mg(ClO_4)_2 + H_2O + CO_2 + 2NH_3$$

The product thus obtained is a powder and not suited because of this fact to use as a drying agent but may be used in special applications such as deammonification. For use as a drying agent it is dissolved in water and processed by a slightly modified procedure as under (a) above.

(c) **Electrolytic Oxidation of Magnesium Chlorate.** For this purpose a half saturated solution of magnesium chlorate, slightly acidified, is electrolyzed using platinum electrodes. A current density of 20-25 amperes at 6-7 volts is employed and the current efficiency under suitable conditions reaches 90-95%. The solution when completely oxidized is then allowed to accumulate and treated to obtain crystals as under (a).

DESIGN AND CONSTRUCTION OF SPECIAL VACUUM DRYING APPARATUS FOR DEHYDRATION OF HYDRATED MAGNESIUM PERCHLORATE

The equipment now to be considered was described by Smith and Rees.[40] The principles of construction of vacuum drying equipment for use in the large scale dehydration of materials of low vapor pressure, such as the magnesium perchlorate hydrates, which must be dehydrated at relatively high and graded temperatures are not met by any commercially available equipment. First, since advantage must be taken of the increase in vapor pressure with increase in temperature, provision must be made for an electrically heated vacuum chamber. Temperatures of 200° to 300°C. are for some dehydrations advantageous. Second, since advantage must be taken of rapid removal of the water

[39] Hardy, "The Preparation of the Anhydrous Perchlorates of Magnesium and the Alkaline Earth Metals by the Use of Reactions of the Solid State," Diss. University of Illinois (1932).

[40] Smith and Rees, "Design and Construction of Special Vacuum Drying Apparatus for Dehydration of Products With Low Vapor Pressure." *Ind. Eng. Chem.*, 23, 1328 (1931).

vapor formed where the vapor pressure is low at the temperature permissible, pressure reduction to a maximum of a few millimeters of mercury is essential.

The present section has for its object the description of the design, construction, and operation of a vacuum-drying unit providing for the demands essential to the dehydration of products having low vapor pressure, as indicated in the above paragraph.

General Characteristics of Design. Requirements to be fulfilled in the apparatus to be described are:

(1) A heating unit, other than steam, preferably electricity, by means of which temperature from 150° to 300° can be maintained.

(2) Provision for evacuation under continuous operation to pressure not greater than a few millimeters of mercury.

(3) Provision for very efficiently uniform heat distribution.

(4) High tray surface area per cubic foot of vacuum chamber.

(5) Design to provide abnormally large exit port between vacuum chamber and condenser.

(6) Provision for exceptionally efficient vapor condensation, by use of condenser of special design having the cooling liquid refrigerated using brine circulation with standard-type thermostatically controlled refrigerating system.

(7) The use of a rotary vacuum oil pump of high efficiency.

(8) The general assembly and connection of the various units of the whole outfit using welded joints, tube turns, etc.

The assembled apparatus built to fulfill the above qualifications is shown in Figure 5. In the foreground is shown the brine tank, with sulfur dioxide boiler enclosed, together with the brine circulatory system and the rotary oil vacuum pump (Kinney type) mounted above. The condenser is contained within the brine tank and is shown connected to the vacuum chamber which is in the background mounted on a concrete base. The condenser system is shown connected to the vacuum chamber by use of a 6-inch distillate conduit. This is an important dimension. Back of the vacuum chamber and concrete base in the right foreground (not shown in Figure 5) is the sulfur dioxide compressor pump (Frigidaire water-cooled type). Further description of the various units of the entire system is left to the following discussion of the semi-detailed drawings. The entire assembly occupies a floor space of 6 by 6

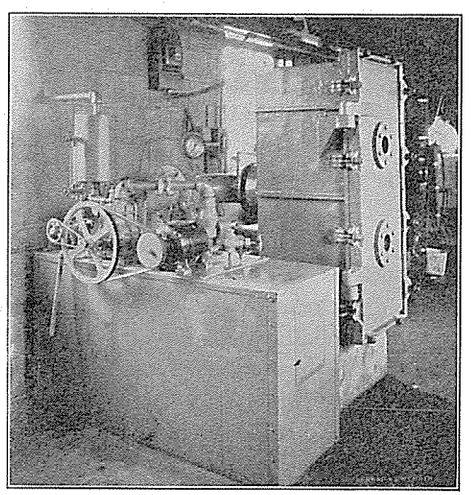


FIGURE 5—ASSEMBLED APPARATUS

feet with an over-all height of 5 feet and 8 inches. The vacuum chamber and the door have a weight of approximately 1800 pounds and the unit pictured in Figure 5 was cast in two parts—the vacuum chamber proper and the door separate. The use of boiler plate with welded seams, door supports, and bolt attachments is thought to be feasible. The union between the door and the vacuum chamber is made vacuum-tight by use of the tongue and groove with a lead gasket grooved bottom. The vacuum chamber and door are shown before heat-insulation material, which should be applied, had been provided, thus emphasizing detail.

Line drawings without detail of dimensions are shown of the front, side, and plain view respectively, of the assembled apparatus in Figures 6, 7 and 8. Attention is called to the 6-inch exhaust port connecting the vacuum chamber with the condenser, to the fact that twelve bolts force the door against the door jamb, and that an exhaust chamber of generous dimensions exists between the back vertical line of the tray bank in the vacuum chamber and the exhaust port leading to the condenser. This space varied in width from 1.5 to 4 inches with the narrow dimensions at the four edges of the back of the vacuum chamber. The 6-inch exhaust port is attached to the vacuum chamber by means of a standard 6-inch pipe flange.

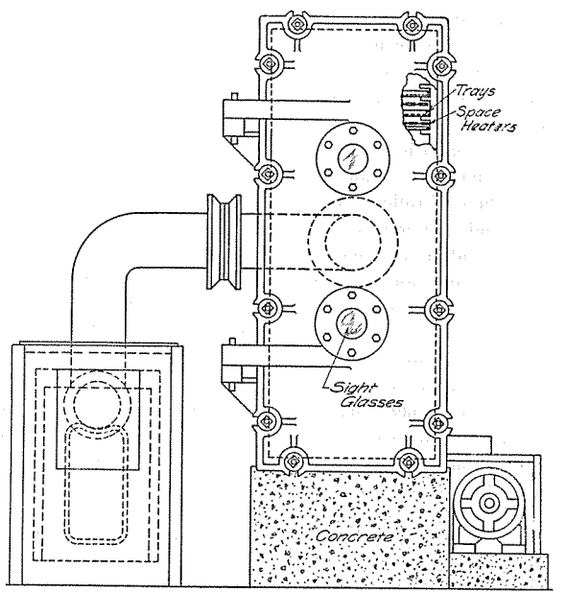


FIGURE 6. FRONT VIEW

As the available tray space is 49 inches high, the vacuum chamber proper is approximately 7 cubic feet in volume. With the volume of the space provided back of the trays leading to the 6-inch exhaust port, together with the condenser volume of 3.5 cubic feet, there result approximately 12 cubic feet of total volume to be evacuated.

As is shown in the upper right hand corner of Figure 2, the right and left inside walls of the vacuum chamber have narrow shelves, 0.5 by 1.5 by 19 inches (25 on each side), cast into the side walls to serve as tray supports. Starting at the top of the vacuum chamber, the space between tray supports is alternately 1.75 and 1 inch apart, respectively. This unequal division provides for mounting space-heater tray banks in the larger space divisions, leaving each tray equally distant from the heat supply. Forty-seven square feet of tray surface is thus provided.

Heater Arrangement and Power Consumption. The electrical space heaters are of the type having a heating value of 350 watts at 110 volts. Eight space heaters were mounted in one tray by use of cross supports. The eight units were connected in such a way as to provide 700 watts at 110 volts, or 1400 watts at 220 volts, and a total consumption of energy of 4500, 9000, 9100, or 18,200 watts. Bus bars are provided for connecting the thirteen trays of space heaters to the power-supply leads. Each bank of space heaters serves as the heat supply for two drying trays, one above and one below.

Condenser Design. The condenser employed is of multiple-tube design with the tubes electrically welded into a rectangular metal housing. The condenser ends are 13 inches wide by 19 inches high, and the side walls are 24 inches long. The shell of the condenser is made of 0.25-inch cold-rolled sheet iron, and the 6-inch exhaust conduit is welded into the top side at one end. The exhaust pump for the system connects to the opposite end of the condenser chamber, and three baffle plates within the condenser chamber provide for uniform distribution of exhaust gases through the condenser proper.

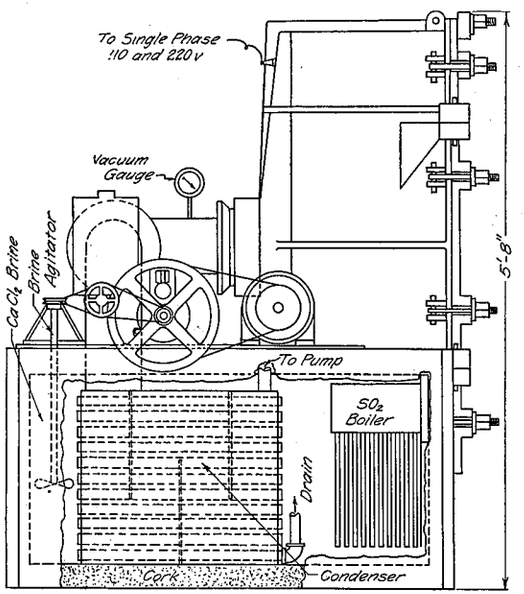


FIGURE 7. SIDE VIEW

Eighty-four condenser tubes of 1.25 inches outside diameter and 24.5 inches in length are electrically welded into the condenser chamber to provide circulation of the cold condenser brine from one end of the condenser to the other. A drain pipe to remove condenser liquid makes the third opening in the condenser described. The condenser chamber is immersed in salt brine together with brine circulator and sulfur dioxide boiler for refrigeration, as shown in Figure 3. The metal covered cork insulated condenser cabinet serves to mount the rotary vacuum pump and motor, as well as the brine circulation equipment. The operation of the mechanical refrigeration unit is thermostatically controlled.

Tray Construction and Its Relation to Drying Operation. Trays for support of material to be dried are conveniently made of perforated nickel sheet with 0.63-inch flange on all the edges. The type of product for which this vacuum equipment is designed should not be charged into the trays to a greater thickness than 0.5-inch. The apparatus described is not provided with automatic circuit breaker and oven-temperature thermostatic control, which could, of course, be easily pro-

vided from standard stock equipment. The condenser and automatic refrigerating equipment are operated at a temperature only slightly above 0°C., and temperatures are automatically controlled.

Operation of Dehydration Equipment. The practical operation of the dehydration equipment described was tested, using as the reaction the dehydration of magnesium perchlorate hexahydrate to form anhydrous magnesium perchlorate. The successive steps in the dehydration of this product to form the super-drying reagent sold under the trade name of Anhydrone are the following:

$$[Mg(OH_2)_6]\ (ClO_4)_2 = [Mg(OH_2)_4]\ (ClO_4)_2 = [Mg(OH_2)_2]\ (ClO_4)_2 = Mg(ClO_4)_2 \text{(Anhydrous)}$$

The vapor pressure of the hydrated magnesium perchlorate with four of the coördination valences of magnesium satisfied is zero at temperatures less than 50°C. The vapor pressure of the perchlorate with but two of its normal of six coördination valences satisfied is zero at all temperatures less than 130°C. The final stage of the dehydration to form anhydrous magnesium perchlorate (Anhydrone) is carried out at temperatures between 200° and 250°C. The equipment described has a capacity of 100 pounds of the finished product, and such a charge requires approximately 20 hours of continuous evacuation and the liberation of between 40 and 50 lbs. of water as condensate. The known tendency of this product to fuse during dehydration under conditions other than that of uniform heat distribution attest to the efficiency of the apparatus described in overcoming this troublesome factor.

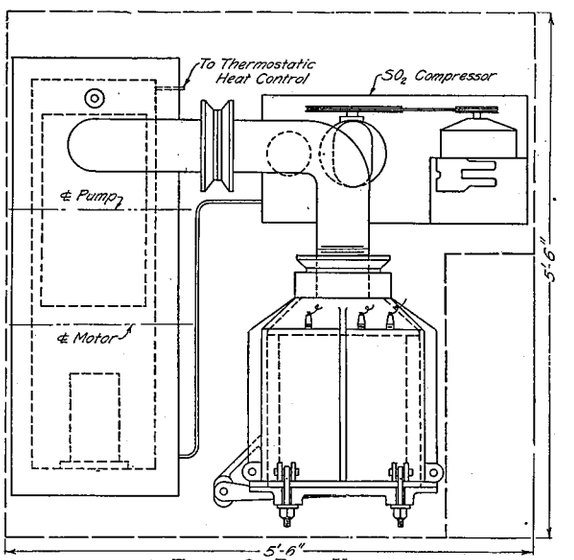


FIGURE 8. PLAN VIEW

For this dehydration a favorable working pressure is 5 mm. of mercury. Pressures in excess of this value are prohibitive for the manufacture of Anhydrone, since the temperature cannot be increased to a value greater than 250°C. because of decomposition. At this temperature the vapor pressure is thought to be approximately 10 mm. of mercury. The use of the equipment described for large-scale generation and regeneration of Anhydrone for use in commercial drying of gases to produce a bone-dry product is suggested.

For continuous operation and for the dehydration of other hydrated perchlorates, such as barium perchlorate trihydrate the Kinney vacuum

pump shown in Figure 5 has been substituted by the next larger size Kinney pump. By its use the vacuum can be maintained at a lower R.P.M. rating. This equipment with some substitutions and changes to provide for the presence of ammonia gas in the system, the synthesis of the anhydrous perchlorates by the method of Smith and Hardy [39] can be applied commercially.

It is clear from this description of the type of apparatus required for the dehydration of hydrated magnesium perchlorate that the anhydrous salt can be spent and then regenerated. The process has been applied commercially in the case of the spent drying agents from the manufacture of high pressure tank oxygen.[5] The equipment required does not encourage regeneration on the part of users who use less than a hundred pounds of drying agents in a reasonable period of time. For these users arrangements should be made with the manufacturers of anhydrous magnesium perchlorate for its regeneration at a cost representing a saving. Manufacturing processes which may develop requiring the use of anhydrous magnesium perchlorate on a 1000-lb. basis should arrange for the installation of their own regeneration equipment through its designers. For the use of the small scale consumer the regeneration of fractions of one pound of anhydrous magnesium perchlorate can be made in the vacuum metal desiccator now to be described.

DESICCATOR DATA

A study dealing with the dehydrating efficiency of laboratory desiccators has been made by Booth and McIntyre (1). The desiccants employed were barium oxide, (BaO), phosphorus pentoxide, (P_2O_5), calcium chloride. ($CaCl_2$) and sulfuric acid, (H_2SO_4). The time required for a large, 7-8 liter desiccator and desiccant, to completely dehydrate the air within, starting with air saturated with water vapor at ordinary laboratory temperature, was determined. The time interval found was in excess of 90 minutes. There was no essential preference in favor of any above listed desiccant.

The description of the apparatus employed and the explanation of the experimental technique, was adequate to justify the conclusions drawn from the experiments as described.

The findings of Booth and McIntyre in their study (1) are, however, not acceptable to the experienced analyst. In consideration of the kinetic theory of gases and the known effinity of the desiccants tested to absorb water, the results reported (1) are completely untenable.

It is the purpose of the present work to repeat the study of Booth and McIntyre using an entirely different technique. In place of the determination of the decrease in pressure with absorption of water vapor as applied by Booth and McIntyre, a direct determination of residual moisture within the desiccator at stated time intervals was employed. The results thus obtained restore to the desiccator

its deserved rating as an entirely adequate working tool. This conclusion from the report of Booth and McIntyre had been almost completely dispelled.

Drying Agents Employed. Anhydrous magnesium perchlorate, $Mg(ClO_4)_2$, barium oxide, (BaO), calcium chloride, ($CaCl_2$), and Drierite (calcium sulfate hemihydrate) were selected as desiccants.

Apparatus Used. The desiccators were Pyrex, vacuum type with external sleeve with standard taper and exhaust tubular, size C, of 160 mm. inside diameter and overall height 255 mm., and size D, of 240 mm. inside diameter and overall height of 340 mm. The respective volumes were approximately 3000 and 7500 ml. including the space provided by the convex lid.

Turner absorption tubes (87 mm. tall and 40 mm. wide at the base) charged with anhydrous magnesium perchlorate were used to measure the water vapor retained by the desiccator at any stated time interval.

A 5000 ml. gas sampling flask with two stop cock tubulars for evacuation and for gas displacement fused in place.

An efficient mechanical vacuum pump capable of attaining a pressure of at least 0.001 mm. and differential mercury manometer gauge were used.

All glass tubular connections except those leading to the Weighed Turner tube were of the ball and socket type.

A double bore capillary sampling tube to serve as a rate adjuster tubular to implement gas sampling under reduced pressure aspiration was employed.

The schematic drawing of the apparatus is not given under the assumption that its description as given is adequate The description of the experimental procedure employed is a further clarification.

Experimental Procedure

The desiccator was provided with 115 grams of desiccant and evacuated together with the gas sampling bottle to vacuum of 0.1 mm. of mercury or less. The gas sampling flask was then closed off and the desiccator opened to admit the moist air of the laboratory and the time noted. At the expiration of a given time interval the desiccator was opened to the 5 liter evacuated sampling bottle and the pressure allowed to equalize. A few seconds only was required for this operation. The residual water vapor in the air of the sampling bottle was then determined.

For the determination of the water vapor in the gas sampling bottle the air was pumped out of the flask through a weighed Turner tube of anhydrous magnesium perchlorate until the pressure in the system was again a small fraction of a mm. The Turner tube was then allowed to come to atmospheric pressure through the admission of bone dry air and weighed using as a tare weight an identical Turner tube and the necessary small total of additional balancing weights.

The use of anhydrous magnesium perchlorate as desiccant in the absorption of residual moisture sampled in the evacuated 5 liter gas holder is seen to be justified as shown in the data of Table 6. No water vapor is shown to have escaped absorption by the anhydrous magnesium perchlorate as shown by its passage over P_2O_5.

The use of anhydrous magnesium perchlorate as desiccant gave the performance shown from the results in triplicate as given in the data of Table 7. Additional results for the various desiccants are given in Tables 8 and 9.

TABLE 6

EXPERIMENTAL DETERMINATION OF THE EFFICIENCY OF MOISTURE ABSORPTION UNDER VACUUM GAS DISPLACEMENT

Relative Humidity of Air %	*Turner Tube Wt. at Start* *Tare + g*	*Turner Tube Wt. + H_2O* *Tare + g*	*Water Vapor Found* *mg.*	*Second Turner Tube with P_2O_5 at Start* *Tare + g*	*Second Turner Tube with P_2O_5 and H_2O* *Tare + g*	*Water Vapor Unabsorbed by Mg $(ClO_4)_2$* *mg.*
45	0.2605	0.3105	50.0	.....	.....	
45	0.3105	0.3606	50.1			
45	0.3606	0.4106	50.1	.....	.....	
45	0.4106	0.4606	50.0	.....	.....	
45	0.4606	0.5106	50.0	.....	.....	
38	0.1642	0.2122	48.0	0.6235	0.6235	0.0
38	0.2122	0.2603	48.1	0.6235	0.6235	0.0
38	0.2603	0.3083	48.0	0.6235	0.6235	0.0
38	0.3083	0.3563	48.0	0.6235	0.6235	0.0

TABLE 7

TIME RATE OF ABSORPTION OF MOISTURE IN 3000 ML. DESICCATOR BY ANHYDROUS MAGNESIUM PERCHLORATE

Relative Humidity of Air %	*Turner Tube Wt. at Start* *Tare + g*	*Turner Tube Wt. + H_2O* *Tare + g*	*Residual Water Vapor Found* *Time 0.5 min.* *mg.*	*Time 5 min.* *mg.*	*Time 7.5 min.* *mg.*	*H_2O Blank No Desiccant* *mg.*	*H_2O Absorption Efficiency* %
45	2.4672	2.4721	4.9	....	....	.....	61.1
	2.4721	2.4771	5.0	....	....	.....	60.3
	2.4771	2.4780	4.9	....	....	.....	61.0
	2.4666	2.4668	....	0.2	....	.....	98.4
	2.4668	2.4670	....	0.2	....	.....	98.4
	2.4670	2.4672	....	0.2	....	.....	98.4
	2.4670	2.4670	....	....	0.0	.....	100.0
	2.4670	2.4670	....	....	0.0	.....	100.0
	2.4670	2.4670	....	....	0.0	.....	100.0
	2.4288	2.4414	....	....	....	12.6	
	2.4414	2.4540	....	....	....	12.6	
	2.4540	2.4666	....	....	....	12.6	

TABLE 8

TIME RATE OF ABSORPTION OF MOISTURE IN 3000 ML. DESICCATOR USING BARIUM OXIDE, ANHYDROUS CALCIUM CHLORIDE AND CALCIUM SULFATE HEMI-HYDRATE

Relative Humidity %	*Desiccant*	*Water Vapor Blank* *mg.*	*Residual Water Vapor in Mg.* *Time 0.5 Min.*	*Time 5.0 Min.*	*Time 7.0 Min.*	*Time 10.0 Min.*	*Time 25.0 Min.*	*Absorption Efficiency in %* *0.5 Min.*	*5.0 Min.*	*7.0 Min.*	*10.0 Min.*	*25.0 Min.*
43	Barium Oxide	12.2	7.3	0.2	0.0	0.0	....	42.5	98.4	100	100	.....
40	Calcium Chloride	10.8	4.1	0.5	....	0.4	0.4	62.0	95.0	.....	96.0	96.0
62	$CaSO_4 . ½ H_2O$	17.5	12.3	1.0	0.7	0.1	....	29.7	94.3	96.0	99.4	.....

TABLE 9

TIME RATE OF ABSORPTION OF MOISTURE IN 7500 ML. DESICCATOR USING $Mg(ClO_4)_2$, BaO, $CaCl_2$, and $CaSO_4 . ½ H_2O$

Relative Humidity %	*Desiccant*	*Water Vapor Blank* *mg.*	*Residual Water Vapor in Mg. Time in Minutes* *0.5*	*5.0*	*10.0*	*15.0*	*20.0*	*Absorption Efficiency in % Time in Minutes* *0.5*	*5.0*	*10.0*	*15.0*	*20.0*
75	$Mg(ClO_4)_2$	34.4	21.0	1.7	0.7	0.0	....	40.2	95.0	98.0	100	.....
42	BaO	17.5	11.1	5.1	1.4	1.0	0.6	36.0	70.9	92.0	94.3	96.6
55	$CaCl_2$	28.8	11.0	2.0	1.4	0.5	....	61.8	93.1	95.2	98.6	.....
55	$CaSO_4 . ½ H_2O$	25.2	15.5	3.5	2.5	1.0	0.0	38.5	86.1	90.0	96.0	100

Interpretation of Experimental Data

Desiccators, contrary to the conclusions of Booth and McIntyre, are not inefficient laboratory dehydration equipment. The proper use of laboratory desiccators at ordinary laboratory air humidities with opening to the air at short intervals only, re-establishes a bone dry condition to the air contained therein promptly if suitable desiccants are employed.

Anhydrous magnesium perchlorate, barium oxide, calcium sulfate hemihydrate and, to a lesser extent anhydrous calcium chloride, are adequate as desiccator drying agents. The use of a moderate sized desiccator with a modern amount of desiccant, (125 grams or more), provides for the establishment of a bone dry atmosphere in less than from 7.5 to 15 minutes in all cases except with anhydrous calcium chloride. These data assume complete displacement of the air in the desiccator when it is opened to laboratory air of ordinary humidity. Since as ordinarily employed desiccators are only opened momentarily it may be logically assumed that the required time interval for desiccation is much less than that experimentally attained in proving the point as described. Anhydrous calcium chloride, while incapable of producing a bone dry condition, is rapid in action and absorbs very nearly all, (96%), of the water vapor in 15 minutes.

For large size desiccators the dehydration efficiency is not materially less rapid or less thorough.

The stigma of inefficiency formerly placed upon the laboratory desiccator as an efficient item of analytical equipment has been refuted. Modern desiccator designs were used in this investigation.

SUMMARY

The time rate of dehydration of air in laboratory desiccators has been determined by direct measurement of residual moisture at given time intervals. Using the commonly employed desiccants $Mg(ClO_4)_2$, BaO and $CaSO_4 \cdot \frac{1}{2} H_2O$ a 3000 ml. desiccator produces a bone dry atmosphere within 7.5 to 15 minutes. Anhydrous calcium chloride was found to be rapid in reaction but not quite 100 percent efficient. In large desiccators the time rate of dehydration is but slightly reduced. Previously published data interpreted to indicate an opposite result has been refuted. The data on Desiccator Data was experimentally determined by D. N. Bernhart and V. R. Wiederkehr, as partial fulfillment of the requirements for the degree B.Sc. in Chemistry. Thesis U. of I. 1950.

40a. Booth and McIntyre, Ind. Eng. Chem. Anal. Ed., 8, (1936) 148.

SECTION 4

THE IMPROVED DEHYDRATION OF AIR FOR USE IN THE MANUFACTURE OF HIGH PRESSURE TANK OXYGEN USING ANHYDROUS MAGNESIUM PERCHLORATE

The production of large quantities of bone dry air (moisture quantitatively removed) has not been described following any known system of dehydration other than by the process using anhydrous magnesium perchlorate next to be considered. The large scale manufacture of the following products using the process of liquifaction of air are all processes in which bone dry air must be prepared if satisfactory conditions are attained in the operation of the liquefaction equipment employed.

Product Manufactured	*Compressor Operation Lbs./sq. in.*	*Important Uses*	*Method of Distribution*
Liquid Air	650-2500	Low Temperature Production	Metal Dewar Bottle
Argon	4000-4500	Incandescent Lamp Manufacture	High Pressure Tank
Oxygen	2000-2200	Welding, Artificial Respiration, Altitude Flying	High Pressure Tank
Nitrogen	2000-2200	High Temperature Bright Annealing. Cable Sheath Dehydration	High Pressure Tank
Liquid Oxygen	2500	Blasting, Welding	Metal Dewar Bottle

The higher the pressure employed in the manufacture of the above products the lower the cost for dehydration of the air used. This fact naturally follows the principle that the higher a gas is compressed the less the percentage by weight of gaseous moisture it retains. The excess moisture is eliminated by its liquefaction after which it is mechanically removed. At average humidity and temperature, air contains approximately 0.22 lbs. of water vapor per 1000 cu. ft. if at one atmosphere pressure. Air at 300 atmosphere pressure, such as that used in the manufacture of argon for use in gas filled incandescent lamps, the moisture content is reduced to 0.0015 lbs. per 1000 cu. ft. Drying costs under these conditions are very low. The cost of dehydrating air for liquefaction to produce liquid oxygen for use in blasting is only roughly twice as great since the air is liquefied after compression to approximately 2500 lbs. per sq. in. The liquefaction of air for use in the manufacture of high pressure tank oxygen, in which case the liquefied air is

fractionated to give as products oxygen and nitrogen at atmospheric pressure, the major part of the operation is at 650 to 750 lbs. per sq. in. Here the drying costs for dehydrating the compressed air increase. The nitrogen and oxygen thus produced are recompressed at 2000 to 2200 lbs. per sq. in. in which case their dehydration cost is again low.

In those cases in which the dehydration operation involves the removal of a considerable quantity of water because operating pressures are low, the usual scheme involves a two-stage dehydration. The compressed gas is passed through drying bottles charged with fused caustic potash. This operation preliminarily dries the gas to a low vapor pressure depending upon conditions of pressure and temperature. The gas is then finally completely dehydrated by use of a pressure bottle charged with anhydrous magnesium perchlorate. The air thus dried has zero vapor pressure at any temperature below 275°F. and at any pressure.

Up to the present time the high pressure tank oxygen and nitrogen industry have been required to adjust their operating conditions to meet the demands of compressed air incompletely dehydrated. Many difficulties in this case are encountered. Using anhydrous magnesium perchlorate in the manner about to be described, eliminates these difficulties.

Oxygen and nitrogen obtained from the liquefaction and fractionation of air is finally collected at atmospheric pressure and is commonly stored in water seal gasometers until ready to be tanked. The common practice is to recompress the nitrogen and oxygen with delivery to the trade in pressure bottles at approximately 2200 lbs. per sq. in. The gas in this case is not generally dehydrated before bottling. As a result the consumer in the use of his product is provided with a gas of variable and increasing moisture content. This fact is often extremely undesirable. Reduction valves may give trouble as a result of the freezing out of moisture in their minute orifices. Welding operations may be interfered with as a tank of high pressure oxygen gets low in pressure. High temperature annealing operations using tank nitrogen may fail. The trade should protect itself by demanding anhydrous compressed oxygen and nitrogen. Additional manufacturing costs using anhydrous magnesium perchlorate are not a sufficient cost item to justify an increased sale price.

The influence of change in pressure on the moisture content of nitrogen delivered at various pressures from a tank of high pressure

[41] Walker and Ernst, "Moisture Content of Compressed Nitrogen." *Ind. Eng. Chem. Anal. Ed.*, 2, 139 (1930).

nitrogen was determined by Walker and Ernst.[41] Their data are reprinted in Table 10.

The following description of the dehydration of air for use in the manufacture of high pressure tank oxygen is reprinted with very few changes, such as reference numbers and the elimination of portions of the last three paragraphs which would be repetitions from other material of this booklet, from the paper on the same subject by G. Frederick Smith[5] published in the Journal of the Society of Chemical Industry. The title of this paper is taken as the title for the present chapter of this booklet.

TABLE 10

MOISTURE CONTENT OF NITROGEN AT ATMOSPHERIC PRESSURE AFTER EXPANSION AT 24°C. FROM A CYLINDER IN WHICH NO LIQUID WATER IS PRESENT
DATA BY WALKER AND ERNST[41]

Time After Start Min.	*Tank Pressure*		*Relative Humidity Obs'd Per cent*
	Atmos.	*lbs. sq. in.*	
0	150	2200	0.78
235	75	1100	1.55
353	37.5	550	1.75
411	18.8	275	2.16
441	9.4	137.5	2.75
453	4.7	68.8	3.25
463	2.35	34.7	3.96
468	1.18	17.2	4.65
470 App.	0	0	6.5 App.

The manufacture of high-pressure tank oxygen by the process of liquefaction of air and fractionation to separate the nitrogen and oxygen requires a preliminary purification of the air to remove carbon dioxide and water vapour quantitatively. The types of equipment employing chemical purification to dehydrate the air which are generally used in Europe and America are manufactured by Heylandt in Berlin, Messer in Frankfort, and Franke in Bremen. The general operating characteristics of the equipment of all three manufacturers are the same. Air is first freed from carbon dioxide at ordinary atmospheric pressure using either caustic potash or soda counter-flow scrubbers. The air is then highly compressed during which most of the moisture is removed. Moisture not removed by compression is then further removed by fused caustic potash which, however, only dehydrates the air to a vapour pressure of 0.5-2.0 mm. of mercury. The air is then liquefied by expansion, the Joule-Thompson effect, after passing through a Siemens' heat exchanger. The liquefied air is then fractionally distilled into nitrogen and oxygen using a single or double rectification fractionating column. The nitrogen, containing oxygen as impurity, is ordinarily discarded and the oxygen fraction allowed to expand to atmospheric pressure through the heat exchanger to lower the temperature further in the exchanger. The oxygen is then stored in the usual type of gasometer using a water seal. The oxygen is finally recompressed, with or without dehydration, into steel cylinders, and is then ready for distribution to the consumer.

The usual type of equipment has a capacity of 700-2100 cu. ft. of 99.5% to 99.8% pure oxygen per hour. Larger capacity plants are uncommon. The period for continuous operation of the usual equipment is dependent, almost entirely, upon the efficiency at which the air used has been dehydrated. A plant having a larger hourly capacity, in general has a shorter period of continuous operation. A plant operated above its rated capacity would naturally have a curtailed period of continuous operation. Owing to the lack of complete dehydration of the air, the great lengths of fine bore heat exchanger tubing are eventually obstructed by the accumulation of "rime" or water vapour frost. The process must then be discontinued and the apparatus warmed for defrosting. Without duplicate equipment the process is necessarily intermittent.

The object of this section is to describe a method by which the air can be completely dehydrated and the accumulation of rime entirely prevented. To do this, a finishing drier, anhydrous magnesium perchlorate, is used in addition to fused caustic potash. Besides eliminating the inefficiency of intermittent operation the process has the following advantages:

(1) The efficiency of the heat exchanger is greatly increased.

(2) The yield of oxygen is materially increased with a simultaneous decrease in power consumption. The oxygen purity is not changed.

(3) The slightest alteration or addition to the present plant equipment is not needed.

(4) The plant equipment may be "shut down" for short periods without requiring premature defrosting as is necessary in present operating practice.

(5) The benefits attained, as outlined, more than balance the additional cost of the chemical drier, even if the increased yield of oxygen alone is considered.

General Description of the Plant Equipment. The operation of a small scale liquid air machine of the Hampson model has been described by Hudson and Garland.[42] A commercial installation having a capacity of 1000 cu. ft. of oxygen per hour has been described by Wikoff.[43] A general description of the process employed with Heylandt, Messer, Franke, and Linde equipment is contained in the text by M. Laschin.[44] The Joule-Thompson effect in relation to heat exchanger operation at pressures up to 200 atmospheres and at temperatures from + 10 to—175°C. has been discussed by I. H. Hausen.[45]

Process Flow Data. Typical Operation Using Caustic Potash as Drier. The plant employed for the following experimental demonstration (the additional use of anhydrous magnesium perchlorate for walnut size fused caustic potash as dehydrating agent) had a capacity of 2190 cu. ft. of oxygen (99.8% purity) per hour. This plant was formerly operated using the same equipment as that described by Wikoff.[43] The original equipment is still installed and is held in reserve in case of failure of the larger and more efficient units now in operation. The

[42] Hudson and Garland, University of Illinois. *Eng. Exp. Sta. Bull.*, 21, March, 1928.

[43] Wikoff, *Met. and Chem.*, 30, 181 (1924).

[44] M. Laschin, Der Sauerstoffe, Carl Marhold, Halle, 1924.

[45] Dr.-Ing. Helmuth Hausen, Der Thompson Joule Effekt und die Zustrandgrossen der Luft bei Drucken bis zu 200 at., V.D.I.-Verlag, G.m.b.H, Berlin, S.W. 19, 1926.

two major alterations consist in the use of an Ingersoll-Rand compressor and a separate unit heat exchanger and double rectification fractionating column of the Messer design. The double column carbon dioxide scrubbers and multiple unit dehydrating chambers are the same as described in the reference given except that the drying battery consisted of twin sets of four bottles each instead of three. This plant was habitually operated with a 10-12% overload and hence the period of continuous operation was thereby diminished.

The plant assembly and flow diagram are shown in Figure 9.

Air for compressor (C) is drawn from the tandem counter flow carbon dioxide scrubbers which are charged with coke and through which caustic potash solution is circulated. The scrubbers are shown at (A) and (B). When the caustic potash solution in (B) is partially spent it is transferred to (A) and finally discarded in the form of an alkaline solution of potassium carbonate. A fresh supply of caustic potash solution is substituted in (B) from the waste solution in the drying bottles. Compressor (C) has four stages of compression shown as (C-1) to (C-4). The capacity of this compressor is 275-300 cu. ft. per minute under a series of pressures up to and including 200 atmospheres (3000 lb. per sq. in.). Each stage is water-cooled and the gas is compressed isothermally. Provision is made for the second stage of compression to be at the drive shaft end of the compressor to prevent a slight contamination by impure air. The air, after compression and at ordinary temperatures, is passed into the series of dehydration bottles (E). The first of these bottles is an oil and water spray trap. The intake is at a point approximately half the distance from the bottom to top of the bottle, and the outlet is from the top. A retarded counterflow of the compressed air causes the deposition of spray and then the air passes into a series of pressure bottles, four in number, containing walnut size fused caustic potash. Here the gas is dried as completely as possible. Each bottle contains 180 - 200 - lb. of caustic potash.

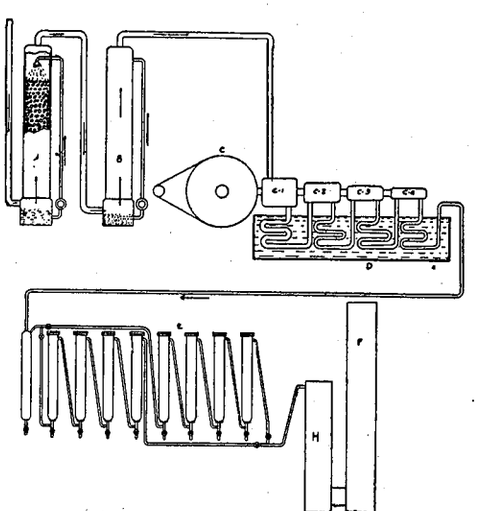


FIGURE 9

From the driers the compressed gas passes into the heat exchanger (H) and then into a second heat exchanger coil which is placed at the bottom of the fractionating column (F) immersed in liquid oxygen. The column (F) is of the double rectification type capable of a yield of approximately 17% of the atmosphere's total oxygen in a purity of 99.8% at its rated capacity of 60 cu. m. (2100 cu. ft) per hour. The plant is habitually operated at an output of 59.67 cu. m. per hour. The impure nitrogen is allowed to be discarded through the heat exchanger. The liquid oxygen is evaporated through the heat exchanger and collected in a storage gasometer. Building up the required quantity for the

double rectification column (F) is carried out under a compression of 2600 lb. per sq. in. After final adjustment, the rectification column functions with a working pressure of 42.7 atmospheres (607 lb. per sq. in.) in the heat exchanger excluding the preliminary period. An average of nine hours is required to build up sufficient liquid air to "bring the column in" and to adjust the double rectification fractionating column to the production of oxygen of the required purity from a fresh start. The average starting pressure (2600 lb. per sq. in.) is maintained during the first eight hours. After approximately four days continuous operation, the accumulation of rime on the inside walls of the Siemens' heat exchanger is sufficient to necessitate a gradual increase in working pressure until at 1000 lb. per sq. in. it is not practical to operate longer. The liquid air and oxygen are withdrawn from the rectification columns, the heat exchanger tower and the rectification column are allowed to warm up, and the rime in the former volatilized by the use of a stream of warm air. The removal and replacement of caustic in the drying bottles and the defrosting of the heat exchanger in the plant investigated requires an inactive period of 12-15 hours. If, for any reason, the plant had to be shut down for a period much over that of one hour, or sometimes even less, the defrosting of the heat exchanger had to be carried out as at the completion of a normal run.

Wikoff [48] estimated that it requires 1.5 lb. of caustic potash for each 1000 cu. ft. of oxygen produced. For a 96-hour run, 788 lbs. of caustic potash are required. Two drying bottles of caustic potash, approximately, are therefore used for each period of continuous operation. At an estimated cost of 12 cents per lb. for the quality of caustic potash required, the drying costs for each period are approximately $40.00. Since four bottles of caustic potash are used in series, two bottles of 180-200 lb. capacity, each of the dimensions given below, are necessary for maximum efficiency (intensity) of drying at the average rate of flow, 4.73 cu. ft. of compressed gas per minute.

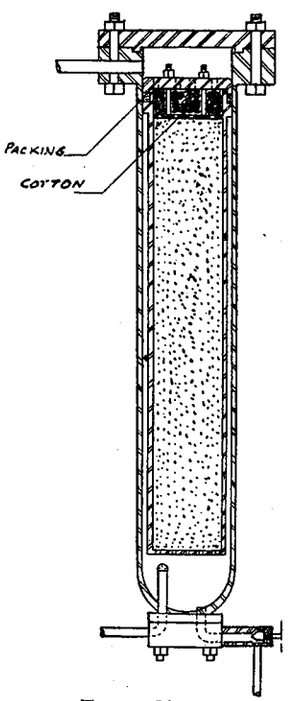


FIGURE 10

A detailed cross-sectional view of one of the drying bottles is shown in Figure 10. The walnut-size caustic potash is contained in a long inner cylindrical drum with perforated bottom. The top of the bottle is sealed by collars and flanges packed as shown. Compressed air enters through the left-hand bottom port and passes out at the top. A space between the bottom of the potash holder and the bottom of the bottle proper is provided to retain the caustic potash solution draining down from the spent caustic. The valve at the lower right permits the collected solution to be drawn off at frequent intervals. If this is not done the entrance port will be blocked. Four drying bottles are connected in series and two such series are provided. If one change of potash is sufficient to operate the equipment for four days before the heat exchanger clogs,

two heat exchangers must be provided for continuous operation. In case the heat exchanger and rectification columns are a single unit, two such complete units would be required. If the combination heat exchanger and rectification column is used, the accumulated liquid air and oxygen would be transferred and operating resumed using the second series of drying bottles.

In the plant under discussion double heat exchanger or double units of heat exchanger and rectification column were not provided. The plant was operated for a period of four days with a 12-15-hour shut-down, and, after defrosting, a second run of three days was made without changing the caustic postash in the drying bottles. At the end of this time about 200 lb. of caustic potash were left in a condition satisfactory to use again.

Characteristics of Walnut Size Fused Caustic Potash as a Drier. Fused caustic potash has been shown [30] to have a vapour pressure of 0.002 mm. of mercury at temperatures less than 50°C. However, under the conditions outlined above, we

TABLE 11

COMPARISON OF POWER AND YIELD DATA IN THE USE OF POTASH AND PERCHLORATE DRYING AGENTS

Drier Used	*Time of Run, Hours*	*Time to Adjust Col'mn to Ave. Condition of Balance*	*Time to Bring O_2 Production to Average*	*Yield of O_2 Av. cu. ft./hr.*	*Pct. Pwr. used in Prelim. Period*	*Operational Pressure-Average, lb./sq. in.*
KOH	110	9 hr. at 2350 lb. sq. in.	10 hrs.	1983	24	746.6
$Mg(ClO_4)_2$	192	6 hr. at 2514 lb. sq. in.	6 hrs.	2336	12	652

are dealing with the much higher vapour pressures of saturated solutions of caustic potash since the absorption of moisture soon coats the surface of the potash with a film of solution. The vapour pressure of this film is increased with temperature. For a plant of the capacity under discussion, the operators estimated that it required 4 lb. of water passing the driers to force the defrosting operation. For a run of 110 hours at 275 cu. ft. of air per minute, the vapour pressure of the air delivered to the heat exchanger was 2.0 mm. of mercury if this air contained 4 lb. of water. Without a drier, the equipment described will operate about 12 hours before clogging. These figures correspond to the requirement of 4 lbs. of moisture known to produce the same effect using air dried as described. Some authorities claim drying of the air to a vapour pressure of 0.5 mm. with caustic potash, but under such conditions the plant should operate for a continuous period of approximately four times as great.

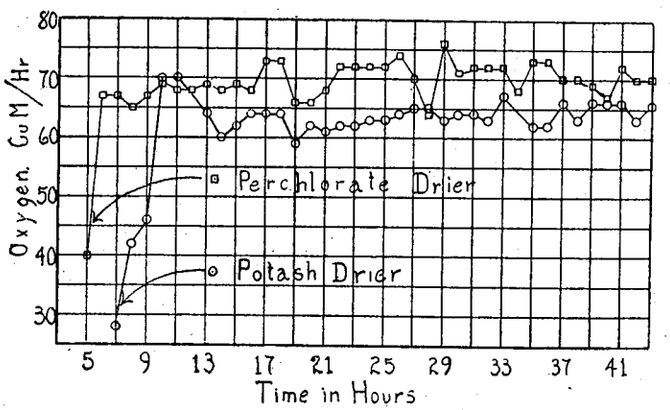
When using caustic potash of shelled corn size, the plant would operate 55 hours before defrosting was necessary. When using flake caustic, the plant could be operated 27 hours. With no drier a 12-hour period was the limit. The improvement in drying efficiency using caustic potash cannot, therefore, result from decreasing the size of the potash. To increase the surface by the use of a larger number of drying bottles is not practicable. The solution of the problem, therefore, is found in the use of an additional drier of greater drying efficiency.

Comparison in Plant Operation Using Caustic Potash Alone as Drier Against Caustic Potash With Anhydrous Magnesium Perchlorate. The plant as described was operated for comparison first using four bottles of caustic potash charged

with walnut-size fused caustic potash (total charge, 720 lbs.). The comparison run was made using two bottles (360 lbs.) of the same grade of fresh caustic potash followed by two bottles (150 lbs.) of anhydrous magnesium perchlorate. With caustic potash alone, the plant operated 110 hours before a run required shut-down. Then, using only two bottles of perchlorate but with changes of caustic potash, the plant was operated for four periods of 110 hours each, being shut down over the week ends. A final run was made using the same bottles of perchlorate for 192 hours, continuously, before a shut-down was necessary to defrost the heat exchanger. This was the only defrosting operation during the series of runs with perchlorate as drier. The comparison in results between the run in which caustic potash alone was used and the final run of 192 hours with the combined driers is found in Table 11.

The time required to adjust the equipment to average operating pressure (column 3, Table 7) using caustic potash alone as drier was typical of the plant

FIGURE 11



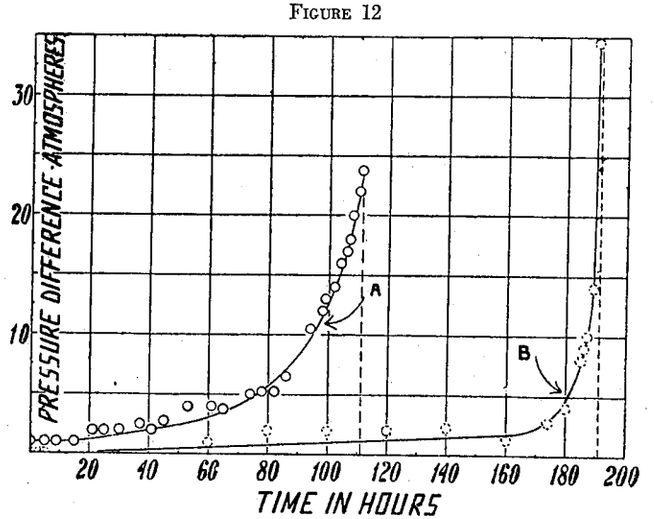
for a period of operation over more than two years. The data given using the combined driers represent a plant average during four months' intermittent operation. The comparison is therefore not a particular but a general one. The period of 110 hours was the maximum ever found using caustic potash alone as drier. The 192 hours run was the only example of a forced shut-down using the combined driers. This period was purposely restricted by intentional failure to replace the spent perchlorate for the purposes of experimentation. By properly alternating the drying bottles and changing driers there need be no periods of forced shut-down.

Hourly Production of Pure Oxygen With and Without Perchlorate Drier. The hourly production of oxygen using caustic potash as drier with and without anhydrous magnesium perchlorate is shown by graph in Figure 11. The first 41 hours of operation are plotted in each case. The remainder of the separate runs show a precise extension of these data. It will be observed by examination of the figure that the time required to "bring the column in" is less using the perchlorate drier and the production rises to normal more rapidly. The highest hourly rate of oxygen production (76 cu. m.) represents at 25% increase in the rated

capacity of the column. The average production of oxygen is approximately 17% over the rated capacity using the perchlorate drier. The maximum and average values using caustic potash alone are respectively 12% and 8% over rated capacity. These latter values indicate the reason for a short period of continuous operation when using potash alone. The increase over rated capacity using the perchlorate drier does not limit the period of operation, although the increase is twice as great as that for the caustic potash.

Influence of Column Balance on Rate of Oxygen Production. It will be noted from Figure 11 that the fluctuation in oxygen production is much greater in the run using the perchlorate drier than in the run using potash alone. Both runs were made with the same average gauge readings in the fractioning column. It is reasonable to expect that this situation calls for a readjustment of the column balance to provide conditions wherein the heat exchanger is cooled less by the Joule-Thompson effect and more by the expanding gases from the fractionating

FIGURE 12



column, since rime is not present to impair the efficiency of heat transfer in the coils of the heat exchanger. The operators of the equipment, however, insisted upon maintaining the usual gauge readings in this portion of the apparatus, and thus eliminated probably the most promising saving of power that might be expected. These considerations are fundamental in the study of the problem and point the way to a closer approach to an ideal thermodynamic balance than that ordinarily attained. All the benefits outlined could be predicted to follow upon complete elimination of rime or frost in the heat exchanger. At the same time, the question of the accumulation of detrimental amounts of frost in the fractionating column would be removed.

Comparison of Rime Accumulation in the Heat Exchanger Using Caustic Potash Alone as Drier and With Perchlorate. Two pressure-gauge readings tabulated in the daily plant report for this equipment indicate the magnitude of rime

accumulation in the heat exchanger. The one gauge precedes the heat exchanger and the other follows it. The accumulation of rime is shown for the two comparison runs in Figure 12. From an examination of the figure it may be seen that the rime accumulation using only the potash drier (curve A) is gradually but persistently increased over the entire run. Using the perchlorate drier (curve B) rime accumulation is negligible almost to the completion of the run. By properly charging drying bottles, therefore, no pressure increment is introduced in the system by the heat exchanger. Using caustic potash alone, this loss is continually increasing and can never be eliminated.

The many desirable features in the use of this drying agent adapt it admirably to many large-scale industrial operations in the commercial drying of gases. It is a neutral drying agent, and can be used for the drying of such gases as sulphur dioxide, carbon dioxide, halogen acid gases as hydrochloric acid gas, chlorine gas, saturated hydrocarbons, hydrogen, nitrogen, methyl chloride, air, etc. The intensity (completion) of its drying action has not been questioned in its numerous applications nor its capacity for water absorption. The two important characteristics not previously demonstrated in its association with large-scale operations are its speed of dehydration and its resistance to gas flow when associated with large volumes of gas in large-scale drying towers especially when operated under pressure.

SECTION 5

ANHYDROUS BARIUM PERCHLORATE AND MIXED MAGNESIUM AND BARUM PERCHLORATES AS DEHYDRATING REAGENTS

The following section is based upon a paper by the author of this booklet previously published.[46] The need for a drying agent which is easily regenerated obviously calls for a product which cannot be excessively efficient as a desiccant. To be easily regenerated in a form that is granular and porous requires that the hydrated product of the spent drying agent retain its structure upon dehydration. The drying agent hydrate should dissociate to liberate water without fusion. The more stable the anhydrous drying agent is towards heat the less close the temperature of dehydration need be regulated.

Barium perchlorate in the anhydrous form absorbs water to form the tri-aquo salt just as it forms a triammine as previously described. The capacity to absorb moisture is therefore approximately 16 per cent of its dry weight. The trihydrated barium perchlorate when heated to 100-200°C. is easily restored to the dry anhydrous salt. This process does not result in fusion during dehydration and the large granular crystal aggregates are not altered in form. If the salt should be heated between 200-400°C. it is undecomposed. The temperature of top efficiency in its use as a drying agent is low and rapidly decreases as the temperature rises. For reasons of its other fine qualities this condition is not an eliminating circumstance. By means of the addition of hydrated magnesium perchlorate to anhydrous barium perchlorate all of the advantages previously stated for anhydrous barium perchlorate are retained by the mixed perchlorates. The drying efficiency is much increased, however, and the temperature at which it can be regenerated is correspondingly increased.

Mixed Barium and Magnesium Perchlorates. The infusibility of barium perchlorate trihydrate upon vacuum dehydration at 100-140°C. may be considered to result from the high molecular weight of the anhydrous salt as compared with the trihydrate, together with its comparatively low dehydration temperature, both conditions preventing the material from dissolving in its own water of crystallization upon dehydration. The comparatively high dehydration temperature of magnesium perchlorate hexahydrate, which forms the trihydrate *in vacuo* and the anhydrous salt only at approximately 250°C., does not materially alter the

[46] Smith, "Anhydrous Barium Perchlorate and Mixed Alkaline Earth Metal Perchlorates as Dehydrating Reagents." *J. Ind. Eng. Chem.*, 19, 411 (1927).

infusibility of barium perchlorate trihydrate including mixtures containing 25 to 35 per cent of the hexahydrated magnesium salt. As a result of these conditions, the state of granulation of a mixture of barium perchlorate trihydrate and magnesium perchlorate hexahydrate subsequent to dehydration at 250°C. depends entirely upon the particle size of the first material prior to such treatment. The barium perchlorate trihydrate, upon treatment at this comparatively high temperature, rapidly dehydrates completely, leaving a granular, porous medium for the absorption of the magnesium perchlorate hexahydrate which fuses at a temperature less than 145°C. Upon continued treatment at 250°C., the magnesium salt is completely dehydrated and the granular condition of the mixed reagents unchanged.

The particular process of manufacturing the mixed drying agents may be varied quite materially without appreciably affecting the characteristics of the finished product. For example, in addition to the method of preparation described above, the granular barium salt may be dehydrated separately at 100-140°C., followed by mixing with the desired amount of magnesium salt and dehydration to the anhydrous condition at 250°C. Other methods might be employed and the resulting product possess a very satisfactory toughness of texture, which is favorable in causing the product to retain its original state of granulation.

Mixtures of the magnesium salt with the barium reagent up to 35 per cent of the magnesium salt give a product that does not more than sinter slightly upon dehydration. Fifty per cent of each component results in an unsatisfactory product. Eight hours at 250°C. and 4 inches of mercury pressure is ample time to dehydrate such a mixture in trays with 10-mesh wire-cloth bottoms covered to a depth of ½ to ¾ inches with ½-inch clearance between trays. A higher vacuum is desirable in speeding up the dehydration. A variation of 10° in temperature is without material consequence.

MECHANISM OF DRYING, USING MIXED ANHYDROUS BARIUM AND MAGNESIUM PERCHLORATES

Consider a single particle of the mixed dehydrating agents a granular support or carrier of anhydrous barium perchlorate comparable to a sponge partially saturated with anhydrous magnesium perchlorate uniformity throughout its structure. The mechanism of the drying action of such a single particle is then as follows:

Upon contact with moist gases permeating the whole of each individual granule of material as the gases pass through a column of it, the molecules of anhydrous magnesium perchlorate absorb water to the hexahydrate condition, requiring 32.62 per cent of water of crystallization. At this stage of hydration the supporting material, anhydrous barium perchlorate, hydrates to the extent of three molecules of water of crystallization, or 13.85 per cent, at which stage it no longer absorbs additional water. Further contact between the moist gases and the mixed drying agents results in the hexahydrated magnesium perchlorate further absorbing moisture. This accounts for dehydrating capacities greater than the theoretical for any given mixture of these materials.

The dehydration and regeneration of such spent granules result in a removal of water in the reverse order. For this purpose the evacuation and heating of the spent material should be carried out in such manner that the temperature is gradually raised to the point at which the moisture in excess of that theoretically

necessary in the formation of the true hydrates has been driven off. The regenerated material thus retains its original granular condition and drying tubes and towers can be used repeatedly without recharging.

For an exact determination of the dehydrating efficiency of a given dehydrating agent, the partial vapor pressure of air retained in contact with such reagent until equilibrium is established should be ascertained. The procedure previously followed is applicable here. For the purpose of obtaining more serviceable data a different procedure was employed wherein the gas rate of flow was greatly increased, using small-length columns of desiccant. This resulted in failure to obtain equilibrium conditions, but provided data concerning both speed and efficiency.

TABLE 12

TESTS OF DRYING EFFICIENCY OF MIXED ANHYDROUS BARIUM AND MAGNESIUM PERCHLORATES AT HIGH RATES OF GAS FLOW AND 60 PER CENT SATURATION

Test	*Rate per Hour*	*Time*	*Gas Dried*	*Temp.*	*Mg(ClO₄)*	*Dimensions of Drying Column*	*Water Absorbed**	*Water Unabsorbed*	*Water Unabsorbed*
	Liters	*Hours*	*Liters*	*° C.*	*Per cent*	*Inches*	*Grams*	*Mg.*	*Mg. per liter*
1	68	1	68	23	20.5	9 × 1	0.60	0.55	0.008
2	68	1	68	23	23.5	10 × 1	0.61	0.50	0.007
3	80	2	160	23.5	23.5	12 × 1	1.86	1.60	0.010
4	55	8	440	26	26.5	14 × 1	5.70	1.85	0.004
5	53	5.5	181	27.5	26.5	6 × 1	3.32	1.00	0.004
					$Ba(ClO_4)_2$				
6	36	5.5	198	27	100	12 × 1	2.17	58.1	0.29
7	55	2	110	27.5	100	12 × 1	1.16	44.3	0.42

* From the length of column of spent reagent the drying capacity of the 20.5, 23.5, and 26.5 per cent magnesium perchlorate reagents was estimated to be 30, 35, and 40 per cent by weight.

A gas stream saturated with moisture was considered too severe a test to represent working conditions ordinarily encountered. The air dried in connection with the present investigation was passed through saturator bottles containing a saturated aqueous solution of sodium bromide, giving a gas 60 per cent saturated with water vapor. The only difference between the use of such a partial vapor pressure and that of a saturated gas at the given temperature was concerned with the regeneration of the spent reagent. In each instance the drying efficiency was the same at a given rate of gas flow, but in the second case the spent reagent became appreciably more moist at the point of first contact and difficult to regenerate. In the case of the 60 per cent saturation the spent granules of reagent never attained such a state of saturation as to result in the slightest tendency for the individual particles to coalesce.

Experimental Procedure. The air to be dried was taken from the regular laboratory air-pressure line and passed through the saturator bottle and saturated solution of sodium bromide to establish 60 per cent humidity and then passed directly into the reagent to be tested. The reagent was placed in drying tubes, either straight or of the U-tube type providing for columns of reagent 25 mm. (1 inch) in diameter and from 8 to 30 cm. (7 to 12 inches) in length. Glass wool plugs at the exit end of the reagent tube provided a filtering medium for the dry gases emitted and permitted regeneration of the spent reagent tube. The dried air from the test reagent tube was passed into a second, much smaller, U-tube, containing alternate layers of purified ignited asbestos and 13-mm. (0.5-

inch) layers of phosphorus pentoxide. The phosphorus pentoxide tube was protected against back flow of moisture by a second tube containing the same material.

The temperature of the drying agents and the gases dried were not controlled but were those of laboratory conditions, 25°C. or more. The gain in weight of the absorption tubes of test reagents was determined with an accuracy of a decigram. The weighed phosphorus pentoxide tube was counterpoised by a duplicate tube, a No. 10 Troemner balance and Bureau of Standards calibrated set of weights being employed. The weighings were made following determinations only after the tubes had been allowed to stand an adequate length of time on the balance pans and after both the weighed tubes and the counterpoise tubes were momentarily opened prior to the final weights.

The rates of gas flow were determined at the exit end of the gas train using the method of water displacement with timing by a stop watch. In nearly all experiments gas flow of from 50 to 80 liters per hour was maintained. Temperatures often reached 28°C. or over. The volume of gas passed was kept at 70 to 400 liters. The rate of flow and the extreme avidity of the drying agent for moisture caused the drying tubes to become appreciably warm at points in the tube nearest the admission of moist air.

The results of the tests, listed in Table 8, show that for high rates of gas-flow the most efficient reagent consists of 26.5 per cent anhydrous magnesium perchlorate, the remainder being anhydrous barium perchlorate. Test number 5 shows that even a column of drying agent 15 by 2.5 cm. (6 by 1 inches) is capable of drying air 60 per cent saturated with moisture passing at the rate of approximately one liter per minute as efficiently as a column of the same reagent twice as long. This indicates that the longer column may be exhausted, through use, to the extent of more than half its length before regeneration is required. This condition attests to the pronounced speed of absorption. (The speed of absorption is also evident from the regular advance of the spent reagent in the drying tube with no tendency to channel.) Test numbers 2 and 3 demonstrate the slight decrease in efficiency with increase in gas flow. Numbers 6 and 7 show the tests of equal-length columns of pure anhydrous barium perchlorate as compared with the mixed reagent.

The drying tube of experiment 5 was regenerated by heating to 250°C. and excavating to 102 mm. (4 inches) of mercury pressure and retested with no appreciable change in efficiency. The regenerated material had the same granulation after generation as before.

It is probable that with higher percentages of the magnesium salt the dehydrating efficiency of the resulting material would be in excess of that found for the 26.5 per cent reagent investigated. This point was not tested because the cost of the preparation of these mixed anhydrous salts materially increases with increasing percentage of the magnesium salt. The reason for this condition becomes apparent from the details of the preparation of the magnesium salt. As a result of the possibility of drying the mixed perchlorate desiccating agent under vacuum and at 250°C., the time of drying is greatly reduced and the cost is minimized. In all samples tested drying at 250°C. and 102 mm. pressure during 8 hours was employed.

SECTION 6

SULFURIC ACID AS A FORE-DRYING MEDIUM. OTHER FORE-DRYING MEDIA

The use of lump caustic potash as a fore-drying medium has been considered in a preceding section. Concentrated sulfuric acid is another common fore-drying medium. Both reagents are inexpensive and being of opposite chemical properties are often not interchangeable. Both products can be utilized in their spent form for other purposes. Sulfuric acid can be regenerated by the addition of fuming sulfuric acid. Caustic potash is more desirable as a fore-drier because it is a solid. Sulfuric acid is to be preferred in some cases because its drying efficiency is altered but slightly with moderate changes in temperature. The decrease in drying efficiency with caustic potash is very appreciable for slight increase in temperature.

Sulfuric acid and lump caustic potash are properly classified as dehumidifiers and not dehydrating agents. It is not within the scope of this book to include data on dehumidification. Since discussion was made in a preceding section of lump caustic potash as fore-drier, some material is included here on the properties of concentrated sulfuric acid as a preliminary drier or dehumidifier. Other fore-drying media are also considered.

HUMIDITY EQUILIBRIA OF VARIOUS TYPICAL FORE-DRIER SYSTEMS AT 25°C

Humidity equilibria for various fore-drying systems at 25°C. are shown graphically in Figure 16. In these data from the work of Wilson and Fuwa [9] the per cent relative humidity for gases in equilibrium with various drying systems at a given stage of saturation is plotted on the horizontal from zero to 100 per cent relative humidity. The per cent of water in the systems of dehumidifying reagents is shown on the vertical dimensions of the figure. In this figure sulfuric acid is shown to have the greatest efficiency for acid strengths above 75 per cent. The drying efficiency of calcium chloride is considerably less than that of sulfuric acid up to approximately 20 per cent relative humidity and at the point where 40 per cent of water has been absorbed by the system. From this point up to 100 per cent humidity both aqueous sulfuric acid and calcium chloride have practically the same drying capacity and intensity.

Dehumidification, 50 per cent efficient, is attained in both cases at approximately 60 per cent drying capacity.

Anhydrous sodium sulfate and calcium chloride are the same type of dehumidifiers. The drying efficiency of the former, however, is much lower. It is capable of dehumidifying a gas only between 80 and 100

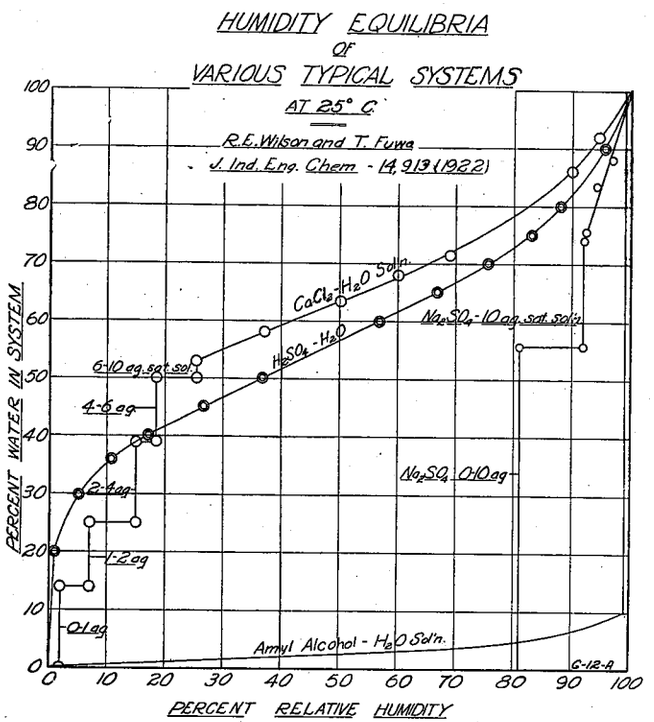


FIGURE 13

per cent relative humidity. In this range its capacity is approximately equal to that of calcium chloride at 50 per cent relative humidity.

Amyl alcohol is shown to have a maximum capacity of 10 per cent at 100 per cent relative humidity. To maintain any appreciable degree of drying efficiency, large quantities of amyl alcohol as a scrubber would have to be employed.

The high drying efficiency of sulfuric acid cannot be maintained unless its acid concentration is kept above 80 per cent. Its effective drying capacity, therefore, is 20 per cent. The drying efficiency of calcium chloride is approximately 15 per cent. It dehumidifies a gas to the extent of 98 per cent in the range $CaCl_2$ to $CaCl_2 \cdot H_2O$. Sodium sulfate

(Glauber's salt) is shown by the diagram to be most valuable as a humidifier. Its saturated aqueous solution humidifies to the extent of 80 per cent relative humidity.

The position that would be occupied by anhydrous magnesium perchlorate were its performance plotted together with the data of Figure 16 is interesting. Its drying efficiency up to 45 per cent absorption capacity would be such that the graph of its performance would be super-

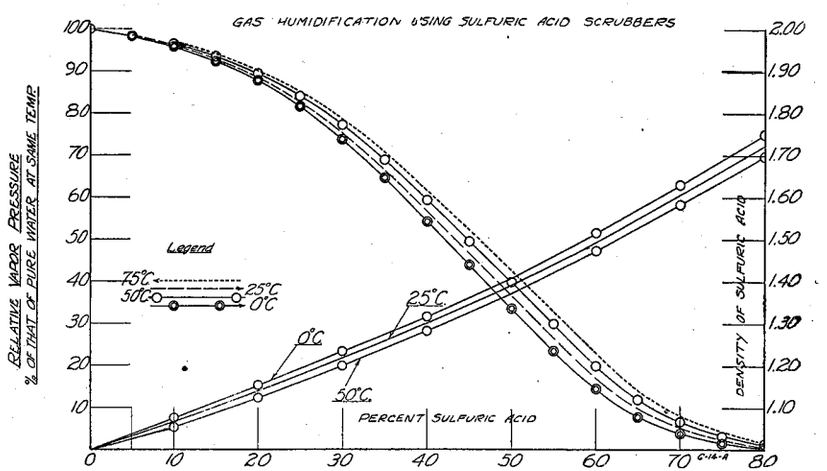


FIGURE 14

imposed on the vertical axis. The vapor pressure of its saturated aqueous solution, or that of its under-saturated solutions are not known and the data cannot be included in the figure. It does not belong among such data since it is a finishing drier rather than a fore-drier.

The data for sulfuric acid as shown in Figure 13 is reproduced in Figure 14. This figure is taken from the studies of Wilson.[8] In Figure 14 the dehydration efficiency is plotted on the vertical left hand axis. The percentage composition of sulfuric acid is plotted on the horizontal axis. The density of sulfuric acid of these various percentage strengths is plotted on the right hand vertical axis. Various temperatures 0, 25, 50 and 75 degrees centigrade are shown for the data dealing with dehydration efficiency. The same temperatures variable, not including 75°C., are shown for the density of the various strength acids.

The data of Figure 14 are given in tabular form in Tables 13, 14 and 15.

TABLE 13

BEST VALUES FROM VAPOR PRESSURE CURVES FOR SULFURIC ACID SOLUTIONS

H_2SO_4 Per cent	Relative Vapor Pressure Values at 0°C. Per cent	25°C. Per cent	50°C. Per cent	75°C. Per cent
0	100.0	100.0	100.0	100.0
5	98.4	98.5	98.5	98.6
10	95.9	96.1	96.3	96.5
15	92.4	92.9	93.4	93.8
20	87.8	88.5	98.3	90.0
25	81.7	82.9	84.0	85.0
30	73.8	75.6	77.2	78.6
35	64.6	66.8	68.9	70.8
40	54.2	56.8	59.3	61.6
45	44.0	46.8	49.5	52.0
50	33.6	36.8	39.9	42.8
55	23.5	26.8	30.0	33.0
60	14.6	17.2	20.0	22.8
65	7.8	9.8	12.0	14.2
70	3.9	5.2	6.7	8.3
75	1.6	2.3	3.2	4.4
80	0.5	0.8	1.2	1.8

TABLE 14

STRENGTH OF H_2SO_4 REQUIRED TO GIVE DEFINITE HUMIDITIES

Per cent	Relative Humidity—Per cent Sulfuric Acid Required at 0°C.	25°C.	50°C.	75°C.
10	63.1	64.8	66.6	68.3
25	54.3	55.9	57.5	59.0
35	49.4	50.9	52.5	54.0
50	42.1	43.4	44.8	46.2
65	34.8	36.0	37.1	46.2
75	29.4	30.4	31.4	32.4
90	17.8	18.5	19.2	20.0

TABLE 15

FACTORS TO BE APPLIED TO RELATIVE VAPOR PRESSURE AT 25° TO GIVE RELATIVE VAPOR PRESSURE AT TEMPERATURES INDICATED

Per cent H_2SO_4	0°	50°	75°	100°
20	0.992	1.007	1.014	1.020
30	0.978	1.020	1.038	1.054
40	0.956	1.043	1.082	1.116
50	0.912	1.084	1.163	1.236
60	0.848	1.156	1.314	1.478
70	0.749	1.289	1.608	(1.968)
80	0.601	1.556	(2.295)	(3.240)

SECTION 7

PRACTICAL APPLICATIONS IN THE USE OF THE MAGNESIUM PERCHLORATE DRYING AGENTS IN QUANTITATIVE ANALYSIS

Large scale use of anhydrous magnesium perchlorate in commercial installations has been described in the earlier pages of this booklet. The small scale laboratory uses are also important. The present chapter includes the discussion in brief of the use the perchlorate driers as applied to the gas purification and analysis trains used in the determination of carbon dioxide in acid soluble carbonate minerals and in the determination of carbon in iron and steel by high temperature combustion in oxygen. Other applications such as in the combustion analysis of organic compounds for carbon and hydrogen, metabolism experiments using small animals in physiological chemistry, the determination of carbon in soil analysis by direct combustion and the use in desiccators will also be mentioned. The treatment is to be in no sense exhaustive and the literature on the subject will be frequently recalled.

THE DETERMINATION OF CARBON DIOXIDE BY EVOLUTION

Introduction. Naturally occurring products containing carbon dioxide as a major constituent are numerous. Carbonate rocks such as limestone, $CaCO_3$, and dolomite, $CaMg(Co_3)_2$, as well as magnesite, $MgCO_3$, are common. Siderite is the carbonate of ferrous iron, $FeCO_3$, a commonly occurring iron ore. Other carbonate minerals are rhodochrosite or manganese carbonate and cerucite, $PbCO_3$. In many cases for proximate analysis the carbon dioxide is estimated following the determination of the loss on ignition. This type of determination although satisfactory for routine analytical control is often not sufficiently accurate for some purposes. Natural carbonates, besides containing organic matter, often contain appreciable amounts of ferrous iron or iron pyrites, combined water and other matter which is either oxidized, oxidized and dissociated, or volatilized to such an extent that the determination of the loss on ignition is not a sufficiently accurate index of the carbon dioxide content. In these cases the most common method of determination involves the solution of the sample in an acid followed by the evolution of carbon dioxide completed by the passage of a stream of air freed from carbon dioxide. The carbon dioxide is commonly absorbed after purification of the gas stream from volatile impurities using either a wet

or dry absorbing composition. The evolved carbon dioxide is then determined by weight. In some cases the CO_2 is displaced from solution of the sample in acid, if it is a water-soluble carbonate, and the evolved gas measured. In special cases such as for low concentration of carbon dioxide the gas may be precipitated by a suitable reagent such as barium hydroxide and the insoluble $BaCO_3$ filtered out of contact with atmospheric CO_2. The precipitate is then dried, ignited, and weighed. The acid usually employed for solution of the sample is dilute hydrochloric.

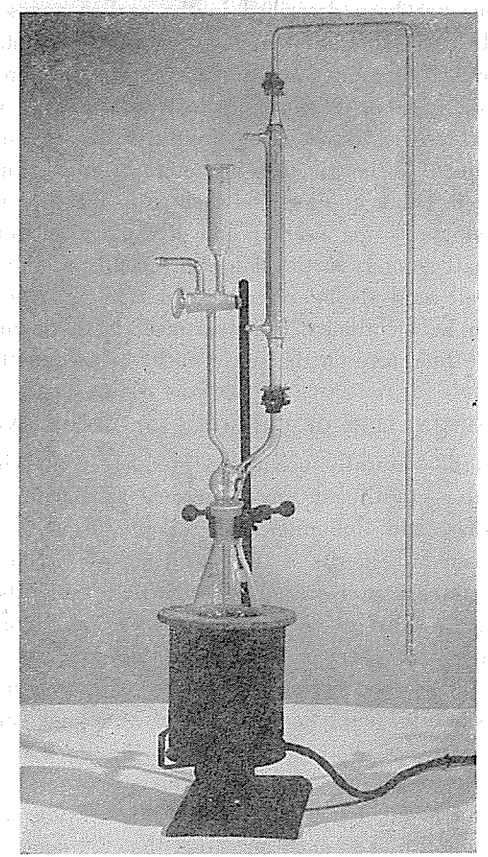


FIGURE 15

For some cases dilute perchloric acid is to be preferred because of its superior solvent action as for instance in the analysis of cerucite in which the mineral is more readily soluble in perchloric acid because of the presence of lead. The method described in the following material

comprises the solution of the sample in dilute acid, evolution of the CO_2 and final determination by weight after absorption in a suitable reagent.

Apparatus Employed. The sample solution and CO_2 evolution flask is shown in Figure 15. This is a modernized version of that described by Hillebrand and Lundell, (Applied Inorganic Analysis, John Wiley, 1929, p. 623). It consists in a 250 ml conical flask, electrically heated and a reflex condenser. Solvent hydrochloric acid is added through a reservoir surmounting three way stop cock with provision for passage of flushing hydrogen into the reaction chamber to displace evolved carbonic acid. The reagent delivery and gas flushing tube reach to the bottom of the reaction chamber. All glass connections are either ground glass or ball and socket ground glass units. The gas absorption and purification train is shown in Figure 16. The absorption units in Figure 16 are from left to right a mercury trap, a sulfuric acid drying tube, two anhydrous copper sulfate drying and HO absorption tubes, a weighed ascarite—anhydrous magnesium perchlorate absorption tube and lastly a back diffusion prevention tube of anhydrous magnesium perchlorate. All absorption tubes are connected by means of ground ball and socket joints.

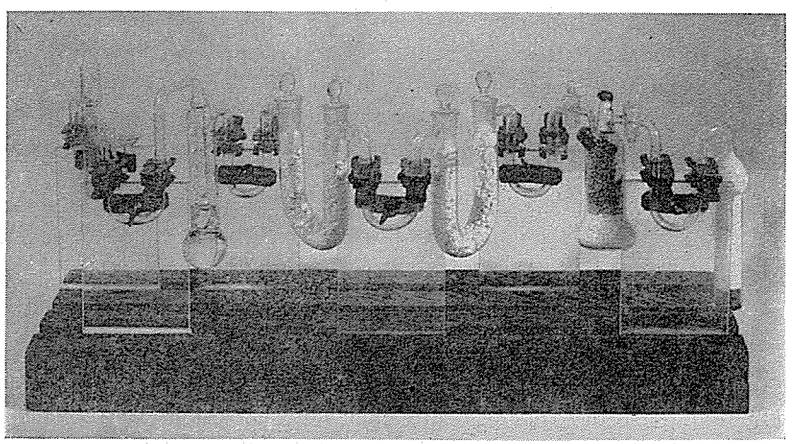


FIGURE 16

Procedure for Analysis. Weigh one gram of the sample carbonate for analysis from a small weighing bottle into the reaction flask, *A*, taking the weight by difference. Add enough water, 50-100 ml., to cover the bottom end of the separatory funnel tube, and assemble the apparatus as shown in Figure 18 with the train disconnected before the first weighed Wesson tube, *J*. Now pass a stream of CO_2 free air into the apparatus until CO_2 present is removed. A slow stream for 10 minutes should be sufficient. Discontinue the air stream, and connect in the remainder of

the absorption train in preparation for the solution of the sample. With the heat ready for application but not as yet applied, add 1 : 1 hydrochloric acid to the dropping funnel (50 ml. in all should be used) and deliver it to the solution in small portions governed by the rate of CO_2 evolution until the entire quantity has been added. When the CO_2 evolution discontinues in the cold reaction flask, adjust the cooling water in the consenser and apply heat to continue the evolution of CO_2 finally bringing the contents of the flask to a very gentle boil. Resume the passage of a slow stream of CO_2 free air, gradually reducing the intensity of the heat applied and finally removing the source altogether, taking care to prevent reduced pressure due to condensation of steam in *A*. Continue the passage of air until the CO_2 is completely swept through the train a second time, and then weigh the Wesson bulbs using a similar bulb as a tare. The increase in weight is CO_2. Repeat the analysis until closely agreeing duplicates are obtained.

When charged with Ascarite the Wesson bulbs absorb large quantities of CO_2, and the degree to which they are spent is shown by the accumulation of a white coating progressively from the entrance to the exit end. The spending of Anhydrone is similarly noticed by the moist appearance after saturation. Since Ascarite has an appreciable vapor pressure it should always be used with a protector drying tube. The second Wesson bulb should not gain in weight but is used as protection in case either reagent in the first Wesson bulb should be saturated. The back flow of moisture into the second Wesson bulb is possible in spite of the counter flow of gas. The back flow of moisture from Ascarite in the second Wesson bulb into the first is not likely since the vapor pressure of Ascarite is so low. If such is occurring there will be a loss in weight of the second bulb.

The anhydrous copper sulfate used in best made by drying $CuSO_4 \cdot 5H_2O$ over Anhydrone in a vacuum at 180-190°C. This leaves a granular structure, the original crystal form not being changed, and is better than the use of pumice impregnated with a solution of copper sulfate and dehydrated as is ordinarily employed. The vapor pressure of $CuSO_4 \cdot H_2O$ is less than 1 mm. at 180°C. and that of Anhydrone still less. Heating $CuSO_4 \cdot 5H_2O$ at 180-190° *in vacuo* in contact with excess Anhydrone, therefore, removes the water of crystallization without fusion. The resulting material is extremely porous since it retains the same granular structure. The metal vacuum desiccator previously described is particularly well adapted to this preparation of anhydrous copper sulfate.

MAGNESIUM PERCHLORATE IN THE DETERMINATION OF HYDROGEN AND CARBON IN ORGANIC COMPOUNDS BY COMBUSTION

Improved methods in the analysis of organic compounds by the usual combustion methods use the magnesium perchlorate driers for the absorption of the hydrogen after combustion to form water. The application includes the macro and semi-micro procedures. Microcombustion methods as yet have not in general taken advantage of this use due undoubtedly to the influence of the origin of these methods in Europe. The description of macro-organic combustion analysis using magnesium perchlorate as drying agent was published first by Smith, Brown and Ross.[47] Steel combustions for carbon determination were also included in this work. A description of the microanalytical determination of carbon and hydrogen in organic compounds is given by Niedehl and Roth.[48] Anhydrous magnesium perchlorate was similarly employed by Kirk and McCalla.[49] In the study by Smith, Brown and Ross 15 analyses of 5 samples of Bureau of Standards analyzed steels were made by the use of the usual absorption and purification trains employing ascarite and dehydrated magnesium perchlorate in place of the formerly used ascarite and P_2O_5 combination. Excellent results were obtained. The use of anhydrous magnesium perchlorate in this determination has become almost a universal practice in routine and research steel works analyses. Also in the paper under discussion the analysis of 8 organic compounds by the macaro-combustion method showed excellent results using ascarite and dehydrated magnesium perchlorate in an improved combustion train using only dry reagents.[47] The general use of this improved method is rapidly displacing the former use of caustic potash solutions with calcium chloride as drying agent in macro-combustion methods. At the University of Illinois the formerly employed Leibig potash bulb together with a U-tube of calcium chloride has been completely replaced by the use of Wesson bulbs containing ascarite and anhydrous magnesium perchlorate. Semi-microanalytical work as a substitute for macro-combination analyses likewise use the same combination of reagents.

THE DETERMINATION OF WATER AND CARBON DIOXIDE IN METABOLISM TESTS AND OTHER ANALYTICAL APPLICATIONS IN THE USE OF ANHYDROUS MAGNESIUM PERCHLORATE

In the study of small animal metabolism experiments a need for the determination of moisture and carbon dioxide in quite large volumes of air is required. A study has been made of improvements in these determinations by Lee and Brown.[50] The method of direct combus-

[47] Smith, Brown and Ross, "Magnesium Perchlorate Trihydrate. Its Use as Drying Agent for Steel and Organic Combustion Analysis." *J. Ind. Eng. Chem.*, 16, 20 (1924).

[48] Niedehl and Roth, "Microanalytical Determination of Carbon and Hydrogen. A Simplified Method. *Ind. Eng. Chem. Anal. Ed.*, 6, 272 (1934).

[49] Kirk and McCalla, "A Convenient Micro Combustion Method for Carbon and Hydrogen Determination." *Mikrochemie*, 12, 88 (1932).

[50] Lee and Brown, "The Use of Magnesium Perchlorate Trihydrate (Dehydrite) and Asbestos Sodium Hydroxide (Ascarite) in Gravimetric Metabolism Determinations of Water and CO_2 Absorption." *J. Biol. Chem.* 73, 69 (1927).

tion in oxygen for determination of carbon in soil using a purification and absorption train of all solid reagents including anhydrous magnesium perchlorate has been described by Winters.[51]

Methods of analysis of gaseous hydrocarbons employ anhydrous magnesium perchlorate in certain drying reactions. Such use is described by Tropsch and Mattox.[52] Anhydrous magnesium perchlorate is used in place of P_2O_5 since it has been shown that partially spent P_2O_5 absorbs olefin hydrocarbons which is not the case with the use of the perchlorate drier.

Gas masks using absorptive charcoals of various types require the dehydration of the gases before contact with the adsorptive carbon for efficient performance. The perchlorate driers have been found desirable in this case but as yet have not been employed because of the former cost. With a materially reduced sale price this objection is eliminated.

THE USE OF ANHYDROUS MAGNESIUM PERCHLORATE IN STEEL AND IRON COMBUSTION ANALYSES FOR DETERMINATION OF CARBON

It is beyond the scope of this booklet to give a complete discussion of the determination of carbon in iron and steel by direct combustion in oxygen. A very complete and authoritative treatment of this most important subject is to be found in the treatise by Lundell, Hoffman and Bright.[53] The use of anhydrous magnesium perchlorate has become practically a universal practice in the case of all the later forms of purification and analysis trains.

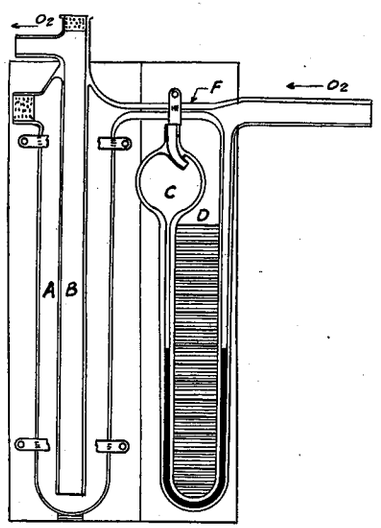


FIGURE 17

A new form of preliminary purification is shown in Figure 17. The oxygen from the high pressure cylinder following the pressure reducing valve and gauge passes into the capillary tube F and the rate of flow is regulated as desired by use of the flow-meter E. From the venturi-meter the oxygen passes into section A containing ascarite and then into section B containing anhydrous magnesium perchlorate and then into the tube furnace combustion tube over the sample to be analyzed.

[51] Winters and Smith (R. S.), "Determination of Total Carbon in Soils." *Ind. Eng. Chem. Anal. Ed.*, 1, 202 (1929).

[52] Tropsch and Mattox, "Analysis of Gaseous Hydrocarbons A Method for Determining Gaseous Paraffins and Olefins." *Ind. Eng. Chem. Anal. Ed.*, 6, 235 (1934).

[53] Lundell, Hoffman and Bright, "The Chemical Analysis of Iron and Steel," Chapter 9, pp. 154-187 incl., John Wiley and Sons Inc., New York, 1931.

The newer form of absorption tube not described by Lundell, Hoffman and Bright is shown in Figure 17 as designed by Turner.[54] This absorption tube is 3½ inches tall and tapers from 1⅛ inches at the top to 1½ inches at the bottom. A ground glass cap 1 inch wide has an intake and exhaust tube fused into each side. By turning the ground glass cap the intake and exhaust ports contact respectively the inner-sealed intake extension on one side reaching to the bottom of the tube and the exhaust indentation at the top of the ground joint on the opposite side.

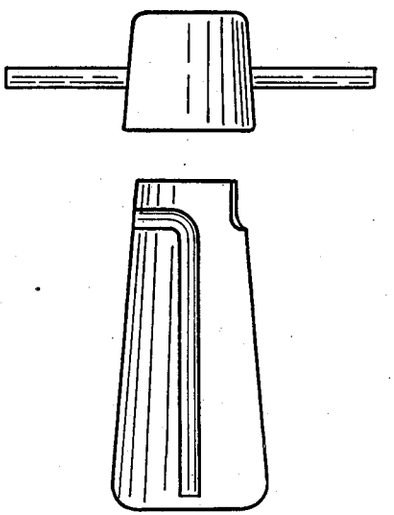


FIGURE 18

The Turner tube is parted and ascarite placed into the bottom 2 inches of its contents. The bottom half is then filled the remainder of its height with anhydrous magnesium perchlorate. A ⅛-inch layer of cotton is placed in the top inside of the ground cap which is then placed in position after a very small amount of stop cock grease has been applied to the ground glass surface of the lower half. The empty tube weighs approximately 50 grams and the charged tube approximately 100 grams. A duplicate tare is used in weighing the tube and the ground cap requires to be turned only a short distance to open or close the tube for use in absorptions or for weighing at the balance.

The Turner tube has all desirable advantages for use in the determination of carbon in iron and steel by direct combustion or for the determination of carbon in organic macro-combustion methods. It may be charged completely with anhydrous magnesium perchlorate for moisture determinations and many other uses can readily be devised. It has the advantage of being easily charged and recharged. It has a high capacity in terms of active ingredient absorbed, requires no support or suspensions on the balance pan and is not fragile or excessive in cost.

[54] Turner, "An Improved Absorption Tube for Combustion Analysis." *Ind. Eng. Chem. Anal. Ed.*, 3, 63 (1931).

Its total height is used as absorptive column. This design is patented and the apparatus is supplied by Eimer and Amend of New York City.

Modern equipment for use in the determination of carbon in iron and steel is shown assembled in Figure 19. The furnace here shown is a "globar" carborundum resistor furnace shown in the center foreground of the illustration. A Leeds and Northrup potentiometer indicator with platinum-rhodium thermocouple is shown in front of the furnace. A 1½ inch McDanel combustion tube is used with furnace and the preliminary purification train in Figure 17 is shown together with pressure cylinder and reducing valve at the right of the furnace. The furnace is energized using a large variac voltage regulator.

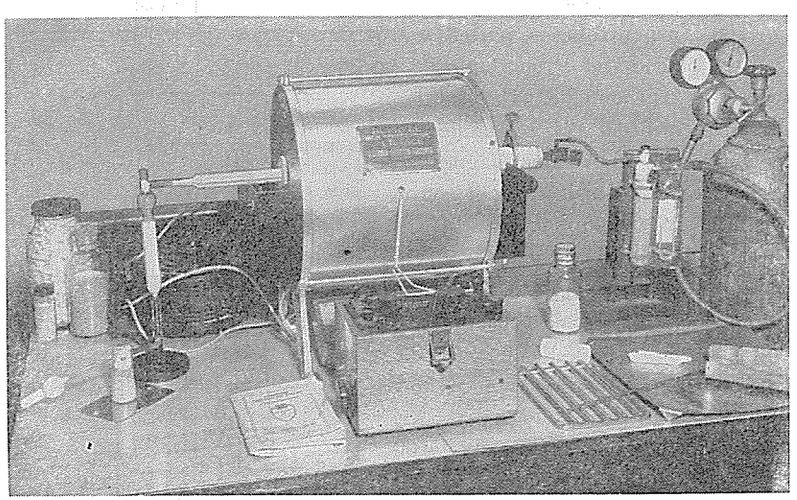


FIGURE 19

The analysis train including Turner tube is shown at the left of the furnace.

The description of the determination of carbon in iron and steel is given in detail by Lundell, Hoffman and Bright.[53] An exhaustive study of the determination of total carbon in low carbon steels is described by Yenson.[55] The determination of carbon in high sulfur steels is described by Bright and Lundell [56] and the determination of carbon in high melting alloys using the induction furnace has been described by Smith and Hockenyos.[57]

[55] Yenson, "Carbon in Iron," *Trans. Am. Elec. Soc.*, 37, 227 (1920).

[56] Bright and Lundell, "Determination of Carbon in High Sulfur Steels by Direct Combustion," *Bur. of Stands. Jour. of Research*, 5, 943 (1930).

[57] Smith and Hockenyos, "Determination of Carbon in High-Melting Alloys Using the High Frequency Induction Furnace." *Ind. Eng. Chem. Anal. Ed.*, 2, 36 (1930).

This chapter on the small scale laboratory uses of the perchlorate driers could not be closed more appropriately than by quoting from the text by Lundell, Hoffman and Bright,[58] page 24, as follows:

"More attention should be paid to the choice of a desiccant and its condition than is usually given by the analyst, not only when the desiccant is to be used in absorption chains as in the determination of water or of carbon dioxide, but also for general drying purposes, as in desiccators. The indiscriminate use of desiccants in absorption chains can not but lead to trouble, for the extent and the speed of their drying powers vary. Air that has been passed through calcium chloride will give up water to sulphuric acid, and air that has passed through phosphorus pentoxide will take water away from calcium chloride; two different desiccants may have the same drying power at a slow rate of air flow and differ considerably when the passage of air is rapid. Two or more desiccants can be used in an absorption chain provided they are progressively more efficient and the final desiccant is the same as that employed in the weighed system. It is self-evident that desiccants should be renewed often enough to insure maximum performance. To this end a record should be kept of the weight of water absorbed if this is feasible, or else the date of filling the apparatus should be recorded.

The common drying agents are calcium chloride, sulphuric acid, phosphorus pentoxide, anhydrous magnesium perchlorate (Anhydrone), and magnesium perchlorate trihydrate (Dehydrite). Less commonly used are ignited alumina, calcium chloride and fused potassium hydroxide."

SUGGESTIONS ON DESICCATOR DRYING AGENTS

Following the general operation of the ignition of a precipitate preparatory to weighing it is necessary to cool the crucible with its contents in a desiccator for a given period of time. Quoting Lundell, Hoffman and Bright,[53] pp. 91-92:

"If the residue is moderately hygroscopic, as lime or alumina, it must be cooled and weighed in a crucible having a snugly-fitting cover, and it is desirable to reignite it and make a second weighing with the previous weights already set, so that the weight can be quickly obtained. *With such residues it is important that the desiccator contain a fresh charge of a powerful desiccant such an anhydrone (anhydrous magnesium perchlorate), never calcium chloride.*"*

* The italics are by the author.