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CARBON DIOXIDE

By

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AND

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American Chemical Society
Monograph Series

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GENERAL INTRODUCTION

American Chemical Society Series of Scientific and Technologic Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in cooperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, Secretary of the American Chemical Society, Washington, D. C.; John E. Teeple, Treasurer of the American Chemical Society, New York City; and Professor Gellert Alleman of Swarthmore College. The Trustees have arranged for the publication of the American Chemical Society series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company (Reinhold Publishing Corporation, successors) of New York City.

The Council, acting through the Committee on National Policy of the American Chemical Society, appointed the editors, named at the close of this introduction, to have charge of securing authors, and of considering critically the manuscripts prepared. The editors of each series will endeavor to select topics which are of current interest and authors who are recognized as authorities in their respective fields. The list of monographs thus far secured appears in the publisher's own announcement elsewhere in this volume.

The development of knowledge in all branches of science, and especially in chemistry, has been so rapid during the last fifty years and the fields covered by this development have been so varied that it is diffi-

cult for any individual to keep in touch with the progress in branches of science outside his own specialty. In spite of the facilities for the examination of the literature given by Chemical Abstracts and such compendia as Beilstein's Handbuch der Organischen Chemie, Richter's Lexikon, Ostwald's Lehrbuch der Allgemeinen Chemie, Abegg's and Gmelin-Kraut's Handbuch der Anorganischen Chemie and the English and French Dictionaries of Chemistry, it often takes a great deal of time to coordinate the knowledge available upon a single topic. Consequently when men who have spent years in the study of important subjects are willing to coordinate their knowledge and present it in concise, readable form, they perform a service of the highest value to their fellow chemists.

It was with a clear recognition of the usefulness of reviews of this character that a Committee of the American Chemical Society recommended the publication of the two series of monographs under the auspices of the society.

Two rather distinct purposes are to be served by these monographs. The first purpose, whose fulfillment will probably render to chemists in general the most important service, is to present the knowledge available upon the chosen topic in a readable form, intelligible to those whose activities may be along a wholly different line. Many chemists fail to realize how closely their investigations may be connected with other work which on the surface appears far afield from their own. These monographs will enable such men to form closer contact with the work of chemists in other lines of research. The second purpose is to promote research in the branch of science covered by the monograph, by furnishing a well-digested survey of the progress already made in that field and by pointing out directions in which investigation needs to be extended. To facilitate the attainment of this purpose, it is intended to include extended references to the literature, which will enable anyone interested to follow up the subject in more detail. If the literature is so voluminous that a complete bibliography is impracticable, a critical selection will be made of those papers which are most important.

The publication of these books marks a distinct departure in the policy of the American Chemical Society inasmuch as it is a serious attempt to found an American chemical literature without primary regard to commercial considerations. The success of the venture will depend in large

part upon the measure of cooperation which can be secured in the preparation of books dealing adequately with topics of general interest; it is earnestly hoped, therefore, that every member of the various organizations in the chemical and allied industries will recognize the importance of the enterprise and take sufficient interest to justify it.

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PREFACE

The writing of this book was started several years ago because we believed that a treatise was needed in which much of the available information concerning carbon dioxide should be assembled in a usable form. The result of this labor is now passed on to those interested in the subject, with a hope that it may fill this need to some extent.

While selecting and arranging the material of which this work is composed we have aimed at a very broad treatment of the many phenomena in nature and industry in which carbon dioxide is an important factor. We have attempted to keep in mind the needs of the industrial worker, the research student and the general reader who is attempting to gain some information concerning the subject. Rapidly changing conditions, especially in the carbon dioxide industry, have made it difficult to satisfactorily attain all of these objectives. We have made no special effort to paint a picture of the carbon dioxide industry as it exists today; mainly because such a picture would have only historical interest in a very short time. The attempt to put into one volume such widely divergent ideas as the natural occurrence of carbon dioxide in Yellowstone National Park, the treatment of skin diseases with solid carbon dioxide and the blasting down of coal with the liquid form, makes a well-coördinated discussion difficult, if not impossible. We believe, however, that our treatment is justified, because after all, the subject treated, is "Carbon Dioxide."

Many persons have assisted either directly or indirectly in this project. Several plant executives with important industrial connections have read all or part of the manuscript. For obvious reasons these men have requested that we do not use their names in acknowledging this aid. We wish, however, to express our gratitude to them as well as to those who so kindly permitted plant inspections by the senior author.

We wish also to extend our thanks to the following persons who have given us exceptional aid: Dr. George Thomas, President of the University of Utah, who made it possible for one of us to devote one whole summer to this work, Dr. Walter D. Bonner, Professor of Chemistry, University of Utah, who read the manuscript and offered many excellent suggestions, Dr. E. B. Auerbach, of the Ira J. Owen Organization, Inc., Chicago, who made a very careful review and pointed out omissions and corrections, Mr. Edwin Johnson of the Safety Mining Company, Chicago, who furnished considerable material relating to the use of carbon dioxide in the coal mining industry, and Mrs. Helen Y. Mackintosh of the library staff of the University of Utah who made the index to this volume.

E. L. Q.
C. L. J.

June 29, 1935

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Chapter I

The Early History of Carbon Dioxide

The intimate relation between carbon dioxide and living things on the earth would lead one to expect its history to start with the history of man. There is hardly any doubt that the primitive people were aware of the presence of this gas, but instead of a material substance they considered it to be an evil spirit or demon having the power to slay without leaving any evidence of violence on its victim. In the first century of our era, Pliny[1] mentioned the exhalation of lethal vapor—*spiritus lethales*—from certain caverns, especially the dog grotto near Naples.

The actual recorded history of this substance, however, starts with the writings of J. B. van Helmont (1577-1644). These papers, assembled by his son after van Helmont's death, were published under the title of *Ortus medicinae*. This work makes it clear that van Helmont recognized carbon dioxide as a gas, distinct from other gaseous substances, and that he was able to study many of its properties.

Van Helmont discovered that the burning of charcoal produced, besides an ash, a substance which he called *spiritus sylvestre*, and furthermore, that this spiritus sylvestre is identical with the gas given off during the process of fermentation. Other names applied to this substance by van Helmont were *gas carbonum, gas vinorum, gas uvarum, gas musti*, etc. In addition to these two sources of carbon dioxide, van Helmont discovered four others: one from the action of acids on carbonates, (he used vinegar and crabs stones); a second from caves, cellars, and mines; a third from mineral waters, especially those from Spa, and the fourth, a product of gastric fermentation in the intestines. Van Helmont was unable to collect and preserve this gas and even declared that it could not be held in any vessel. Nevertheless, this early investigator was the first to note the disappearance of air when a candle was burned in a jar, inverted over water, and his conclusions were, that he was able to produce a void in nature which filled immediately with the material substance, water.

Soon after the time of van Helmont, Fr. Hoffman[2] carried on an investigation with the gas escaping from certain effervescing mineral waters which he named *spiritus mineralis*, although he also referred to it as *spiritus sulphurus, spiritus aethereus, and spiritus elasticus*. He observed that water charged with carbon dioxide had the power of reddening certain blue vegetable coloring matters which he placed in it, and from this he

[1] Pliny, *Historiae naturalis*, 2, 95 (A. D. 77).

[2] Hoffman, "De methode examinandi aquas salubres," Lugduni Batavorum, (1708).

concluded that the gas caused the water to have weak acidic properties. However, L. Libavius,[3] in 1597, had also noticed the acid character of charged water, and attributed it to the presence of imponderable spiritus of great volatility.

Next Hales,[4] in the year 1724, carried on a large number of experiments on plant transpiration and the distillation products of vegetable matter. While Hales added nothing new regarding carbon dioxide, he produced the gas and handled it much as we do today. His apparatus for collecting gases was his best contribution to the science and with slight modifications, it is still used, even by those beginning the study of the subject.

Fr. Venel,[5] Professor of Chemistry at Montpellier, in 1750, presented to the Academy of Sciences two memoirs, the object of which was to prove that Seltz water and other acidulous waters owe their pungent taste, as well as the escaping gas bubbles to a quality of air, dissolved in them. Venel, however, confused this air or gas with ordinary atmospheric air, and his writings added nothing to the existing knowledge of the subject.

About 1757, Joseph Black[6] found that carbon dioxide was a constituent of the carbonates or mild alkalies, being combined in them in the fixed or solid state; and for that reason he called it *fixed air*. Black's skillful experimentation proved much which at that time lacked experimental verification. He confirmed the ideas of van Helmont regarding combustion of carbonaceous matter and showed that respiration was a process that removed part of ordinary atmospheric air and transformed it into fixed air. Black discovered the deadly effect that this gas had on animal life and he performed many experiments with it on birds and small animals.

McBride,[7] about 1764, also investigated the formation of fixed air during the process of fermentation and putrefaction, and made certain valuable observations on its presence in the blood and in the atmosphere.

Two years later, Cavendish[8] published certain observations which he had made on fixed air, especially the fact that fixed air precipitated calcium carbonate from a solution of calcium hydroxide and then on the continued addition of the fixed air the precipitate went back into solution.

While Joseph Priestley's fame is due largely to his discovery of oxygen, he really added considerable valuable information to the knowledge of carbon dioxide. The presence of a brewery near Priestley's home, stimulated him to study the gaseous product of the fermentation vats. While attempting to make, artificially, a water similar to the famous Pyrmont product, he found that pressure favored the solution of carbon dioxide in water and for this discovery he may be considered the inventor of artifically

[3] Libavius, "De judico aquarum mineralium," Francofurti, (1597).

[4] Hales, "Vegetable Staticks," London, (1727).

[5] Venel, *Mém. Acad.*, **53**, 80, 337 (1750).

[6] Black, "Experiments upon magnesia alba, quicklime, and other alcaline substances," Edinburgh, (1777); Alembic Club Reprints, 1 (1893).

[7] McBride, D., "Experimental Essays on the Fermentation of Alimentary Substances and on the Nature and Properties of Fixed Air," London, (1764).

[8] Cavendish, H., *Phil. Trans.*, **56**, 141 (1766).

carbonated water. Priestly also found that plants were able to live in this fixed air whereas animals perished, and further that plants gave to the fixed air, properties of common air under the influence of light, but that this action ceased at night.

Regarding the influence of living plants and living animals on the composition of the atmosphere, Priestley, from a series of experiments, drew conclusions which have withstood the test of time. These ideas are even more remarkable when one considers the fact that oxygen, at that time, had not been discovered and rather vague ideas prevailed regarding nitrogen. Priestley's conclusions can best be given in his own words:[9]

> "These proofs of a partial restoration of air by plants in a state of vegetation, though in a confined and unnatural situation, cannot but render it highly probable, that the injury which is continually done to the atmosphere by the respiration of such a number of animals, and the putrefaction of such masses of both vegetable and animal matter, is, in part at least, repaired by the vegetable creation, and, notwithstanding the prodigious mass of air, that is corrupted daily by the above mentioned causes, yet, if we consider the immense profusion of vegetables upon the face of the earth, growing in places suited to their nature, and consequently, at full liberty to exert all their powers, both inhaling and exhaling, it can hardly be thought, but that it may be sufficient counterbalance to it, and, that the remedy is adequate to the evil."

Shortly after the publication of this long dissertation by Priestley, concerning the properties of this gas, an exhaustive work on the history and nature of carbon dioxide came out under the authorship of Tobern Bergman,[10] who about 1770 made an exhaustive study of the properties of this elastic fluid. Bergman found that water dissolves nearly its own volume of fixed air at 10° C. and that the solubility of the gas decreases as the temperature increases. He carefully determined the density of a saturated solution of carbon dioxide in distilled water, and found it to be 1.015 at a temperature of 2° C. He demonstrated again by the taste and action on litmus that this solution was a weak acid and he proceeded to produce water artifically, which imitated that of Seltz, Spa and Pyrmont. He used this artificial mineral water for several years and claimed very pleasing results. Because of the acid nature of its water solutions Bergman called carbon dioxide, *acid of air*. Some of Bergman's quantitative work on compounds containing carbon dioxide was of a degree of accuracy that might be considered good today. He determined the composition of various carbonates such as barium, calcium and magnesium and noted that the last two were soluble in water solutions of acid of air.

Bergman was the first to formulate a rational opinion on the composition of the atmosphere. He considered it as consisting of three elastic fluids;

[9] Priestley, J., *Phil. Trans.*, **62**, 127-264 (1772).

[10] Bergman, T., Opusc., I., 1, "De acido aereo." (1774).

first, acid of air, which exists in very small amounts; second, what he called vitiated air, which served neither for combustion nor for the respiration of animals; and third, an air absolutely necessary for fire and animal life, that makes up about a quarter of the atmosphere and which he regarded as pure air. The density of carbon dioxide, Bergman found, was greater than ordinary air, and this explained the phenomenon of asphyxia that takes place near the ground, in many places where the gas exists in abundance. He cites for example, the fountain in Pyrmont, opened in 1717, where the geese, having very long necks, were able to swim without inconvenience; the sources of Schwalback and the dog grotto near Naples. Bergman's experiments with animals in an atmosphere of carbon dioxide were very remarkable. The exactness of his observations, his skill as an experimenter and the care with which he examined the animals after death, threw much light on the physiological action of carbon dioxide. His experiments showed that carbon dioxide kills, not only by depriving the victim of respirable air, but in exercising a harmful effect on the organism, particularly on the blood and the circulatory system.

Lavoisier[11] proved the composition of fixed air by showing that it was produced when carbon was heated in oxygen. He then renamed it *acide carbonique* a term which, with its English equivalent, *carbonic acid,* has come down to the present time. However, the term carbon dioxide is more generally used now for the gas and carbonic acid for its water solution. Lavoisier and Laplace[12] found that acide carbonique was composed of 23.5 to 28.9 parts of carbon with 71.1 to 76.5 parts of oxygen. Lavoisier produced this compound by the combustion of the diamond in oxygen.

While most of the determinations of the compositions of carbon dioxide up to this time, were made by the method of synthesis, Smithson Tennant, in 1797, determined its composition by an analytical method. He heated a small piece of phosphorus with powdered calcium carbonate in a glass tube. The phosphorus changed to an oxide at the expense of the oxygen of the carbon dioxide, and the liberated carbon was deposited in the tube in the form of a black powder.[13]

The Industrial Development of Carbon Dioxide. The industrial development of carbon dioxide may be considered to start with the purely scientific experiments of Faraday on the liquefaction of gases. It is true that much interest was shown before this time in the preparation of artificially carbonated mineral water,[14] which was considered especially valuable as a medicine, yet the industry as it is today could not exist without the process of liquefaction.

Faraday's[15] experiments with bent glass tubes, in which he liquefied various gases, one of which was carbon dioxide, are well known even to

[11] Lavoisier, A. L. Opuscules physiques et chimiques, Paris, (1774); *Mém. Acad.*, 564, 591 (1772); 520 (1775); 185, 363 (1777); 448 (1781); 593 (1784).

[12] Lavoisier, A. L., and Laplace, P. S., *Mém. Acad.*, 359 (1780); 387 (1784).

[13] Tennant, Smithson, *Phil. Trans.*, (1791).

[14] Nooth, *Phil. Trans.*, 65, 59-66 (1774).

[15] Faraday, M., *Phil. Trans.*, 193 (1823).

beginners in the science. It is, perhaps well, however, to emphasize at this point the important consequences of his work and how it affected the future of the industry.

The idea of making liquids from gases had an immediate appeal to a large number of investigators who proceeded to study various gases from many different points of view. Thilorier[16] repeated Faraday's liquefaction experiments on a much larger scale, using a cast-iron retort instead of a glass tube for the gas generator. Two of these retorts were connected together, one serving for the generator, in which sodium bicarbonate was treated with sulfuric acid, and the other acting as a receiver and condenser for the gas as it came over under very high pressure from the generator. While Thilorier was able to produce considerable liquid by this method, his apparatus was quite unsuited to withstand the terrific strain imposed on it and eventually it exploded. This explosion took place before a class at the Ecóle de Pharmacie, Paris, and the fragments of the shattered cast-iron receiver cut off both legs of the unfortunate operator, M. Hervy[17] who, at the time, was swinging the generator to and fro for the purpose of mixing the charge. From this injury, Hervy died a short time after. Thilorier, however, made many valuable observations on the dilation, vapor pressure, density and heat change of this liquid during vaporization. While vaporizing the liquid, Thilorier[18] produced solid carbon dioxide for the first time. He obtained this as a white flocculent mass, resembling snow, which, like snow, was readily compressed. Thilorier gives the following description of this interesting substance: "When the solid is exposed to the air it disappears insensibly by slow evaporation, without melting. A fragment of the solid, slightly touched by the finger, glides rapidly over a polished surface, as if it were sustained by the gaseous atmosphere with which it is constantly surrounded. The vaporization of solid carbon dioxide is complete; it leaves but rarely a slight humidity which may be attributed to the action of air on a cold body, the temperature of which is far below that of freezing mercury. The snow can be handled without harm, but when pressed on the skin for a few seconds or more, it produces blisters."

Mareska and Donny[19] improved Thilorier's liquefying apparatus and made it much safer by constructing it of lead and surrounding the lead retorts with copper jackets reinforced with wrought-iron bands. Two of these cylinders were connected together with a small flexible copper tube in order that the one serving as a generator could be rocked backwards and forwards for agitating the mixture. The generating cylinder was charged with sodium bicarbonate while the sulfuric acid, necessary for the reaction, was inclosed in a small internal cylinder. Mixing was accomplished by tilting the generator until the acid flowed into the bicarbonate solution.

[16] Thilorier, M., *Ann. chim. phys.*, (2) **60**, 427 (1835).

[17] Anon., *J. Chem. Med.*, **17**, 61.

[18] Thilorier, M., *Ann. chim. phys.*, (2) **60**, 432 (1835).

[19] Mareska, J. and Donny, F., *Mém. Couron. Bruxelles*, **18**, 1 (1845); *J. prakt. Chem.*, (1) **35**, 226 (1845); *Compt. rend.*, **20**, 817 (1845).

During the year 1845, several important steps were taken in the direction of the commercial utilization of carbon dioxide. Addams[20] had previously been able to produce liquid carbon dioxide with a hydraulic pump. This apparatus now served Faraday[21] for the preparation of large amounts of the liquid from which he was able to make considerable solid carbon dioxide. Faraday mixed this solid carbon dioxide with ether and by means of a vacuum pump was able to decrease the gas pressure over the mixture, reducing the temperature thereby to a value somewhat below −100° C. This freezing mixture was used in the famous research which Faraday published at this time on the liquefaction of gases. Then Johann Natterer[22] working under the direction of Professor Pleischl in Vienna, developed a mechanical compressor with which he was able to produce liquid carbon dioxide. His machine was of the single-acting compression type and several hours of hard work were required to produce a pound of the liquid. Nevertheless, in spite of its crudeness, it was the forerunner of the modern multi-stage compressors.

In 1873, the United States Navy Department purchased a "Lay Torpedo" with the Lay apparatus for producing the liquid carbon dioxide necessary for propelling and steering it. Walter Hill,[23] working at the Naval Station at Newport, R. I., was assigned the task of producing the required carbon dioxide with this apparatus and testing the torpedo. The Lay process was similar to that already used by previous investigators, in which sodium bicarbonate was treated with sulfuric acid and Hill soon found that it was quite impractical for producing the large quantity of liquid needed for the operation of the torpedo. Seven hundred pounds of this liquefied gas were necessary for filling the torpedo, and to accomplish the work necessary for compressing this vast amount of gas, Hill obtained a compressor from the Burleigh Rock Drill Company, Fitchburg, Massachusetts. In 1874, in less than two working days, 315 lbs. of this liquid had been made, using marble dust and sulfuric acid for producing the gas, and the mechanical compressor for reducing it to a liquid. A few weeks later, 380 pounds more were compressed, thus completing the charge necessary for the torpedo. Several hours after this work was finished, one of the flasks containing the liquid carbon dioxide burst, while lying in a shed used for housing the torpedo. The other flask was condemned as unsafe and immediately destroyed. New flasks were made, but no more liquid was produced until 1875. Hill, at this time, was able to compress carbon dioxide at a rate of 46 lbs. per hour at a cost of 24.9 cents per pound for the first, and not over 21 cents per pound for the second lot. He estimated that the liquid could be made for less than 15 cents per pound, with an apparatus similar to the one he used.

[20] Addams, R., *Report of Brit. Assoc.*, 70, (1838).
[21] Faraday, M., *Phil. Trans.*, 155 (1845).
[22] Natterer, Johann, *J. prakt. Chem.*, (1) 31, 375 (1844).
[23] Hill, Walter, "Liquid Carbonic Acid," Newport, (1875).

In the year 1877, Dr.Hendryk Beins, in Groningen took out a patent on the production of liquid carbon dioxide by heating sodium bicarbonate. He was interested in the liquid, which he called "carboleum," as a motive power. In his discussion of the advantages of "carboleum" over other forms of power, Beins said "It can be used: (1) for locomotives; (2) for steam boats; (3) for small factories such as sewing machines, pumps, and lathes; (4) in fire extinguishers as a gas or solution; (5) as a source of power for electrical machines for street lighting, lighthouses, telegraphs, etc.; (6) as a 100 times cheaper projectile propeller than powder; (7) in the accomplishment of scientific undersea navigation for war purposes and perhaps for operating air ships; (8) for ice machines; (9) for mineral water as well as a source of pure carbon dioxide."

Beins' experiments with carbon dioxide as a propelling medium for submarines, interested the Dutch Navy to such an extent that the Minister of Marine, after an intelligent official test, which found it feasible, furnished financial assistance for carrying out the project.

An important event took place on August 28, 1879, when carbon dioxide was put to practical use on rather a large scale. On this day, Dr. W. Raydt, in Germany, attached a deflated balloon to an anchor on the bottom of the sea, in Kiel harbor, inflated it with carbon dioxide gas, and in just eight minutes had raised the anchor to the surface of the ocean, a distance of 10 meters. Then Raydt tried to raise some sunken steamers, but finally turned to the use of carbon dioxide for raising beer, and for making soda water. The anchor episode, while of no great importance in itself, turned the eyes of many inventors and scientists to the compound responsible for it, and from this time on, carbon dioxide received a great deal of attention as a potential article of commerce. Five years later, Raydt had established a factory for the production of liquid carbon dioxide, and part of the product from that factory was used by the Krupp Iron Works for compressing liquid iron into the molds. Raydt's factory became of great economic importance in later years, and this fact, more than his experiments with the anchor, is responsible for the statement, often made, that he is the father of the liquid carbon dioxide industry.

In 1882, Raydt[24] constructed an apparatus for carbonating water under pressure, for use as a fire extinguisher. This apparatus was tested at the Krupp Steel Works and by the Fire Department in Berlin, and in both cases was found to be superior to any other type of extinguisher at that time in existence. The fire director and chief of the department of the Krupps in Essen, writes as follows, regarding the Raydt system: "The principal advantage of the Raydt method lies in the fact, that one can, immediately, on the breaking out of a fire, without any preparation produce any desired pressure and form a very effective solution of carbon dioxide, which can be handled by a very much smaller service crew. The author has convinced us that very large theater, factory, and ship fires can be

[24] Raydt, W., *Polyt. Notizbl.*, **37**, 196 (1882).

avoided by the use of the Raydt solution apparatus when taken at the right time." Then followed Raydt's patent on the ice and refrigerating machine (D. R. P. No. 33168) in the year 1885. Other patents followed in rapid succession, until Raydt became by far the most important figure in the industry.

At this time, the liquid carbon dioxide industry depended upon two factors for development, first the development of compressors capable of compressing large quantities of the gas, and second the development of a market sufficient to absorb the product. Plenty of carbon dioxide came from the earth in many places, especially in Germany, so the manufacture of the gaseous compound was of small importance. However, to avoid transportation of the heavy cylinders and their contents, the need for other methods of manufacturing the gas was soon evident and in 1889 the Kolensäure-Werke in Erkner near Berlin started making carbon dioxide by the coke process.

The names of many men were closely associated with the industry at this time. The Beins brothers, H. Beins and his brother T. F. Beins, had devised an apparatus for producing mineral water and had established a company for manufacturing it. Dr. Hugo Kunheim was very active both as a manufacturer and as an investigator. Hugo Baum was the first to use natural carbon dioxide from a well in Burgbrohl in the Eifel. C. G. Rommenhöller became a leading figure as a manufacturer of carbon dioxide and was connected with many enterprises using both natural and coke process carbon dioxide.

Chapter II

Carbon Dioxide in Nature

Notwithstanding the very low concentrations of carbon dioxide in the earth's atmosphere, its importance to plants and animals as a part of the life process cannot be over-emphasized. Being a food for the vegetable kingdom and a waste produce from animal life, it is, to a certain extent, a connecting link, which by its regulatory powers, controls the extent of life in each. The situation, however, is very complex. The information at present available is both scant and to a certain extent inaccurate. It is, therefore, not to be expected that a complete and well founded exposition of nature's *modus operandi,* with respect to carbon dioxide, can at this time be given.

Occurrence in the Atmosphere. The exact concentration of carbon dioxide in air over wooded areas, desert land, in the atmosphere near the north and south poles, over the seas, lakes, etc., becomes of great importance to those working in the field of photosynthesis and perhaps only to a lesser extent in many other fields.

In 1769, H. B. de Saussure[1] made an investigation of the carbon dioxide content of the air in the mountains and on the plains of Switzerland. Later, his son, N. T. de Saussure[2] continued this investigation and arrived at some very interesting conclusions, regarding the variability in amounts of this gas in the atmosphere and some of the factors influencing its concentration. His most remarkable observation concerned the difference in concentration of carbon dioxide during day and night. His values obtained at night were somewhat higher than those obtained during the day.

These early determinations are more valuable for their historic significance than for their scientific utility. A few other analyses collected by Mellor[3] are also interesting as they were made on air from many different part of the earth. These values, shown in Table 1, vary between rather wide limits, i. e. from 2.43 to 3.90 volumes per 10,000 volumes of air. This deviation is somewhat greater than one might expect and is, perhaps, due to lack of refinement in the technique of sampling and analyzing, rather than to actual variation in the carbon dioxide concentration.

Certain disturbing factors may greatly affect the carbon dioxide concentration of the atmosphere at any one point and unless these are guarded

[1] de Saussure, H. B., "Voyages dans les Alpes," *Geneve,* **4,** 202 (1796).

[2] de Saussure, N. T., *Ann. chim. phys.,* (2) **38,** 411 (1828); (2) **44,** 5, (1830).

[3] Mellor, J. W., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," **6,** page 3. Longmans, Green and Co. (London.) (1925).

TABLE 1.—*Concentrations of Carbon Dioxide at Various Points on the Earth.*

Source of sample	Vols. CO_2 per 10,000 vols. of air	Observer
Paris	3.027	J. A. Reiset
Dieppe	2.942	J. A. Reiset
Bloomington, Ind.	2.816	T. C. van Nüys and B. F. Adams
Country of Belgium	2.944	A. Petermann and J. Graftiau
Gembloux	3.700	A. Petermann and J. Graftiau
Sheffield	3.90	W. C. Williams
1.5 miles west of Sheffield	3.27	W. C. Williams
Mont Blanc, 1080 m.	2.62	M. de Thierry
Mont Blanc, 3050 m.	2.69	M. de Thierry
Belfast	2.91	E. A. Letts and R. F. Blake
Kew (max. and min.)	2.43 to 3.60	H. T. Brown and F. Escombe

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Reiset, J. A., *loc. cit.*
Petermann, A. and Graftiau, J., *Mém. Acad. Belg.*, **47**, 2 (1892).
Williams, W. C., *Chem. News*, **76**, 209 (1897); *Ber.*, **30**, 1450 (1897).
de Thierry, M., *Compt. rend.*, **129**, 315 (1899).
Letts, E. A. and Blake, R. F., *Proc. Roy. Soc. (Dublin)* (2) **9**, 107 (1900).
Brown, H. T. and Escombe, F., *Proc. Roy. Soc. (London)*, **76**, B 118 (1905).

against the determinations may have but little value. Thus, Reiset[4] made several analyses, 8 kilometers from the city of Dieppe and obtained an average value of 2.917 vols. of carbon dioxide per 10,000 vols. of air. When, however, a drove of sheep entered the region of sampling, the carbon dioxide concentration rose to 3.178 volumes. Samples taken near the ground are affected by the character of the soil, the presence of decaying organic material, and the presence of water. The effect of proximity of human habitation to the source of sampling is shown in the results of Haehnel[5] who made a series of determinations of the carbon dioxide concentration in the air of Berlin. This investigation was made in an attempt to determine the cause of weathering of stone and metal structures. His results showed a value of 24 parts of carbon dioxide per 10,000 parts of air which is so far above the amount usually found, even in cities, one is led to suspect that the samples did not represent true averages. Florentine[6] collected 27 samples at various seasons of the year in the streets of Paris and found that the carbon dioxide concentration ranged from 3.4 to 6.2 vols. per 10,000 vols. of air. Confirmation of these results were made by Cambier and Macy[7] who nearly a year later obtained values from 3.4 to 6 parts carbon dioxide per 10,000 parts of air. The samples were taken two meters above the ground in the streets of Paris.

[4] Reiset, J. A., *Compt. rend.*, **88**, 1007 (1879).
[5] Haehnel, O., *Z. angew. Chem.*, **35**, 618-20 (1922).
[6] Florentine, D., *Compt. rend.*, 185, 1538-41 (1927).
[7] Cambier, R., and Macy, F., *Compt. rend.*, **186**, 918-21 (1928).

One of the most valuable investigations of the carbon dioxide tension of the air was made by Benedict[8] on 212 samples, taken under conditions well removed from disturbing influences and over a period extending from April 1911 to January 1912. His samples, from which he obtained an average of 3.1 vols. per 10,000 vols. of air, were collected under various conditions of weather, pressure of the atmosphere, temperature, humidity and wind velocity, furthermore, the experiments were made before, during and after the vegetation season. The agreement between the individual determinations was remarkable and essentially the same results were obtained from air taken from the top of Pike's Peak in Colorado and samples taken over the ocean. The air of crowded city streets showed much higher concentrations and in subway stations in New York and Boston, he found about twice the normal amount.

A series of determinations made by Lundegårdh on the island of Hollands Väderö, 3.2 kilometers from the mainland of Sweden, show only a very slight variation over a series of years when the same method of analysis was used. The results he obtained were:

1920	3.295	vols. per	10,000	vols. of	air.
1921	3.031	vols. per	10,000	vols. of	air.
1922	2.843	vols. per	10,000	vols. of	air.
1923	3.000	vols. per	10,000	vols. of	air.

Moss[10] found the air over the Arctic to be richer in carbon dioxide than that over England. Krogh[11] found the concentration of this gas in the air over Greenland to vary between 2.5 and 7 vols. per 10,000 vols. of air. Schulz[12] reports values over the North Sea and Baltic ranging from 2.7 to 3.2 with a mean value of 2.93. Müntz and Lainé[13] determined the carbon dioxide content of air in the Antractic regions. Between 64° 49′ and 70° 5′ the average carbon dioxide content of the air is 2.0524; at 69° 30′ only 1.447 and at 70° 5′, 1.702 parts per 10,000 parts of air. The explanation of this decrease depends upon the fact that the dissociation pressure of bicarbonates decreases with a decrease in temperature and is extremely small at temperatures of 0° and below. Legendre[14] analyzed the sea air off the coast of France and obtained a value of 3.35 vols. of carbon dioxide per 10,000 vols. of air.

All of these determinations, with the wide variation in results, leave one rather confused as to the most probable concentration of carbon dioxide in the atmosphere. Reinau[15] attaches considerable importance to these variations and has attempted to account for them by means of an elaborate

[8] Benedict, F. G., "The Composition of the Atmosphere with Special Reference to its Oxygen Content," *Carnegie Inst., Washington, Pub.* **166,** (1912).

[9] Lundegårdh, H., "Der Kreislauf der Kohlensaure in der Natur," Jena p. 9 (1924).

[10] Moss, E. L., *Proc. Roy. Soc.* (*Dublin*), (2) **2,** 34 (1878).

[11] Krogh, A., *Medd. Gronland,* **26,** 409 (1904); *Compt. rend.,* **139,** 896 (1904).

[12] Schulz, *Arch. deutsch. Seewarte,* **40,** 16 (1922); **41,** 6 (1923).

[13] Müntz, A., and Lainé, E., *Compt. rend.,* **153,** 1116-9 (1911).

[14] Legendre, R., *Compt. rend.,* **143,** 526 (1906).

[15] Reinau, E., "Kohlensäure and Pflanzen." Halle (1920).

theory. However, it is very likely, as Spoehr[16] points out that these variations are due to errors inherent in the methods used for analysis and it is rather risky to attach too much importance to them. For calculations requiring a knowledge of the concentration of atmospheric carbon dioxide, the value ordinarily used is 3 vols. per 10,000 vols. of air or 0.03 per cent by volume.

From the analytical data already obtained various attempts have been made to estimate the total carbon dioxide in the atmosphere. Clark[17] calculated that the atmosphere of the earth contains 2.2×10^{12} tons of this gas while Krogh gives a value of 2.4×10^{12} tons and van Hise[18] and Dittmar[19] obtain similar estimates. Chamberlin,[20] however, gives a somewhat higher value. The amount taken for calculations involving this factor, is usually about 2.2×10^{12} tons or 2.0×10^{15} kilograms.

Occurrence in the Hydrosphere. By the hydrosphere is meant that layer of liquid water which covers such a large part of the earth's surface. In this liquid, carbon dioxide is soluble and, in addition, it is capable of acting as a medium in which many reactions involving carbon dioxide may take place. That the sea acts as a tremendous reservoir for carbon dioxide cannot be doubted. From this reservoir, carbon dioxide can be liberated to the atmosphere if its partial pressure in the air falls below that exerted by the gas in solution. Or, on the other hand, it can remove the gas from the atmosphere when an increased carbon dioxide tension prevails. The solution of carbon dioxide in ocean waters is not a simple case of gas dissolved in a liquid but rather a gas dissolved in a solution of many substances, some of which act chemically with the carbon dioxide. Not only the inorganic solutes present in ocean water affect the concentration of the gas, but many plants and animals live in these waters and their relation to the carbon dioxide balance is very much the same as that of their counterparts on the land.

From available data, it seems that there is even a wider variation in the concentration of carbon dioxide in the sea than has ever been observed in the atmosphere. Roughly, however, this concentration is about 5 vols. of the gas per 10,000 vols. of sea water. It has been estimated that the sea contains from 20 to 30 times the carbon dioxide existing in the atmosphere, thus making a total quantity as great as 6.6×10^{13} tons.

The carbon dioxide in the sea may exist in the form of carbonates, bicarbonates, carbonic acid and its ions, and the dissolved gas. That part of this compound existing as a carbonate, may be considered as more or less fixed. It is no longer available as a gas unless its compounds undergo some radical treatment by which the carbon dioxide is again liberated. However, half of that in the form of bicarbonates is rather loosely com-

[16] Spoehr, H. A., "Photosynthesis," page 38, The Chemical Catalog Co., Inc., New York (1926).
[17] Clark, F. W., Data of Geo-Chemistry, Washington, (1920).
[18] van Hise, C. R., *Mon. U. S. Geol. Survey*, **47**, 964 (1904).
[19] Dittmar, W., "Report on the Composition of Ocean Water," London, (1883).
[20] Chamberlin, T. C., *Geol.*, **5**, 653 (1897).

bined and will be given up again as gaseous carbon dioxide with a change in temperature or pressure of the gas over the liquid. All of that carbon dioxide, in the form of carbonic acid, is easily recovered if the temperature of the water increases. Each of these forms and their respective ions are related to each other and tend to form an equilibrium in which the carbon dioxide of the atmosphere takes part.

The concentration of carbon dioxide in the sea has been the subject of many investigations. Fox[21] found the concentration to vary from 1 to 7 vols. of carbon dioxide per 10,000 vols. of sea water. The more recent and extensive results of Schultz,[22] obtained during a study of the North Sea and the Baltic Sea, give a much better idea of this value. Some of the results obtained by Schulz are given in Table 2.

TABLE 2.—*Concentration of Carbon Dioxide in the Air, in Fresh Water and in Sea Water.*

In the atmosphere	3	vols. per 10,000 vols. of air
In fresh water, at 0°	5.1	vols. per 10,000 vols. of air
at 20°	2.6	vols. per 10,000 vols. of air
In sea water, at 0° (3.5% NaCl)	4.4	vols. per 10,000 vols. of air
at 20°	2.3	vols. per 10,000 vols. of air

Much evidence[23] points to the fact that the carbon dioxide of the sea is mostly in the form of bicarbonates or its ions and that this compound is in equilibrium with the dissolved carbon dioxide, which in turn, is regulated largely by the carbon dioxide tension of the atmosphere. Also, the carbon dioxide in sea water is not sufficient to transform all the normal calcium carbonate into the form of bicarbonate. According to Dittmar the dissociation pressure of the bicarbonate in sea water is 0.0005 atmos. at a temperature of about 18° to 21° C. and falls off to zero at the temperature of freezing water. As the carbon dioxide tension of normal air is about .0003 atmos., it follows that the colder parts of the ocean are constantly removing carbon dioxide from the atmosphere, while the warmer portions are constantly giving it up.

The question of whether there is ever a complete equilibrium between the carbon dioxide of the air and that in the sea, has, at present, no answer. Perhaps one can do no better than to consult Spoehr's[24] work on "Photosynthesis" for a more complete and detailed discussion of this subject.

Occurrence in the Lithosphere. From numerous eruptive vents and active volcanoes scattered pretty well over the whole earth, gases are pouring forth, and have been, since the beginning of time. Carbon dioxide

[21] Fox, C. J. J., *Trans. Faraday Soc.*, **5**, 68 (1909).

[22] Schultz, B., *Naturwissenschaften*, **12**, 105-113, 126-133 (1924).

[23] Jacobsen, O., Die Ergebinisse der Untersuchangsfahrten Drache, Berlin (1886); *Liebig's Ann.*, **167**, 1 (1873). Hamberg, A., *Svensaka Akad. Handl.*, **10**, 13 (1885); *J. prakt. Chem.*, (1) **33**, 433 (1886). Torneo, H., Den Norske Nordhays-Expedition, Chemistry, Christiania. 1, (1880). Natterer, F., *Monatsh*, **14**, 675 (1893); **15**; 596 (1894); **16**, 591 (1895); **20**, 1 (1899). Dittmar, W., *Challenger Reports, Physics and Chemistry*, **1**, 212, 221 (1884). Buchanan, J. Y., *Proc. Roy. Soc. (London)*, **22**, 192, 483 (1874).

[24] Spoehr, H. A., "Photosynthesis," pages 40-46, The Chemical Catalog Co., Inc., New York (1926).

occurs in practically all of these gases, in quantities which may vary from very low concentrations to a practically pure compound. All igneous rocks contain gases which they give up when strongly heated in a vacuum. Analyses have shown that the principal constituents of the gas obtained in this manner are: water, carbon dioxide and hydrogen while carbon monoxide, nitrogen, methane and hydrogen sulfide are subsidiary. Carbonates of calcium and magnesium, when subjected to volcanic intrusion, give off carbon dioxide because they are dissociated so easily by heat. Bituminous shales, when heated give off the products of dry distillation and in the gases from such a reaction, carbon dioxide is always present. Also, we have what are known as secondary fumaroles, which give off gases produced by the surface water acting on the hot detritus. The water is vaporized by the heat and the steam reacts chemically with the hot detritus, forming various quantities of volcanic gas. Table 3 taken from the extensive data of Allen[25] shows the analysis of a few typical volcanic gases.

TABLE 3.—*Showing the Per Cent by Volume of Carbon Dioxide, Nitrogen, and Oxygen in Various Volcanic Gases.*

Source	Date	CO_2	N_2	O_2
Hawaii, the crater	1912	62.3	13.8	0.0
Vesuvius, edge of great crater	1865	4.8	75.6	19.6
Phlegrean Fields, Torre del Greco, Flow of 1694	1869	90.2	6.2	0.08
Etna, Crater B, fumarole	1865	5.0	77.28	17.27
Sicily, Salinelle of Paterno Acqua Rossa	1856	97.9	2.1	.....
Lipari Isles, Vulcano, near the Chemical Works	1856	86.0	14.0	.....
Santorin, Port of George	1870	98.8	1.8	0.4
West Indies, Guadeloupe fumarole of the North	1904	52.8	36.07	7.5
Colombia, S. America, Puracé Solfatara	1868	98.2	.....	.....
Iceland, Krisuvik, second fumarole	1846	88.24	0.69	.....
Katami, Ten Thousand Smokes, Nova Rupta Basin	1919	70.4	12.8	1.0
Canary Islands, Pico de Teyde, South Fumarole	1907	71.1	26.9	.....

The curious effects produced on plant and animal life by these volcanic gases, where they escape from the earth, have been described by several writers. A few of these descriptions may be worthy of note here.

M. Boussingault describes a visit he made to a locality near the volcano of Tunguragua in 1851 in this manner: "Our horses soon gave us indications that we were approaching it; they refused to obey the spur, and threw up their heads in a most disagreeable fashion. The ground was strewn with dead birds, among which was a magnificent blackcock, that our guides at once picked up. Among the victims were also several reptiles and a multitude of butterflies. The sport was good, and the game did not seem too high. An old Indian, Quichua, who accompanied us, declared that, to procure a good sleep, there was nothing like making one's bed upon the Tunguraville."

Near Naples is found a cave which has become famous under the name of Grotta del Cane (the cave of the dog) from which a gas issues contain-

[25] Allen, E. T., *J. Franklin Inst.*, 193, 29-80 (1922).

ing about 70 per cent carbon dioxide, 24 per cent nitrogen and 6 per cent oxygen. Flammarion[26] thus describes this interesting cave: This grotto is situated upon the slope of a very fertile hill, opposite, and not far from Lake Agnano. The entrance is closed by a gate of which the keeper retains the key. The ground in this cavern is very earthy, damp, black, and at times heated. It is, as it were, steeped in a whitish mist, in which can be distinguished small bubbles. This mist is composed of carbonic acid gas, which is colored by a small quantity of aqueous vapor. The stratum of gas is from ten to twenty-five inches high. It represents, therefore, an inclined plane, the highest part of which corresponds to the deepest portion of the grotto, and this is a physical consequence of the formation of the ground. The grotto, being about the same level as the opening leading into it, the gas finds its way out at the door, and flows like a rivulet along the hillpath. The stream may be traced for a long distance, and a candle dipped into it at a distance of more than six feet from the grotto, is extinguished at once. A dog dies in the grotto in three minutes, a cat in four, a rabbit in seventy-five seconds. A man could not live more than ten minutes if he were to lie down upon this fatal ground. It is said that the Emperor Tiberius had two slaves chained up here, and that they perished at once; and that Peter of Toledo, Viceroy of Naples, shut up in the grotto two men condemned to death, whose end was as rapid."

The Valley of Death in Java, is an old volcanic crater with fissures from which escape large quantities of carbon dioxide. At times this gas covers the floor of the valley like water and the unwary animal venturing into it, increases the number of white skeletons which are scattered over the ground. An excellent description of this valley was given by Loudon.[27]

The Stygian Caves in Yellowstone National Park are interesting, as they have concentrations of carbon dioxide, sufficient to make them dangerous to animal life, yet it is said, that bears safely hibernate in them during the winter months. A few other caves, also of the same origin, that is, fissures of ancient hot springs, have low concentrations of this gas.

The Laacher Lake in Germany is the water-filled crater of a prehistoric volcano, and near by is a depression filled with carbon dioxide. Birds and insects flying in this region are killed by the gas. Many tragedies have resulted because of the carbon dioxide collecting in cellars of houses in the vicinity of this crater.

In former times the accidents caused by carbon dioxide in caves, mines, and even in wells, gave rise to the most extravagant stories. Such localities were said to be haunted by demons, gnomes, or genii, the guardians of subterranean treasures, whose glance alone, caused death, as no trace of lesion or bruise was to be found on the unfortunate persons so suddenly struck down. There is some reason for believing that the convulsions of the pythonesses, charged with expounding the decrees of the gods, were produced by the priests, with carbon dioxide gas.

[26] Flammarion, "The Atmosphere," Harper and Brothers, New York (1873).
[27] Loudon, A., *Edinburgh Phil. J.* (2), **12**, 102 (1831).

Natural waters practically always contain carbon dioxide. These waters may be divided into two general classes: first, those waters saturated, or nearly so, with carbon dioxide under the partial pressure found in normal air, and second, those waters containing carbon dioxide dissolved under pressure which effervesce when the pressure is released as the water comes to the surface of the earth. In the first class, one may place the surface waters of the earth and most wells. In the second class may be included those springs and wells, the waters of which have been charged with carbon dioxide under pressure by some chemical process in the earth. The acidity of these waters, due to the carbon dioxide, increases their dissolving action for rock material thus producing the so-called mineral waters.

Many of our most famous carbonated springs occur in Germany, a country exceptionally well favored with numerous sources of carbon dioxide in the form of springs and even practically dry gas wells. A few of the famous springs of Germany are found at Altwasser, Pyrmont, Reinerz, Salzbrunn and Seltzer. France is supplied with a number of carbonated springs in the Auvergne and in the midst of the Vivarais while this country has many like those located at Saratoga Springs, New York; in the Navajo and Ute Springs, Manitou, Colorado; the Napa Soda Springs, California, and the Hot Springs in Virginia. Apollinaris water, obtained from a spring in the Valley of Aar, near the Rhine, is an example of what is called an acid water, while Vichy, another famous spring water, has an alkaline reaction.

One of the most complete and exhaustive works dealing with mineral waters is that of Bouquet[28] who wrote a long report on the analysis of the mineral waters from many of the sources at Vichy and the vicinity. Seventeen of these sources delivered 610,776 liters of water per day from which 714 kilograms of carbon dioxide was liberated as a gas, and many times that amount was carried away in the form of carbonates and bicarbonates.

Castelli[29] describes some natural carbon dioxide springs in the territory of Montepulciano in the Saint Albino region in Italy. The zone covers an area approximately 500 meters square, and is made up of various Pliocene rocks. The fissures are filled with slightly opalescent water, through which the gas issues, causing the appearance of boiling, though the water is only slightly above 0° C. and the carbon dioxide 5° to 10° C. Several hundred cubic meters of gas is given off each day having the average composition: CO_2, 95.4 per cent; O_2, 0.33 per cent; N_2, 3.13 per cent; combustible gases 0.14 per cent and H_2S, a trace.

The numerous boiling springs found in Yellowstone National Park, give off large amounts of gaseous carbon dioxide to the atmosphere. The gases escaping from these springs, consists of steam mixed with various amounts of gas composed largely of carbon dioxide. One rather interesting formation, "The Dragon's Mouth," was investigated by Quinn who found the vapors responsible for the spewing of hot water from a small cave, to

[28] Bouquet, M., *Ann. chim. phys.* (3), 42, 278-363 (1854).
[29] Castelli, G., *Rass. min. met. chem.*, 58, 14-5 (1923).

include besides steam, a gas containing 34 per cent carbon dioxide. This value is very likely low as the difficulties connected with taking samples made the presence of air in the sample possible. A gas bubbling up through the mud only a few paces from this formation consisted of 96.5 per cent carbon dioxide.

Besides springs of carbonated mineral water, carbon dioxide comes to the surface of the earth, sometimes under great pressure, with various amounts of water. In some cases, the gas is practically dry and pure enough to be used directly for commercial purposes. Many of these sources were used industrially during the early history of carbon dioxide and interest in their commercial application seems to be again increasing.

At Pergine (Tuscany) there is an abundant source of carbon dioxide which was at one time used industrially by the firm of Cesare Pegna and Sons, of Florence. About 1885, a shaft, 52 meters deep, was sunk at Burgbrohl, and also one at Hoenningen on the Rhine. Measurements reported by Heusler,[30] indicated a water flow of 430 liters and a carbon dioxide flow of 1500 liters per minute or 2160 cubic meters per 24 hours. A factory was located at this point for compressing the gas into cylinders and some of it was also used for making white lead. Forbes[31] describes a most interesting spring in Bavaria in this manner: "The brine spring is about a mile from Kissingen, Bavaria. It has 3 per cent salt, and rises in a bore, 325 Bavarian feet deep, in red sandstone; but it is understood that the water flows at about 200 feet in depth. Its temperature is never less than 65°, the mean temperature of springs near being only 50° to 52°. It discharges carbonic acid gas in volumes almost unexampled, keeping the water in a state resembling turbulent ebullition. The enormous supply of gas has led to its use in gas baths, for which purpose it is carried off by a tube connected with a huge inverted funnel, which rests upon the water. It contains scarcely a trace of nitrogen. It is conducted into chambers properly prepared, and thence into baths, in which it lies by its weight, and is used as water would be. But the most remarkable feature still remains. About five or six times a day, the discharge of gas suddenly stops; in a few seconds the surface of the well is calm. The flow of water, amounting to 40 cu. ft. per minute, also stops or rather becomes negative, for the water recedes in the shaft even when the pumps, commonly used to extract the brine, do not work, and the water subsides during 15 to 20 minutes. It then flows again, the water appearing first, then suddenly the gas, which gradually increases in quantity until after three-quarters of an hour, the shaft is full as at first. This discharge has continued with little variation since the bore was made in 1882. Within a short distance is a bore 554 Bavarian feet deep, which exhibits somewhat similar phenomena."

In 1895, C. G. Rommenhöller established a carbon dioxide works in Herste near Driburg in Westfalen. This was the largest plant built up to that time. The giant well poured forth carbon dioxide at a rate of over

[30] Heusler, *J. Soc. Chem. Ind.*, (abst.) 743 (1885).
[31] Forbes, *Am. J. Sci. and Arts*, 35, 293 (1893).

a ton each hour,[32] enough to supply half of Germany with chemically pure gas (according to the analysis of König it was 99.84 per cent pure). On calm days this giant fountain sent its white froth nearly 200 feet high, from which height it fell down in a fine glistening spray. Stones, the size of the fist, when thrown into the fountain, were hurled by the force of the stream high into the air, with a whistling sound similar to that of a meteor falling to the earth. This well was controlled only after considerable difficulty.

The many natural sources of carbon dioxide in the United States have not proved popular as commercial sources of the gas. The Saratoga Springs in New York, were formerly used industrially. The water from these wells brought carbon dioxide to the surface of the earth under a pressure of 21 pounds per square inch. As the pressure was released on the escape of the water, the gas effervesced and was collected in large iron caps placed over the wells in such a manner that the water could escape from the lower part. A few years ago, the use of this gas was discontinued, and the old factory buildings were removed. It is said, however, that interest is again being shown in the commercial utilization of the gas from these wells. At Manitou, Colorado, natural gas is being compressed for commercial use and it is understood that one or two other sources in this country are being utilized at the present time.

Considerable attention has recently been given to certain other natural sources of carbon dioxide in the United States. A well near Price, Utah, produces carbon dioxide about 98 per cent pure and under a pressure of 760 pounds per square inch. This well is being utilized for making solid carbon dioxide on a small scale. Some other wells in eastern Utah and western Colorado produce carbon dioxide mixed with petroleum under such a pressure that the pipe lines freeze due to the evaporation of the carbon dioxide. These wells are sometimes called "ice cream" wells because of the appearance of the gas oil mixture. Martin[33] describes an interesting well near Tampico, Mexico, which delivered carbon dioxide gas under a pressure of about 1000 pounds per square inch. Some solid carbon dioxide produced from this gas was shipped to the United States.

The question of how carbon dioxide came to exist in the earth and the conditions under which it does exist, makes an interesting subject for speculation. Notwithstanding the experimental work which sheds a certain amount of light on these conditions, we know practically nothing about it at this time. It is quite certain that there are many reactions which produce carbon dioxide in the earth and it is not difficult to assign one or more of these reactions as the cause of the gas in certain regions.

As was previously mentioned igneous rocks, calcium and magnesium carbonates and bituminous shales, when heated give off carbon dioxide. It has been demonstrated that if silica and limestone are put together in boiling water, calcium silicate and carbon dioxide are produced.[34] The acid

[32] Wender, "Die Kohlensäure-Industrie."
[33] Martin, J. W., *Ind. Eng. Chem.*, 23, 256-8 (1931).
[34] Hapke, *Z. kompr. flüss Gase.*, 1, 149 (1898).

produced by the oxidation of metallic sulfides by atmospheric oxygen also will liberate carbon dioxide when acting on metallic carbonates in the earth.[35]

In some cases, the rate of carbon dioxide production must be the same as the rate at which it escapes from the earth. In other cases, however, it is quite evident that the supply comes from some sort of reservoir in the earth's crust. The nature of this reservoir can only be conjectured. We know that many wells deliver carbon dioxide at a rate quite beyond all conception as the direct product of a chemical reaction, and in many cases under a pressure which must be at least equal to the vapor pressure of the liquid. Several other facts lead one to believe that this compound may exist as a liquid in rock pockets of tremendous size. Certain wells, e. g., the well drilled at Driburg, Germany, in 1894, have been observed to expel gas with detonations and the formation of ice in large pieces. Such behavior could readily be accounted for on the assumption that the gas came from the boiling liquid. That liquid carbon dioxide can exist in nature, was demonstrated by Brewster[36] in 1823, who observed the presence of liquid carbon dioxide in mineral cavities. Since that time many investigators have made the same observations.[37]

The Carbon Dioxide Balance in Nature. After observing the stupendous quantities of carbon dioxide that are being added to the atmosphere continually from natural gas sources, the question naturally arises as to the factors which prevent a serious fouling of the atmosphere with this gas. The carbon dioxide in nature represents a dynamic equilibrium, the several factors of which tend to increase or to decrease this substance. These factors which increase the carbon dioxide in the atmosphere are: (1) the evolution of carbon dioxide from springs, gas wells, volcanic vents, etc., (2) the combustion of coal, wood and petroleum, (3) the respiration of lower organisms, plants and animals, (4) the decay of organic matter, (5) certain industrial processes such as lime burning and fermentation. The factors which remove carbon dioxide from the atmosphere are: (1) photosynthesis by plants, (2) $CaCO_3$-forming organisms, (3) chemosynthesis of certain bacteria, (4) the weathering of rocks.

Factors Increasing Carbon Dioxide in the Atmosphere. The evolution of carbon dioxide from wells and springs has already been considered because of its economic aspect. It is now best to consider the other factors which play a part in the equilibrium reactions involving this gas.

The combustion of carbonaceous matter adds carbon dioxide to the atmosphere in prodigious quantities, yet over a period of a year, its percentage increase from this source is really very small. Sievers[38] estimates

[35] Eaton, A., *Am. J. Sci.*, **15**, 237 (1829).

[36] Brewster, David, *Trans. Roy. Soc. (Edinburgh)*, **10**, 1 (1823).

[37] Sorby and Butler, *Proc. Roy. Soc. (London)*, **17**, 299 (1869); Hartley, *J. Chem. Soc.*, **29**, 137 (1876); *ibid.*, **30**, 237 (1876); Schorizer, Rudolph, *Centr. Mineral. Geol.*, **1920**, 143-8.

[38] Sievers, E. G., *Gas Age-Record*, **51**, 757-761 (1923).

that in 1920 about 1.317×10^9 kilograms or 1.4517×10^6 tons of fuel in the form of coal of various types such as anthracite, bituminous and lignite were produced on the earth. The carbon dioxide formed by the combustion of this material, assuming a 70 per cent carbon content, amounts to about 3.38×10^9 kilograms. In spite of the magnitude of this number, the existing carbon dioxide in the atmosphere would be increased only 0.16 per cent by its addition if all the opposing factors ceased to operate for that period. The carbon dioxide produced by the combustion of wood and petroleum would also materially increase this value. The quantity of carbon dioxide produced during one of our great forest fires must be enormous.

The respiration of animals and to a much smaller extent, plants, represents vast amounts of carbon dioxide which is being admitted into the atmosphere continually. A human being expires, on an average, about 900 grams of carbon dioxide daily. On the basis of a population of 1750 million human beings on the earth, this would add about 629 million tons of carbon dioxide to the atmosphere each year, or approximately the same amount as produced by burning 230 million tons of coal. Add to this value the quantity produced by the respiration of all other animals, both in the sea and on the land, and then the comparatively small amount produced by the respiration of plants and one gets an idea of the magnitude of this source of carbon dioxide.

The decay of organic matter is, for the most part, a chemical reaction promoted by microörganisms, carbon dioxide being one of the end products of this action. In every acre of fertile soil there are hundreds of pounds of living organisms present. Algae, fungi, actinomycetes, and bacteria may be considered as plants of microscopic size, while protozoa are microscopic animals. Millions of microörganisms exist in every gram of fertile soil. Leaves, dead plants, and animals all furnish food for these various forms of life and the end of it all, including the living forms themselves, is carbon dioxide and water which return to the air and to the soil where they are ready to go through the cycle again.

Soil air from fertile areas always has a high carbon dioxide concentration. The maximum concentration of this compound was found by Youkov[39] to occur 30 cm. below the surface of the soil. This perhaps has no significance except to indicate the point of maximum life activity. Heat, moisture, nature of the soil, and many other factors affect the situation. Marsh[40] observed the rate of evolution of carbon dioxide from fertile soils to be from 23.7 to 162.4 mg. per 72 hours from a sample of 500 grams of soil. The excellent work of Lundegårdh[41] on carbon dioxide evolution gives us much information regarding the respiration of soils. The respiration of agricultural soils in Sweden, varied from 0.125 grams per sq. m.

[39] Youkov, G. I., *Khoziaistvo*, 7, 37-46; through *Intern. Inst. Agr.* (Rome), *Bull. Agr. Intelligence*, 1911, 510-1.

[40] Marsh, F. W., *Soil Science*, 25, 417-54 (1927).

[41] Lundegårdh, H., *Soil Science*, 23, 417-54 (1927).

per hour for sandy soils low in humus and heavy clay soils to 0.411 grams for loams 10 to 15 per cent humus. Forest soils evolve more carbon dioxide than agricultural lands. Most of the carbon dioxide of the soil is evolved in the surface layer (10 to 15 cm.) and is produced chiefly by microflora. Plant roots also produce a considerable quantity, but the amount produced by simple chemical oxidation is of no importance. A soil covered with oats showed 50 per cent increase in carbon dioxide production over the same soil when bare; but it was shown by subsequent experiments with sterilized and non-sterilized soils that a large percentage of the increase was due to bacteria inhabiting the root surfaces rather than to real root respiration. The carbon dioxide concentration of soil air (C) is a function of the absolute carbon dioxide production (A) and the diffusion velocity. The diffusion coefficient (K) is defined by Lundegårdh as the volume in cubic centimeters of gas which passes through a cylinder 1 sq. cm. on the base by 1 cm. high in one second where the difference in partial pressure is 1 atmos. Since diffusion is the moving force of soil respiration the diffusion value (K) is an important characteristic and can be calculated by means of the equation:

$$K = \frac{(Aa \times 15 \times 100)}{(3600 \times (C - 0.03))} \quad \ldots\ldots\ldots\ldots (1)$$

in which $A\,a$ is the total soil respiration in cc. per hour. In general, the value of K is an index of aeration, since as carbon dioxide diffuses upwards oxygen diffuses downward, and most soils take up the same volume of oxygen as the carbon dioxide evolved. Soil respiration shows a seasonal variation attaining a maximum in August or September and is associated with seasonal variation in bacterial activity.

Lundegårdh found no correlation between respiration of soils and temperature or rainfall but Suprunenko[42] states that light rains increase, while heavy rains decrease, the bacterial activity with a consequent corresponding change in the soil respiration. The difference in respiration of sterile and non-sterile soils was found by Vandecaveye[43] to be very great. A non-sterile soil gave twice as much carbon dioxide as a sterile one. Organic manures increase soil respiration markedly and it is believed that a large part of the fertilizing value of manures is due to this fact.

Factors Decreasing the Carbon Dioxide Concentration of the Atmosphere. Without doubt, the process of photosynthesis is the most important factor concerned with the elimination of carbon dioxide from the atmosphere. This interesting and important subject has already been masterfully treated by Spoehr[44] in his work on "Photosynthesis" and in this discussion only a few of its more practical aspects will be considered.

Photosynthesis is essentially a reducing action in which the oxide of carbon is reduced to carbohydrates with the evolution of oxygen and the

[42] Suprunenko, A., through *Intern. Inst. Agr. (Rome), Bull. Agri. Intelligence*, 1911, 511-2.
[43] Vandecaveye, S. C., *Soil Science*, 16, 389-406 (1923).
[44] Spoehr, H. A., *loc. cit.*

absorption of energy obtained from the rays of the sun. This reaction takes place primarily in the green coloring material in the leaves of growing plants and the tree may, therefore, be regarded as a nature-made photochemical absorption apparatus working on extremely dilute gases. In submerged aquatic plants the carbon dioxide dissolved in the water reaches the interior of the plant by diffusion through the outer walls of the epidermal cells. The higher land plants have special differentiated organs called stomata, through which the gaseous carbon dioxide passes to the chlorophyll-bearing cells. The stomata are minute, mouth-like openings in the surface of the leaf, usually situated on the under side. The number of openings in a single leaf runs to enormous numbers, a medium sunflower leaf containing about 13 million stomata. Some idea of the functioning of these minute openings during the gas transfer can be gained from the calculation of Noll who finds that a tree weighing 5000 kilograms (5.5 tons) must have removed the carbon dioxide from about 12 million cubic meters (15.6 million cubic yards) of air.

Another factor tending to decrease the carbon dioxide in the atmosphere is the action of rocks during the process of weathering. Some years ago, Hunt[45] made the statement, based on a calculation, that the production from orthoclase of a layer of kaolin 500 meters thick and completely enveloping the earth, would consume 21 times the amount of carbon dioxide now present in the atmosphere. Whether or not this estimate has any numerical value, it at least gives some idea of the magnitude of the weathering process. It is difficult, if not impossible, to make a reliable estimate of the actual amount of carbon dioxide removed from the atmosphere each year by these decomposing rocks. A water solution of carbon dioxide may react with silicates to produce carbonates or it may react with carbonates of calcium and magnesium to form bicarbonates. In the former case, the silicates which constitute a large part of igneous rocks, are decomposed into simpler and more stable silicates, forming at the same time, carbonates of the alkaline earths and the alkali metals. In the latter case, the carbon dioxide serves to make the alkaline earth carbonates soluble in water, in which condition, they may be transported considerable distances and again deposited as carbonates with the liberation of the carbon dioxide. Thus bicarbonates formed in the mountains may find themselves finally in the ocean where they are washed by the streams and eventually converted into sediments, shells, or coral reefs. The carbon dioxide used for the formation of bicarbonates is in this way liberated again to the atmosphere, but that forming the original carbonates of calcium and magnesium is permanently lost, unless conditions change in such a way as to promote some of the reactions which are believed to be responsible for carbon dioxide wells and springs. Solution and reprecipitation of these carbonate deposits may take place again and again by the action of carbonic acid.

[45] Hunt, T. Sterry, *Am. J. Sci.* (3), **19**, 349 (1880).

The chemical reactions involved in the process of weathering may be illustrated by the equation given by Chamberlin and Salisbury[46] for the action of carbon dioxide on labradorite, a typical rock-forming mineral. The composition of labradorite is represented by the formula:

$$\left\{\begin{array}{l} CaO.\ Al_2O_3.\ 2\ SiO_2 \\ Na_2O.\ Al_2O_3.\ 6\ SiO_2 \end{array}\right.$$

Assuming the two molecules represented by this formula to be equally abundant, and allowing the whole to be acted upon by water and carbon dioxide, we have $CaO.Na_2O.2\ Al_2O_3.8\ SiO_2+4\ H_2O+2\ CO_2=2(Al_2O_3.2\ SiO_2.2\ H_2O)+4\ SiO_2+CaCO_3+Na_2CO_3$. The silicate produced in this reaction is kaolin. The carbonates of sodium or potassium usually react with other substances and appear as sulfates or chlorides.

[46] Chamberlin, T. C., and Salisbury, R. D., "Geology," Henry Holt and Co., New York (1909).

Chapter III

Physical Properties of Carbon Dioxide

The active interest shown in carbon dioxide for the past few years has been directed very largely towards its chemical and physical properties. This interest, however, is not new, investigators since the beginning of the science of chemistry have been adding more and more data until at present it is exceeding difficult to judiciously select the best and most reliable results from the great mass of data. Therefore, in the following discussion this shifting operation has been only partially done. In many cases practically all of the published data have been recorded and it is left to the reader to select those he considers the most useful.

For the convenience of those desiring data in English engineering units many of the tables given in this chapter in metric units have been calculated to the English system. These tables will be found in the appendix at the end of this volume.

Density of Gaseous Carbon Dioxide.—The early density determinations made with this gas were ratios of its weight to the weight of an equal volume of air, hydrogen, oxygen or nitrogen, all of course, measured under the same conditions of temperature and pressure. The accuracy of these determinations depended upon the refinement of weighing equipment and technique at that time available yet there is a remarkable agreement between these earlier results and values obtained more recently. It is customary at present to report the density of gases in absolute values, i. e., the weight in grams of one liter of the gas measured under standard conditions of temperature and pressure (0° C. and 760 mm. pressure). In Table 4 these earlier values are listed in their chronological order together with the absolute densities calculated from them.

Relative densities of carbon dioxide, referred to nitrogen, at high temperatures have been made by Emich.[1] His values were 1.485 at 1000°; 1.497 at 1500° and 1.527 at 2000° C. With carbon dioxide carefully dried over sulfuric acid he obtained 1.557 at 19° and 1.550 at 1875° C.

The absolute density of carbon dioxide has been determined by other investigators besides those listed above. Dietrich[2] obtained a value of 1.9676; Guye and Printza[3] 1.9768 and Jaquerod and Perrot[4] 1.97677. The value most often used at the present time is 1.9769.[5]

[1] Emich, F., *Monatsh*, **26**, 505 (1905).
[2] Dietrich, E., *Z. anal Chem.* **4**, 142 (1864).
[3] Guye, P. A., and Printza, A., *Compt. rend.*, **141**, 51 (1905).
[4] Jaquerod, A., and Perrot, F. L., *Arch Sciences Genève*, (4) **20**, 206 (1905).
[5] "International Critical Tables," **3**, The McGraw-Hill Book Co., New York.

TABLE 4.—*Showing the Absolute and Relative Densities of Carbon Dioxide as Determined by Various Investigators.*

Air=1	H_2=1	O_2=1	Wt. of 1 liter at S. C.	Mol. vol. at S. C.	Observer
1.5245	.....	.....	1.9708	22.345	Berzelius and Dulong
1.5282	.....	.....	1.9756	22.271	Marchand
.....	.....	1.3822	1.9752	22.276	Marchand
1.52037	.....	.....	1.9656	22.385	Wrede
1.5191	.....	.....	1.9639	22.404	Regnault
.....	22.00	.....	1.9771	22.254	Mohr
1.520	.....	.....	1.9650	22.391	Exner
1.529	.....	.....	1.9767	22.259	Wiedermann
1.529 (at 15°)	.....	.....	1 9767	22.259	Bleekrode
1.52897	.....	.....	1.9767	22.259	Crafts
1.52856	.....	.....	1.9762	22.264	Cooke
.....	21.971	.....	1.9745	22.284	Cooke
1.5287	.....	.....	1.9763	22.263	Leduc
1.52909	.....	.....	1.9768	22.258	Rayleigh
.....	.....	1.3833	1.9767	22.259	Guye
1.530	.....	.....	1.9780	22.245	Strutt
1.50 to 1.52	.....	.....	.....	.....	Drenteln

Note. Calculations were made on the basis of Air=1.2928, Hydrogen=0.08987 and Oxygen=1.4290 grams per liter measured under standard conditions (760 mm. pressure and 0° C.).

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Lord Rayleigh, *Proc. Roy. Soc. (London)* **62**, 204 (1897).
Guye, P. A., *Compt. rend.* **112**, 1257 (1891); **144**, 976, 1360 (1907); *J. chim. phys.* **5**, 203 (1907); *Bull. soc. chim.* (4) **5**, 339 (1909).
Strutt, R. J., *Proc. Roy. Soc. (London)* **68**, 126 (1901).
Drenteln, *Z. physik. chem. Unterricht* **17**, 350 (1904).

The change of density with temperature and pressure variations has been calculated by Parr[6] and the results of these calculations are given in Table 5.

The density of dry saturated carbon dioxide vapor at various temperatures has been the subject for numerous researches. A tabulation of the results of these measurements has been made by Plank and Kuprianoff[7] and is shown here as Table 6. The last column of this table shows the most probable density values.

Density of Liquid Carbon Dioxide. Thilorier[8] was one of the first to attempt specific gravity determinations on liquid carbon dioxide. His

[6] Parr, S. W., *J. Am. Chem Soc.*, **31**, 237 (1909).
[7] Plank, R. and Kuprianoff, J., *Z. ges. Kälte-Ind. Beihefte*, **1**, 1 (1929)
[8] Thilorier, M., *Ann. chim. phys.*, (2) **60**, 427 (1835).

TABLE 5.—*Weight of Carbon Dioxide (According to Parr).*

In milligrams per cubic centimeter. Calculated from 1.976—weight of 1 liter carbon dioxide at 0° temperature, 760 mm. pressure and 41° latitude. Corrected for aqueous vapor and barometer readings on glass scale.

t/mm.	720	722	724	726	728	730	732	734	736	738	740	742	744
10	1.7788	1.7838	1.7888	1.7938	1.7988	1.8038	1.8089	1.8139	1.8189	1.8239	1.8288	1.8338	1.8388
11	1.7706	1.7756	1.7806	1.7856	1.7905	1.7955	1.8005	1.8055	1.8105	1.8155	1.8204	1.8254	1.8304
12	1.7623	1.7673	1.7723	1.7773	1.7822	1.7872	1.7921	1.7971	1.8021	1.8071	1.8120	1.8170	1.8219
13	1.7540	1.7590	1.7639	1.7689	1.7738	1.7788	1.7837	1.7887	1.7936	1.7986	1.8035	1.8085	1.8134
14	1.7457	1.7506	1.7555	1.7605	1.7654	1.7703	1.7752	1.7802	1.7851	1.7901	1.7950	1.7999	1.8048
15	1.7373	1.7422	1.7471	1.7520	1.7569	1.7618	1.7667	1.7717	1.7766	1.7815	1.7864	1.7913	1.7962
16	1.7288	1.7337	1.7386	1.7435	1.7484	1.7533	1.7582	1.7631	1.7680	1.7729	1.7778	1.7827	1.7875
17	1.7203	1.7252	1.7301	1.7349	1.7398	1.7447	1.7496	1.7545	1.7593	1.7642	1.7691	1.7740	1.7788
18	1.7117	1.7166	1.7215	1.7263	1.7312	1.7360	1.7409	1.7458	1.7506	1.7555	1.7603	1.7652	1.7700
19	1.7031	1.7079	1.7128	1.7176	1.7225	1.7273	1.7321	1.7370	1.7418	1.7467	1.7515	1.7564	1.7612
20	1.6944	1.6992	1.7041	1.7089	1.7137	1.7185	1.7233	1.7282	1.7330	1.7378	1.7426	1.7475	1.7523
21	1.6856	1.6904	1.6953	1.7001	1.7049	1.7097	1.7145	1.7193	1.7241	1.7289	1.7337	1.7385	1.7433
22	1.6767	1.6815	1.6863	1.6911	1.6959	1.7007	1.7055	1.7103	1.7151	1.7199	1.7247	1.7295	1.7342
23	1.6678	1.6726	1.6773	1.6821	1.6869	1.6917	1.6964	1.7012	1.7060	1.7107	1.7155	1.7203	1.7250
24	1.6587	1.6635	1.6682	1.6730	1.6778	1.6825	1.6872	1.6920	1.6968	1.7015	1.7063	1.7111	1.7158
25	1.6495	1.6543	1.6590	1.6638	1.6685	1.6732	1.6779	1.6827	1.6875	1.6922	1.6969	1.7017	1.7064
26	1.6403	1.6450	1.6497	1.6544	1.6591	1.6638	1.6685	1.6733	1.6780	1.6827	1.6874	1.6922	1.6969
27	1.6309	1.6356	1.6403	1.6450	1.6497	1.6544	1.6591	1.6638	1.6685	1.6732	1.6778	1.6826	1.6873
28	1.6213	1.6260	1.6307	1.6354	1.6401	1.6448	1.6494	1.6541	1.6588	1.6635	1.6681	1.6729	1.6776
29	1.6116	1.6163	1.6210	1.6256	1.6303	1.6350	1.6396	1.6443	1.6490	1.6537	1.6583	1.6630	1.6677
30	1.6018	1.6065	1.6111	1.6157	1.6204	1.6251	1.6297	1.6343	1.6390	1.6437	1.6483	1.6530	1.6577
								1.					

t/mm.	746	748	750	752	754	756	758	760	762	764	766	768	770
10	1.8439	1.8489	1.8539	1.8589	1.8639	1.8689	1.8739	1.8789	1.8839	1.8890	1.8940	1.8990	1.9040
11	1.8354	1.8404	1.8454	1.8504	1.8554	1.8603	1.8653	1.8703	1.8753	1.8803	1.8853	1.8903	1.8953
12	1.8269	1.8319	1.8368	1.8418	1.8468	1.8517	1.8567	1.8617	1.8667	1.8716	1.8766	1.8816	1.8865
13	1.8184	1.8233	1.8282	1.8332	1.8382	1.8431	1.8481	1.8530	1.8580	1.8629	1.8679	1.8728	1.8777
14	1.8098	1.8147	1.8196	1.8246	1.8295	1.8344	1.8392	1.8443	1.8429	1.8541	1.8591	1.8640	1.8689
15	1.8011	1.8060	1.8109	1.8159	1.8208	1.8257	1.8306	1.8355	1.8404	1.8453	1.8503	1.8552	1.8601
16	1.7924	1.7973	1.8022	1.8072	1.8120	1.8169	1.8218	1.8267	1.8316	1.8365	1.8414	1.8463	1.8512
17	1.7837	1.7886	1.7934	1.7984	1.8032	1.8081	1.8130	1.8178	1.8227	1.8276	1.8325	1.8374	1.8422
18	1.7749	1.7798	1.7846	1.7895	1.7944	1.7992	1.8041	1.8089	1.8138	1.8187	1.8235	1.8284	1.8332
19	1.7661	1.7709	1.7757	1.7806	1.7854	1.7902	1.7951	1.7999	1.8048	1.8096	1.8144	1.8193	1.8241
20	1.7571	1.7619	1.7667	1.7716	1.7764	1.7812	1.7861	1.7909	1.7957	1.8005	1.8053	1.8102	1.8150
21	1.7481	1.7529	1.7577	1.7625	1.7673	1.7721	1.7770	1.7818	1.7866	1.7914	1.7962	1.8010	1.8058
22	1.7390	1.7438	1.7486	1.7534	1.7582	1.7630	1.7678	1.7725	1.7773	1.7821	1.7869	1.7917	1.7965
23	1.7298	1.7346	1.7392	1.7441	1.7489	1.7537	1.7585	1.7632	1.7680	1.7728	1.7776	1.7823	1.7871
24	1.7206	1.7253	1.7301	1.7348	1.7396	1.7443	1.7491	1.7538	1.7586	1.7633	1.7681	1.7728	1.7776
25	1.7112	1.7159	1.7206	1.7254	1.7301	1.7348	1.7396	1.7443	1.7490	1.7538	1.7585	1.7633	1.7680
26	1.7016	1.7063	1.7110	1.7158	1.7205	1.7252	1.7300	1.7347	1.7394	1.7441	1.7488	1.7535	1.7582
27	1.6920	1.6967	1.7014	1.7061	1.7108	1.7155	1.7202	1.7249	1.7296	1.7343	1.7390	1.7437	1.7484
28	1.6822	1.6869	1.6916	1.6963	1.7010	1.7057	1.7104	1.7150	1.7197	1.7244	1.7291	1.7338	1.7385
29	1.6723	1.6770	1.6817	1.6864	1.6910	1.6957	1.7004	1.7050	1.7097	1.7144	1.7191	1.7237	1.7284
30	1.6623	1.6670	1.6716	1.6763	1.6809	1.6856	1.6903	1.6949	1.6996	1.7042	1.7089	1.7135	1.7182

TABLE 6.—*Density of Dry Saturated Vapor of CO_2 at Various Temperatures.*
(Data in gm./cc.)

	Experimental values			Calculated values					
Temp. °C.	Cailletet and Mathias	Amagat	Lowry and Erickson	Jenkin and Pye	Mollier	Langen	Eichelberg	Keyes and Kenney	Plank and Kuprianoff*
31	0.396	0.392	0.468					0.460	0.392
30	.354	.334	.338		.338	.333	.338	.337	.334
25	.254	.240	.237		.239	.239	.239	.239	.240
20	.203	.190	.191	.196	.191	.194	.191	.188	.190
15	.167	.158	.159		.159	.160	.159	.152	.158
10	.139	.133	.135	.138	.133	.134	.133	.132	.133
5	.117	.114	.115		.113	.113	.113	.109	.114
0	.099	.096	.099	.100	.096	.096	.098	.096	.096
− 5	.085		.085		.082	.082	.083	.082	.082
−10				.073	.070	.072	.070		.070
−15					.060	.061	.060		.060
−20				.053	.051	.052	.051		.051
−25					.044	.044	.044		.044
−30				.038	.037	.037	.037		.037
−35						.031	.031		.031
−40				.026		.026	.026		.026
−45						.022	.022		.022
−50				.018		.018	.018		.018
−55							.015		.015
−56.6									.014

* Amagats data to 0° C.

values were as follows: +30° = 0.60, 0° = 0.83 and −20° = 0.90. D'Andreef[9] made a number of determinations between −10.82° and 25.38° C. and developed an equation to represent the change of specific gravity with temperature. His results do not agree at all with those obtained by later investigators and at present are considered to have but little value. A few of these determinations are as follows:

Temp. °C.	−10.82	−5.02	−0.84	+4.22	+10.08	+14.79	+20.85	+25.38
Observed	0.9985	0.9712	0.9509	0.9265	0.8938	0.8657	0.8209	0.7790
Calcd.	0.9989	0.9708	0.9510	0.9262	0.8939	0.8652	0.8201	0.7801

The calculated values were obtained from the equation: $D = 0.94695 - 0.0048041\,t - 0.00002936\,t^2 - 0.0000019409\,t^3$. In 1886 Cailletet and Mathias made a series of determinations on the densities of various liquefied gases and their saturated vapors. While they extended the measurements down to −23° C. for carbon dioxide their results are rather erratic and do not serve to plot a smooth curve. They obtained the following results:

Temp. °C. ...	−23	−5	+0.5	+10.1	+15.7	+19.7	+25.0	+30.0	
D of vapor...	0.057	0.085	0.0983	0.141	0.171	0.201	0.254	0.354	
Temp. °C. ...	−34	−25	−11.5	−1.6	+1.3	+6.8	+11.0	+15.9	+22.2
D of liquid..	1.057	1.016	0.966	0.910	0.907	0.868	0.840	0.788	0.726

[9] D'Andreef, M. E., *Ann. chim. phys.*, (3) **56**, 317 (1859).

The classical researches of Amagat[10] have given us the most widely used values above 0° C. and those of Behn[11] have extended the data for the liquid density down to −60° C. Table 7 gives the results obtained by Amagat for both liquid and its saturated vapor. Behn's values for the liquid were as follows:

Temp. °C.	+30	+20	+10	0	−10	−20	−30	−40	−50	−60
Density	0.598	0.772	0.860	0.925	0.981	1.031	1.075	1.116	1.154	1.191

TABLE 7.—*Showing the Density of Liquid Carbon Dioxide and its Saturated Vapor Together with the Vapor Pressure from 0° to its Critical Temperature.*

(Data by Amagat)

Temp. ° C.	Density of liquid gm./cc.	Density of vapor gm./cc.	Vapor pressure atmos.
0	0.914	0.096	34.3
1	0.910	0.099	35.2
2	0.906	0.103	36.1
3	0.900	0.106	37.0
4	0.894	0.110	38.0
5	0.888	0.114	39.0
6	0.882	0.117	40.0
7	0.876	0.121	41.0
8	0.869	0.125	42.0
9	0.863	0.129	43.1
10	0.856	0.133	44.2
11	0.848	0.137	45.3
12	0.841	0.142	46.4
13	0.831	0.147	47.5
14	0.822	0.152	48.7
15	0.814	0.158	50.0
16	0.804	0.164	51.2
17	0.796	0.170	52.4
18	0.786	0.176	53.8
19	0.776	0.183	55.0
20	0.766	0.190	56.3
21	0.755	0.199	57.6
22	0.743	0.208	59.0
23	0.731	0.217	60.4
24	0.717	0.228	61.8
25	0.703	0.240	63.3
26	0.688	0.252	64.7
27	0.671	0.266	66.2
28	0.653	0.282	67.7
29	0.630	0.303	69.2
30	0.598	0.334	70.7
30.5	0.574	0.356	71.5
31.0	0.536	0.392	72.3
31.25	0.497	0.422	72.8
31.35 (Critical data)	0.464	0.464	72.9

[10] Amagat, E. H., *Compt. rend.*, **114**, 1093 (1892).
[11] Behn, U., *Ann. physik.* (4), **3**, 733 (1900).

In 1920 Jenkin[12] published the following data for the density of liquid carbon dioxide:

Temp. °C.	+25	20	15	10	5	0
Density	0.717	0.761	0.819	0.861	0.894	0.925

Lowry and Erickson[13] recently made some very careful determinations of the densities of coëxisting liquid and gaseous carbon dioxide. Their values are:

Density of Liquid Carbon Dioxide

Temp. °C. ..	+31	+30	+25	+20	+15	+10	+5	0	−5
Density	0.4683	0.6016	0.7165	0.7784	0.8236	0.8626	0.8966	0.9273	0.9556

Density of Gaseous Carbon Dioxide

Temp. °C. ..	+31	+30	+25	+20	+15	+10	+5	0	−5
Density	0.4683	0.3380	0.2375	0.1910	0.1594	0.1350	0.1154	0.0993	0.0854

Values calculated from the equations

$$D_l = 0.4683 + 0.001442(t_k - t) + 0.1318\sqrt[3]{(t_k - t)} \quad \ldots\ldots\ldots (2)$$

$$D_g = 0.4683 + 0.001442(t_k - t) - 0.1318\sqrt[3]{(t_k - t)} \quad \ldots\ldots\ldots (3)$$

agree very well with the above data. It will be observed that according to the data of these investigators the critical density of carbon dioxide is 0.4683.

Density of Solid Carbon Dioxide. Solid carbon dioxide is usually made in the form of very fine crystals resembling snow and for that reason is called carbon dioxide snow. The density of this material depends upon the method of its production and upon the pressure to which it is subjected. This compound can be frozen in the form of a transparent, glass-like solid and in this condition has its maximum density at any one temperature. Landolt[14] found values for the compressed snow from 1.188 to 1.199. Bleekrode[15] obtained 1.3 to 1.6 and Schwalbe[16] 1.19. Behn[17] sublimed carbon dioxide under normal pressure into a space cooled below −79° C. and the gas condensed slowly into a transparent mass. Some of these masses weighed from 30 to 50 grams and had a density of 1.56. In a series of determinations carried out with slightly greater precision he obtained an average of 1.53. Dewar[18] obtained 1.6267 at −188.8° and

[12] Jenkin, C. F., *Proc. Roy. Soc. (London)*, **98**, 170 (1920).
[13] Lowry, H. H., and Erickson, W. R., *J. Am. Chem. Soc.*, **49**, 2729-2734 (1927).
[14] Landolt, H., *Ber.*, **17**, 309 (1884).
[15] Bleekrode, L., *Proc. Roy. Soc. (London)*, **37**, 339 (1884).
[16] Schwalbe, B., *Z. physik. chem. Unterricht.* **9**, 1 (1896).
[17] Behn, U., *Ann. Physik.* (4), **3**, 733 (1900).
[18] Dewar, J., *Chem. News*, **85**, 277, 289 (1902); *ibid.*, **91**, 216 (1905).

1.53 at the boiling point. Recent determinations made by Maass and Barnes[19] cover a considerable temperature range. Their values are:

Temp. °C.	−56.6	−60	−65	−70	−75	−80	−85	−90
Density kg./l.	1.512	1.522	1.535	1.546	1.557	1.566	1.575	1.582
Density lbs./cu. ft.	94.39	95.01	95.83	96.51	97.20	97.76	98.32	98.76

Temp. °C.	−95	−100	−110	−120	−130	−183
Density kg./l.	1.589	1.595	1.606	1.616	1.625	1.669
Density lbs./cu. ft.	99.20	99.57	100.2	100.9	101.4	104.2

The current practice of making solid carbon dioxide for the trade is to compress the snow or to cause the crystals of solid to freeze together by the expansion of liquid at the triple point or to combine these. Kuprianoff[20] conducted an exhaustive research under conditions similar to these in which the density was determined as a function of the pressure and time of pressing. Because his data are easily applied to the practical operation of solid CO_2 formation his results are considered in a later chapter (cf. page 209).

Molecular Weight. It is of interest to note that Berthelot[21] as early as 1898 obtained a value for the molecular weight of carbon dioxide which is identical with the formula weight accepted at present. This was obtained by calculation from the relative density of 1.38324, referred to oxygen, and on the basis of oxygen being 32. Lord Rayleigh[22] working at 0° C. and 760 mm. pressure obtained a value of 44.268 and at low pressures a value of 44.014. Jacquerod and Perrot[23] obtained 43.992 at 1067° C. and Lowenstein[24] while determining the percentage dissociation at higher temperatures found 43.8 at 1350° C. The molecular weight of 44.004 recently obtained by Cooper and Maass[25] is without doubt the most reliable on record.

Molecular Volume. From the accepted formula weight of 44.0 and the absolute density of 1.9760 (according to Parr) one calculates the volume occupied by 44 grams of carbon dioxide gas at 0° C. and 760 mm. pressure to be 22.267 liters. Bridgeman considers 22.2613 liters to be the most likely value for this constant.

Molecular Diameter. Jeans[26] has calculated the molecular diameter of carbon dioxide by four different methods with the following results:

From viscosity measurements	3.47×10^{-8} cm.
From conductivity of heat	3.58×10^{-8} cm.
From coefficient of diffusion	3.27×10^{-8} cm.
From deviation from Boyle's law	3.00×10^{-8} cm.

[19] Maass, O., and Barnes, W. H., *Proc. Roy. Soc. (London)*, **A 111**, 224 (1926).
[20] Kuprianoff, J., "Ueber die Herstellung von fester Kohlensaure," Berlin (1931).
[21] Berthelot, D., *Compt. rend.*, **126**, 1415 (1898).
[22] Lord Rayleigh, *Proc. Roy. Soc. (London)*, **62**, 204 (1898).
[23] Jacquerod, A., and Perrot, F. L., *Ann chim. phys.*, **140**, 1542 (1905).
[24] Lowenstein, L., *Z. physik. Chem.*, **54**, 707 (1906).
[25] Cooper, D. LeB. and Maass, O., *Can. J. Research*, **4**, 283-98 (1931).
[26] Jeans, J. H., *Phil. Mag.*, (6) **8**, 692 (1904).

Giving double weight to the viscosity determinations he obtained a mean value of 3.36×10^{-8} cm. Robinson[27] by measurement of the absorption of cathode rays by carbon dioxide calculates a value of 3.44×10^{-8} cm. while Hasse and Cook[28] from viscosity data recently obtained a value of 3.55×10^{-8} cm.

Molecular Velocity. Blaserna[29] calculated the velocity of carbon dioxide molecules at various pressures and temperatures. Some of his values were as follows where V is the velocity in meters per second:

Pressure cm. of Hg..	0	76	100	500	1000	1500	2000
V at 3.3°.....	393.3	392.1	391.8	385.0	374.5	362.9	350.4
V at 100°.....	459.7	459.2	459.0	456.4	452.8	449.4	446.2

Mean Free Path. This value as calculated by Jeans[30] is 4.0×10^{-6} cm.

Velocity of Sound in Carbon Dioxide. Buckendahl[31] gives the following values for the velocity of sound in carbon dioxide:

Temp. °C.	0	100	300	500	670	945	1080
Meters/sec.	258.04	301.54	373.74	434.06	503.28	543.29	572.45

Kneser[32] found that the velocity of sound in carbon dioxide increases with the frequency in the range from 0.5×10^5 to 3.0×10^5 cycles per second. Above the frequency of 3×10^5 cycles the velocity is again constant at the value of 268.2 meters per second at ordinary temperature.

Viscosity. The resistance to flow of carbon dioxide has been determined by many different methods. Those most generally used are: (1) time required for a certain quantity of gas to flow through a small orifice, (2) the oil drop method, and (3) a method based on the deflection of a stationary cylinder inside a whirling one. Viscosity measurements may be expressed in relative units where air is taken as the standard of measurement or in C.G.S. units which are called "poise" and usually designated as η. Some of the relative values obtained by various investigators at a pressure of 760 mm. are as follows:

Observer	Value	Reference
Kundt, A. and Warburg, E.	0.806	*Wied. Ann.*, **17**, 390 (1882).
Graham, T.	.807	*Phil. Trans.*, **136**, 573 (1846).
Maxwell, J. C.	.859	*Phil. Trans.*, **156**, 249 (1866).
Crookes, W.	.9208	*Proc. Roy. Soc. (London)*, **31**, 446 (1881).
Hofsäss, M.	.840	*J. Gasbel*, **62**, 776-7 (1919).

[27] Robinson, J., *Proc. Univ. Durham Phil. Soc.*, **3**, Pt. 4, 195-200.

[28] Hasse, H. R., and Cook, W. R., *Phil. Mag.*, (7) **3**, 977-90 (1927).

[29] Blaserna, P., *Compt. rend.*, **69**, 134 (1869).

[30] Jeans, J. H., "The Dynamical Theory of Gases," Cambridge (1916).

[31] Buckendahl, O., "Ueber Schallgeschwindigkeit und Verhaltnis der spezifischen Warmen von Kohlensaure und Stickstoff bei gewohnlichen und hohen Temperaturen," Heidelberg (1906).

[32] Kneser, H. O., *Physik. Z*, **32**, 179 (1931).

Table 8 gives values of η obtained by various investigators at 760 mm. and the temperature indicated:

TABLE 8.—*Values of* η *Obtained by Various Investigators.*

Temp. °C.	$\eta \times 10^4$	Observer	Reference
0	1.64	Meyer, O. E.	"Die kinetische Theorie der Gase," Breslau (1877).
0	1.383	Wüller, A.	*Wied. Ann.*, 4, 321 (1878).
0	1.366 (CO_2 and N_2O)	Smith, C. J.	*Proc. Phys. Soc.* (*London*), 34, 155-64 (1922).
0	1.382	Klemenc, A. and Remi, W.	*Monatsh*, 44, 307 (1924).
15	1.441 (CO_2 and N_2O)	Smith, C. J.	*Proc. Phys. Soc.* (*London*), 34, 155-64 (1922).
23	1.490	Lasalle, L. J.	*Phys. Rev.*, (2) 17, 354 (1921).
23	1.471	Ishida, T.	*Phys. Rev.*, (2) 21, 550 (1923).
23	1.478	Eglin, J. M.	*Phys. Rev.*, 22, 161-70 (1923).
23	1.472	Van Dyke	*Phys. Rev.*, 21, 250 (1923).
100	1.859	Wüller, A.	*Wied. Ann.*, 4, 321 (1878).
100	1.845 (CO_2 and N_2O)	Smith, C. J.	*Proc. Phys. Soc.* (*London*), 34, 155-64 (1922).

The change of viscosity with a change in temperature is expressed with a fair degree of accuracy by the equation of Sutherland,[33] which may be written

$$\eta = \eta_0 \frac{T_0 + C}{T + C} \left(\frac{T}{T_0} \right)^x \quad \ldots\ldots\ldots\ldots \quad (4)$$

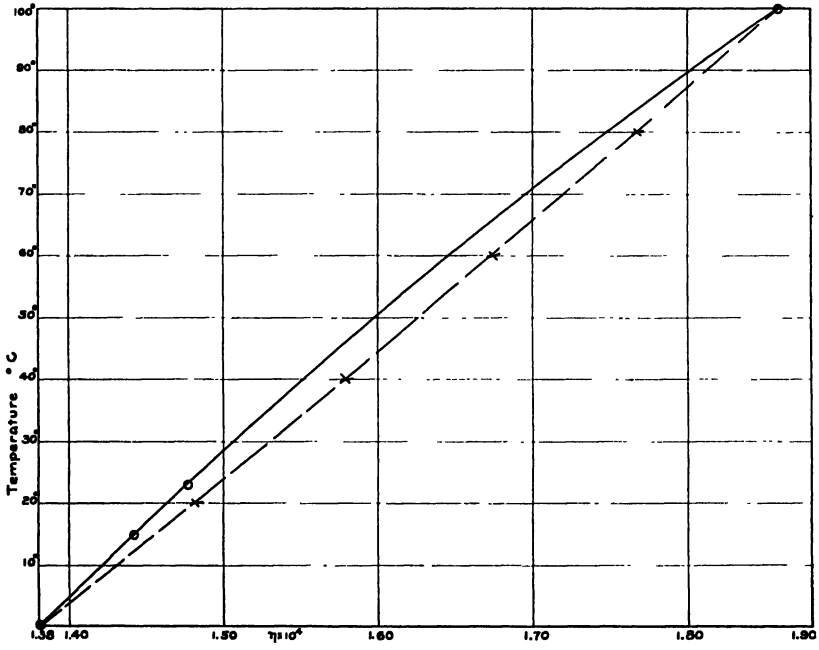

FIGURE 1. Viscosity Curve of Carbon Dioxide.

[33] Sutherland, W., *Phil. Mag.*, (5) 36, 507 (1893).

where η is the viscosity coefficient at the absolute temperature T and η_0 is the coefficient at absolute temperature T_0 while C is a constant. The value of C for carbon dioxide has been reported as 277 by Sutherland, 239.7 by Breitenbach[34] and 263.4 by Klemenc and Remi.

Figure 1 shows a curve drawn with the most probable values of η thus far reported between 0° and 100° C. Unfortunately the number of determinations is very limited, in fact hardly sufficient to determine the course

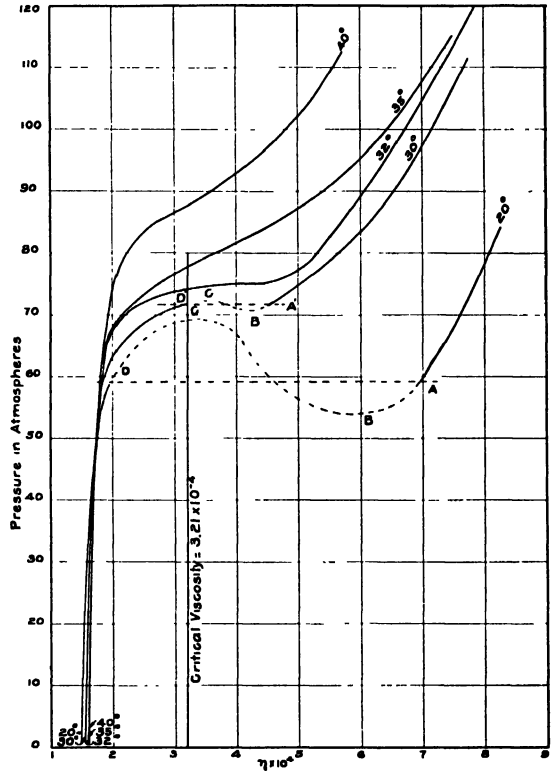

FIGURE 2.

Showing the Change of Viscosity of Carbon Dioxide with a Change of Pressure. (Data by Phillips)

of the viscosity curve. Values for η obtained by calculation with Sutherland's equation, using 263.4 for the value of C, are also plotted and the curve represented by the dotted line. It is rather interesting to note that the use of any of the other values for C, listed above, improves the agreement between these curves but slightly.

The change in viscosity of carbon dioxide with a change in pressure has been studied at several different temperatures by Phillips.[35] His results are tabulated in Table 9 and the curves constructed from these data are shown in Figure 2. It is of interest to note that in Figure 2 the curves

[34] Breitenbach, P., *Ann. Physik.*, (4) 5, 166 (1901).

[35] Phillips, P., *Proc. Roy. Soc. (London)*, 87 A, 48 (1912).

TABLE 9.—*Showing the Change of Viscosity of Carbon Dioxide with a Change in Pressure.*

(Data from Phillips)

P atmos.	Viscosity $\eta \times 10^4$ poise	Density	P atmos.	Viscosity $\eta \times 10^4$ poise	Density
20° C.			30° C.		
83	8.23	0.835	110.5	7.70	0.795
72	7.71	.812	104	7.33	.781
59	6.97	.768	96	6.93	.760
56	1.86	.190	90	6.43	.743
50	1.77	.145	82	5.92	.716
40	1.66	.100	80	5.65	.706
20	1.56	.036	76	5.29	.680
1	1.48	.00183	74	4.95	.664
			73	4.78	.653
			72	4.58	.635
			70	2.29	.287
			60	1.87	.177
			40	1.68	.092
			20	1.59	.0354
			1	1.53	.00177
32° C.			35° C.		
120	7.88	0.790	114.5	6.93	0.755
112	7.41	0.777	109	6.60	.741
104	6.95	.760	96	5.86	.696
93	6.27	.729	88	5.11	.653
87	5.86	.700	85	4.56	.626
84	5.60	.682	80	3.61	.494
80	5.28	.655	75	2.37	.289
76	4.88	.597	70	2.14	.227
75	4.06	.555	60	1.78	.163
74	2.54	.360	40	1.74	.085
70	2.14	.255	20	1.63	.0348
60	1.87	.170	1	1.56	.00174
40	1.75	.090			
20	1.62	.0352			
1	1.55	.00176			
40° C.					
112	5.71	0.699			
108	5.40	.682			
100	4.83	.636			
94	4.14	.582			
85	2.69	.385			
80	2.18	.291			
70	2.00	.204			
60	1.87	.153			
40	1.76	.083			
23.8	1.69	.0408			
1.	1.57	.00173			

cross before the gas is liquefied which indicates that the substance begins to act like a viscous liquid before condensation takes place. The portion of the curves AB and $A'B'$ indicated with dotted lines represent the viscosity of a superheated liquid and the part represented by CD and $C'D'$ represents the viscosity of a supercooled vapor. The critical viscosity is 3.21×10^{-4} and the critical density 0.464.

Coefficient of Diffusion. The Stefan-Maxwell[36] basic differential equation for the diffusion of one gas A into another B is

$$R_A = \frac{-D \ dp_A}{p_B \ dz} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

wherein p_A and p_B are the partial pressure (or mole fractions) of gas A and gas B respectively, z is a length measured in the direction of diffusion, R_A is the "current density" or net rate of diffusion of gas A per unit area, and D is the "diffusivity" or specific diffusion coefficient for the gas system which is substantially independent of the relative concentration of the components. Obviously, the net units of D must depend on those chosen for R_A. Thus if R_A is expressed in gram moles per sec. per sq. cm., D must be expressed in gram moles per sec. per cm., the units for p being immaterial because of the ratio "dp_A/p_B."

The variations of D with temperature and pressure changes may be expressed by the Loschmidt-von Obermayer[37] equation which one may write in the following form

$$D = D_0 \left(\frac{T}{T_0} \right)^m \frac{p_0}{p} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

In this equation D is the coefficient of diffusion at absolute temperature T and pressure p while D_0 is the value of D at T_0 ($=273° K$) and p_0 ($=1$ atmos.). m is a constant having a numerical value which may be taken as 1.75 or 2.00 depending on the nature of the gases involved. The values of D_0 for carbon dioxide and the gases indicated are as follows:

Gas	$D_0 \left(\frac{\text{cm.}^2}{\text{sec.}} \right)$	m	Observers
Hydrogen	0.550	1.75	Loschmidt, von Obermayer and Schmidt.
Carbon monoxide	.137	1.75	Loschmidt, von Obermayer.
Oxygen	.139	2.00	Loschmidt, von Obermayer.
Nitrous oxide	.096	2.00	Loschmidt, von Obermayer.
Air	.138	2.00	Loschmidt, von Obermayer and Waitz.
Methane	.156	2.00	Loschmidt.

The coefficient of diffusion of bromine in carbon dioxide has been measured by Mackenzie and Melville,[38] and a very recent set of calculations

[36] Stefan, J., *Sitzber Akad. Wiss. Uren*, **65**, and **74**, 161 (1879); Maxwell, J. C., *Phil. Mag.*, (4) **35**, 199 (1868); *Phil. Trans.*, **157**, 49 (1867); *Sci. Pap.*, **2**, 26.

[37] Loschmidt, J., *Sitzber. Akad. Wiss. Wien.*, **61**, 367 (1870); *ibid.*, **62**, 468 (1870); von Obermayer, A., *ibid.*, **81**, 1102 (1880); *ibid.*, **85**, 147, 748 (1882); *ibid.*, **87**, 188 (1883).

[38] Mackenzie, J. E., and Melville, H. W., *Proc. Roy. Soc. (Edinburgh)*, **52**, 337-44 (1932).

of diffusional coefficients for several gases and carbon dioxide have been made by Roth.[39] This last investigator points out that the diffusion velocity is not exactly inversely proportional to the square root of the densities as is stated in Graham's law. If this were so the expression $kM_1 \times M_2$, in which M_1 and M_2 are molecular weights of the gases, would be constant. Actually, however, the values for this expression for the mixing of carbon dioxide and air, hydrogen, carbon monoxide, methane and water are: 5.05, 5.10, 4.62, 3.87 and 3.72 respectively. Roth developed the following expression for calculating the content, g_1, of one gas in another as a function of time:

$$g_1 = g_{2a} + \frac{(g_{1a} - g_{2a}) \times 1 + \frac{v_1}{v_2} \times e^x}{\frac{v_1}{v_2}} + l$$

the exponent x is equal to $-\frac{kzq}{l} \times \frac{1}{v_1} + \frac{1}{v_2}$.

In this equation g_{1a} and g_{2a} are the initial contents, v_1 and v_2 the respective volumes, z the time in seconds, q the section of gas considered and k a factor. The values for k in several gas mixtures are as follows: CO_2-air, 0.142; CO_2-hydrogen, 0.544; CO_2-carbon monoxide, 0.131; CO_2-methane, 0.146; and CO_2-water vapor, 0.132.

Diffusion Through Solids. The transference of gases through solid partitions should be essentially the same as simple diffusion through a porous plate, provided that these rates are not complicated by adsorption or solution of the gas in the solid material. In such simple systems the rates of penetration are approximately inversely proportional to the viscosities of the gases. The phenomenon of simple diffusion through porous material has been investigated by Graham and also by Matteucci,[40] who studied the rate of diffusion of carbon dioxide through dry plaster of Paris and by Roscoe[41] who determined the rate of passage of carbon dioxide through bricks. The rate of diffusion of carbon dioxide through soil has been studied by Hannen.[42] While this is not a case of simple diffusion, due to the many other factors which must be considered, it is nevertheless of considerable importance, especially from the point of view of plant food.

The penetration of rubber by various gases, especially carbon dioxide and hydrogen has received considerable attention from research workers. As pointed out by Graham[43] the relative rates of penetration of rubber by different gases bears no relation to their densities nor to their viscosities.

[39] Roth, Walter, *Arch Eisenhüttenw.*, **8**, 401-3 (1935).

[40] Graham, T., *Phil. Mag.*, (4) **26**, 409 (1863); *ibid.*, (4) **32**, 401, 503 (1866); *Proc. Roy. Soc. (London)*, **12**, 611 (1863); *J. Chem. Soc.*, **20**, 235 (1867). Matteucci, C., *Arch. Sci. Genève*, (2) **18**, 103 (1863); *Bull. soc. chim.*, (1) **5**, 546 (1863); *Compt. rend.*, **57**, 251 (1863).

[41] Roscoe, H. S., *J. Chem. Soc.*, **10**, 251 (1857).

[42] Hannen, F., *Biedermann's Zentr.*, **22**, 74 (1893).

[43] Graham, T., *loc. cit.*

He postulated that the penetration mechanism consisted in the solution of the gas on one side of the rubber, with a subsequent diffusion of the dissolved gas through the sheet and vaporization on the other side. This explanation is pretty well accepted at present.

Edwards and Pickering[44] in a carefully planned series of experiments determined the permeability of rubber to carbon dioxide and to other gases. They were able to show that for any one gas the rate of penetration through

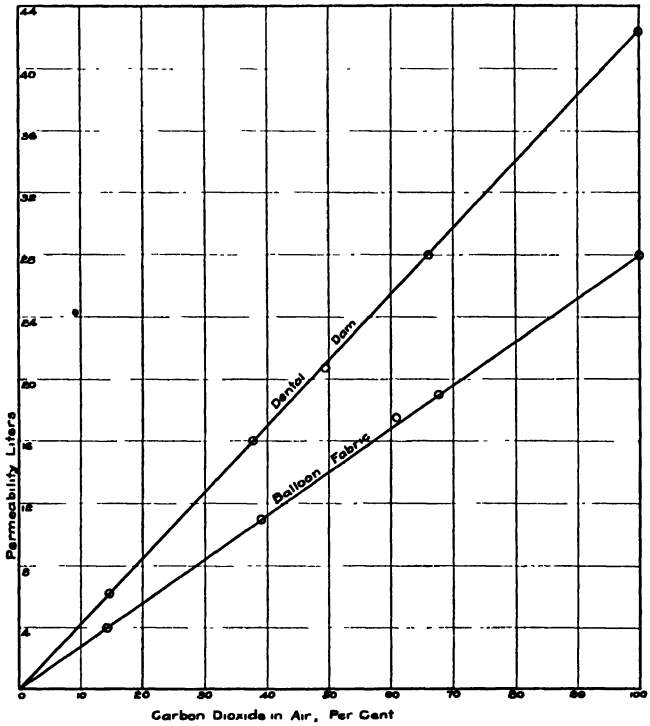

FIGURE 3. Relation Between Permeability and Partial Pressure of Carbon Dioxide.

(According to Edwards and Pickering)

a given sample of rubber is directly proportional to the partial pressure difference and increases rapidly with temperature. In Figure 3 the diffusion curves of carbon dioxide through a sample of rubber and a piece of balloon fabric have been plotted and Figure 4 shows how the rate of diffusion changes with the temperature for carbon dioxide, hydrogen and helium.

The effect of solubility on penetrability has been studied by Venable and Fuwa.[45] They found that the carbon dioxide held by rubber formed a true solution and the amount of gas thus held, within the limits investi-

[44] Edwards, J. P., and Pickering, S. F., *Chem. Met. Eng.*, **23**, 17-21, 71-75 (1920).

[45] Venable, C. S., and Fuwa, T., *Ind. Eng. Chem.*, **14**, 139-142 (1922).

gated, was directly proportional to the pressure and was unaffected by the degree of vulcanization or the presence of compounding ingredients. It was also found that the solubility of carbon dioxide in rubber decreased rapidly with a rise of temperature. This change is clearly shown by means

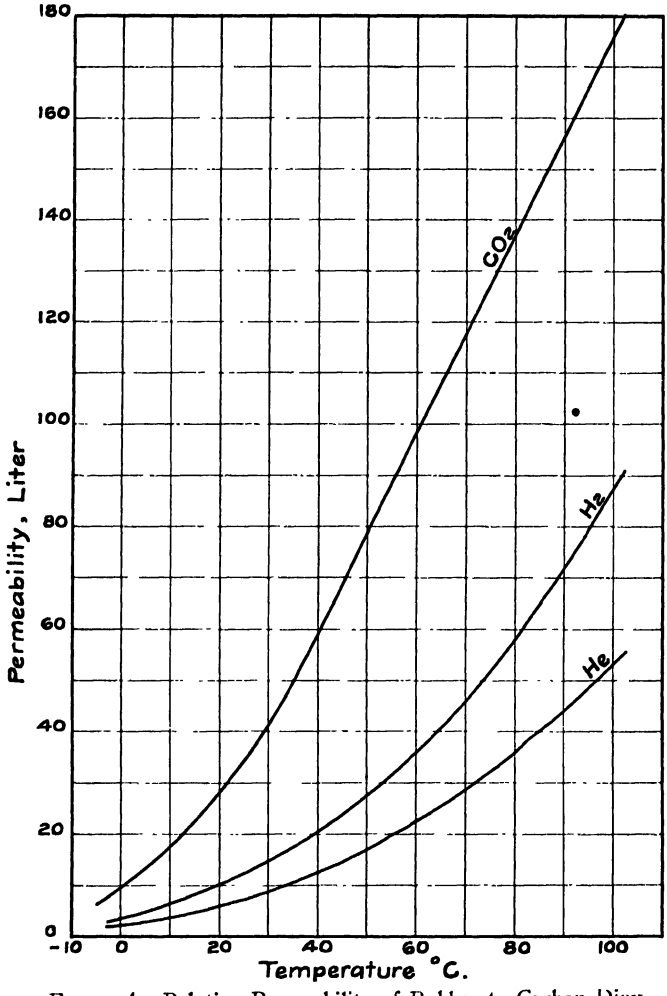

FIGURE 4. Relative Permeability of Rubber to Carbon Dioxide, Hydrogen and Helium at Various Temperatures.

(According to Edwards and Pickering)

of the curve in Figure 5 and likewise the relation between solubility and pressure is indicated in Figure 6.

Steinitzer[46] carried out experiments to determine the action of carbon dioxide when used for inflating pneumatic tires. He reported a decrease

[46] Steinitzer, F., *Gummi-Ztg.*, **26**, 1626-8.

in the tensile strength of the sample and a tendency for it to become tacky. Yammamoto[47] also made solubility measurements of carbon dioxide in rubber. The specimens of tubing he used were cut into bits, dried and tested for increase in weight in carbon dioxide at a pressure of 1 atmos-

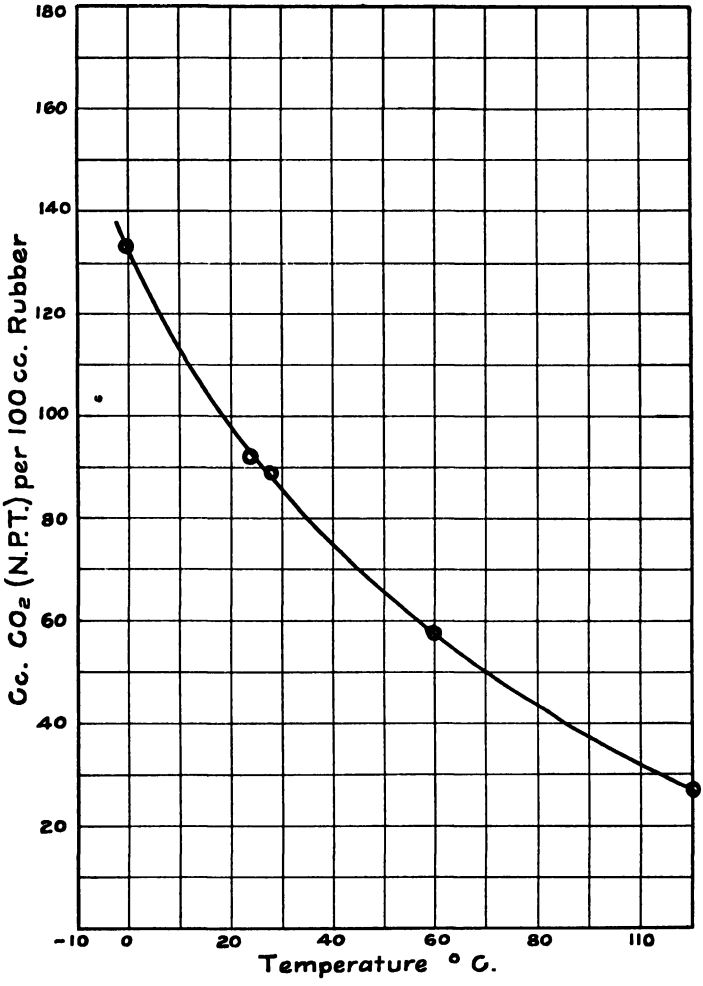

FIGURE 5. Effect of Temperature on Solubility of Carbon Dioxide in Rubber.

(According to Venable and Fuwa)

phere and a temperature of 25° C. He found that black tubing ($d_4^{25}=0.93$) dissolved 0.146 gram of carbon dioxide per 100 grams of rubber (equivalent to 68.8 cc. per 100 cc. at 0° and 760 mm.) and bright brown tubing

[47] Yammamoto, T., *Bull. Inst. Phys. Research (Tokyo)*, **7**, 999-1001 (1928).

($d_4^{25}=0.938$) dissolved 0.166 gram of carbon dioxide per 100 grams of rubber (78.5 cc. per 100 cc. rubber).

Relative diffusional rates of various gases through rubber have been determined by several investigators. In order to compare their results,

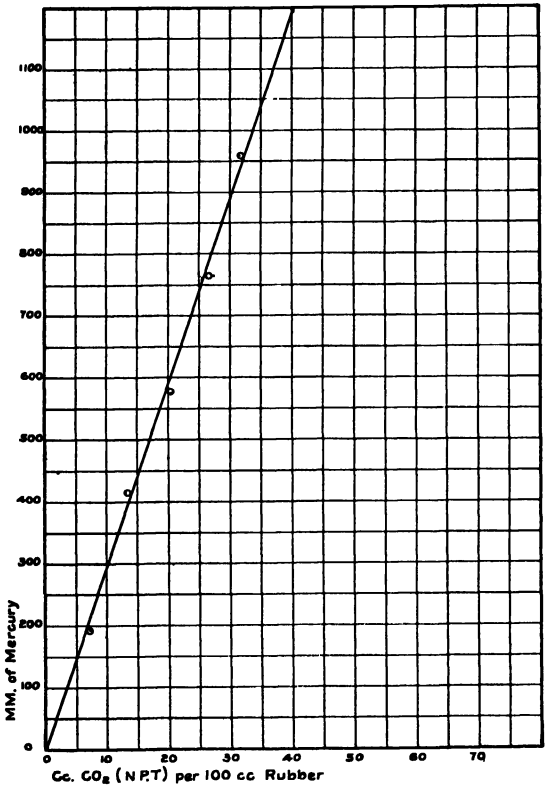

FIGURE 6.

Effect of Pressure on Solubility of Carbon Dioxide in Rubber at 100° C.

(According to Venable and Fuwa)

the reported data have been recalculated to a common basis and the results of these calculations are shown in Table 10.

TABLE 10.—*Relative Rates of Diffusion of Various Gases Through Rubber.*

Observer	N_2	Air	A	He	O_2	H_2	CO_2
	(O_2=1)						
Dewar	0.34	0.50	0.64	0.87	1.0	2.8	7.0
Alexjev and Matalskii	.43	...	...	...	1.0	..	6.0
Edwards and Pickering	.35	.71	.57	1.4	1.0	2.2	6.4

Compressibility. Carbon dioxide deviates considerably from the ideal gas laws and especially is this true at the very high pressure under which it is often measured. Amagat's work on the compressibility of gases produced the most extensive and reliable data obtained to the present time. His values for the product PV covering a considerable temperature and pressure range are given in Table 11 and the plots of these values are

TABLE 11.—*The Product of $P \times V$ at Various Temperatures and Pressures.*

(PV=1 at 0° C. and 1 atmos. pressure)

Press. Atmos.	Temperatures ° C.									
	0	10	20	40	60	80	100	137	198	258
50	0.1050	0.1145	0.6800	0.8500	0.9840	1.0960	1.2065	1.3800	.....	.....
100	0.2020	0.2130	0.2285	0.3090	0.6610	0.8725	0.9535	1.2590	1.5820	1.8470
150	0.2950	0.3090	0.3260	0.3770	0.4850	0.6805	0.8780	1.1585	1.5295	1.8180
200	0.3850	0.4010	0.4190	0.4400	0.5425	0.6600	0.8145	1.0960	1.4960	1.8040
250	0.4740	0.4900	0.5100	0.5580	0.6250	0.7135	0.8355	1.0810	1.4870	1.8060
300	0.5590	0.5775	0.5985	0.6485	0.7100	0.7900	0.8900	1.1080	1.4835	1.8200
350	0.6445	0.6640	0.6850	0.7635	0.7980	0.8725	0.9615	1.1565	1.5210	1.8465
400	0.7280	0.7475	0.7710	0.8320	0.8840	0.9560	1.0385	1.2175	1.5630	1.8830
450	0.8090	0.8310	0.8550	0.9075	0.9690	1.0400	1.1190	1.2880	1.6160	1.9280
500	0.8905	0.9130	0.9380	0.9900	1.0540	1.1250	1.2005	1.3620	1.6775	.....
550	0.9700	0.9935	1.0200	1.0740	1.1370	1.2085	1.2830	1.4400	1.7450	.....
600	1.0495	1.0730	1.0995	1.1270	1.2190	1.2900	1.3655	1.5180	1.8120	.....
650	1.1275	1.1530	1.1800	1.2375	1.3010	1.3725	1.4475	1.5960	1.8835	.....
700	1.2055	1.2325	1.2590	1.3190	1.3825	1.4535	1.5285	1.6760	1.9560	.....
750	1.2815	1.3105	1.3395	1.4000	1.4640	1.5335	1.6100	1.7565	2.0330	.....
800	1.3580	1.3870	1.4170	1.4790	1.5435	1.6140	1.6890	1.8355	2.1080	.....
850	1.4340	1.4625	1.4935	1.5570	1.6225	1.6925	1.7680	1.9150	2.1860	.....
900	1.5090	1.5385	1.5685	1.6325	1.6995	1.7710	1.8460	1.9940	2.2600	.....
950	1.5830	1.6115	1.6430	1.7065	1.7745	1.8470	1.9230	2.0720	2.3350	.....
1000	1.6560	1.6850	1.7160	1.7800	1.8475	1.9210	1.9990	.....	.....	.....

shown in Figure 7 and Figure 8. The latter isotherms have been plotted on an enlarged scale to show better the behavior of the gas at temperatures below the critical point. The dotted line AB represents the vapor-liquid curve and the values of P within this region represent the vapor pressure of the liquid phase. Perhaps one of the most interesting features of this plot is shown by the isotherms at 32° and 35° C. While they are above the critical temperature they show characteristics similar to those of the liquid-gas curve below this point.

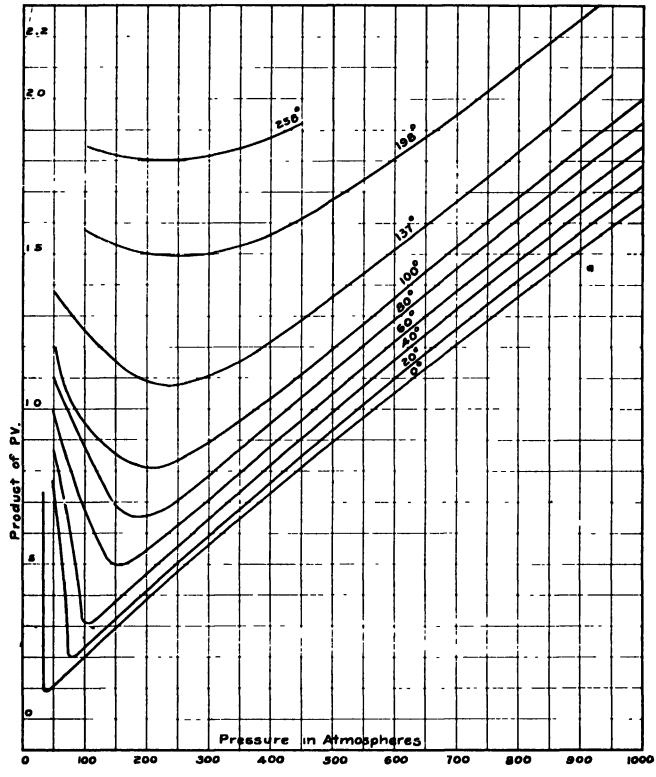

FIGURE 7. Compressibility Data of Amagat.

The work of Keesom[48] some years after that of Amagat also give an interesting series of isotherms. These isothermic values have been plotted in Figure 9.

The compressibility of liquid carbon dioxide has been measured by Jenkin[49] and the results of his measurements are shown by the isotherms plotted in Figure 10. The ordinate of this graph represents the absolute

[48] Keesom, W. H., *Verhandel. Akad. Wetenschappen Amsterdam*, **12**, 391, 544, 616, 621 (1903); *Communications Phys. Lab. Univ. Leiden*, **88** (1903).

[49] Jenkin, C. F., *Proc. Roy. Soc. (London)*, **A 98**, 170 (1921).

pressure in pounds per square inch. The curve *AB* is evidently the vapor-liquid limit curve for the system.

There seems to be a paucity of information concerning the effect of pressure changes on the volume occupied by solid carbon dioxide. Bridgeman has studied the effect of varying pressures on the melting point and his results will be considered in detail under that topic.

FIGURE 8. Compressibility Data of Amagat.

The Coefficient of Thermal Expansion. Among the many reported values for the coefficient of expansion of carbon dioxide we find the following:

Temp. Range °C.	Coefficient of Expansion	Observer	Reference
0°–100°	0.003691	Magnus	*Pogg. Ann.*, **55**, 21 (1842).
0°–100°	0.003710	Regnault	*Mém. Acad.*, **26**, 575 (1862).
0°–100°	0.003724	Leduc	*Compt. rend.*, **148**, 1173 (1909).
0°–100°	0.003724	Chappuis	*Arch. Sci. Genève*, (3) **20**, 5, 153, 248 (1888).
Average	0.003712		

Dewar, Sir James, *Proc. Roy. Inst.*, **21**, 813-26; *J. Chem. Soc.*, **114**, II 186-7. Alexjev, D. and Matalskii, V., *J. chim. phys.*, **24**, 737-41 (1927). Edwards, J. P. and Pickering, S. F., *loc. cit.*

In some of the above cases the pressures under which the measurements were made were not stated. It may be assumed, however, that these values are for one atmosphere. Chappius has determined the coefficient of expansion at several different pressures with the following results:

Pressure in mm.	0° to 20° C.	0° to 40° C.	0° to 100° C.
518	0.0037128	0.0037100	0.0037073
998	0.0037602	0.0037536	0.0037410
1377	0.0037972	0.0037906	0.0037703

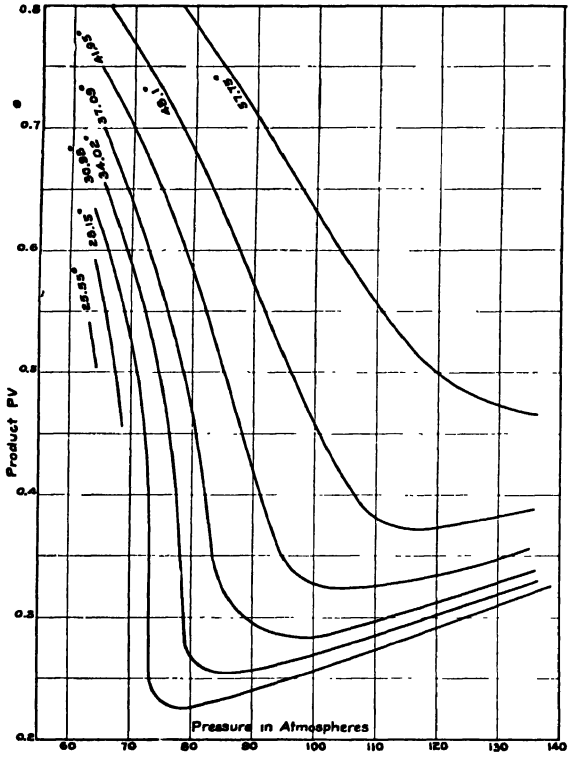

FIGURE 9.

Compressibility Data of Keesom.

At higher pressure the values given by Amagat are very useful. They have been listed in Table 12.

The Equation of State. One of the oldest and best known equations derived for the purpose of showing the relation between P, V and T in non-ideal gases is that of van der Waal. The usual form of this equation when applied to carbon dioxide takes the form

$$\left(P+\frac{.00719}{V^2}\right)(V-.001912)=n\,.081518\,T \quad \ldots\ldots \quad (7)$$

where P is expressed in atmospheres, V in liters, T in degrees Kelvin $(t°+273.1)$ and n is the number of moles of gas taken. The values of

TABLE 12.—*Coefficients of Expansion of Carbon Dioxide at Different Temperatures and Pressures.*

Values given in the table equal $\frac{1}{V} \times \frac{\Delta V}{\Delta t}$

Pressure Atmos.	Temperatures ° C.											
	0 to 10	10 to 20	20 to 30	30 to 40	40 to 50	50 to 60	60 to 70	70 to 80	80 to 90	90 to 100	100 to 137	137 to 198
50	0.00905	.....	0.01394	0.01097	0.00823	0.00695	0.00600	0.00508	0.00520	0.00464	.....	.....
60	0.00800	0.01259	.....	0.01557	0.01081	0 00853	0.00705	0.00604	0.00560	0.00521	.....	.....
75	0.00654	0.01043	0.02166	0.18310	0.02048	0 01258	0 00916	0.00762	0.00643	0.00595	0.00485	0.00369
80	0.00644	0.00951	0.01710	0.14270	0.02963	0 01471	0.01083	0.00854	0.00699	0.00648	.....	.....
85	0.00637	0.00872	0.01425	0.09079	0.04965	0.01813	0 01222	0.00921	0.00753	0.00696	.....	.....
90	0.00632	0.00827	0.01265	0.04450	0.07566	0.02254	0.01376	0.01006	0.00811	0.00724	.....	.....
95	0.00626	0.00786	0.01162	0.02900	0.07388	0.02784	0.01547	0.01116	0.00865	0.00765	.....	.....
100	0.00544	0.00728	0.01159	0.02128	0.05899	0.03462	0.01755	0.01229	0.00908	0.00802	0.00601	0.00420
110	0.00544	0.00709	0.00923	0 01510	0.03142	0.04100	0.02262	0.01428	0.01092	0.00908	.....	.....
125	0.00522	0.00630	0.00772	0.01666	0 01791	0.02911	0 02608	0.01804	0.01304	0.01037	.....	.....
150	0.00474	0.00550	0.00613	0.00922	0.01114	0.01575	0.01855	0 01835	0.01484	0.01247	0.00864	0.00525
175	0.00423	0.00493	0.00550	0.00728	0.00842	0 01061	0.01335	0.01370	0.01374	0.01228	0.00945	0.00565
200	0.00416	0.00449	0.00501	0 00625	0.00695	0.00850	0.00977	0.01083	0.01083	0.01134	0.00934	0.00798
250	0 00337	0.00408	0.00461	0.00459	0.00511	0.00656	0.00672	0.00697	0.00778	0.00865	0.00794	0.00616
300	0.00322	0.00364	0.00401	0.00418	0.00432	0.00495	0.00542	0.00554	0.00601	0.00627	0.00662	0.00570
400	0.00268	0.00314	0 00311	0.00352	0.00346	0.00382	0 00384	0.00414	0.00419	0.00426	0.00466	0.00465
500	0.00253	0.00274	0.00266	0.00313	0.00323	0.00322	0.00322	0.00330	0.00329	0.00349	0.00364	0.00386
600	0.00224	0.00247	0.00255	0.00261	0.00255	0.00274	0.00287	0.00287	0.00283	0.00293	0.00303	0.00317
700	0.00220	0.00219	0.00238	0.00232	0.00235	0.00241	0 00249	0.00258	0.00251	0.00258	0.00261	0.00278
800	0.00214	0.00216	0.00215	0.00218	0.00223	0.00219	0.00224	0.00228	0.00226	0.00233	0.00234	0.00243
900	0.00197	0.00195	0.00200	0.00199	0.00210	0.00206	0.00206	0.00210	0.00206	0.00213	0.00216	0.00223
1000	0.00175	0.00184	0.00180	0.00191	0.00184	0.00198	0 00198	0.00197	0.00198	0.00204	0.00234	.....

a and b (.00719 and .001912 respectively) were calculated from the data of Amagat. Unfortunately this simple equation does not represent the actual relations between P, V and T over any considerable range of temperature and pressure.

In an attempt to obtain an equation which more accurately represents the changes in condition of carbon dioxide Kammerlingh-Onnes[50] modified the equation of van der Waals until it took the following form:

$$PV = n\,.081507\,T\left[1+\frac{1}{V}\left(.001912-\frac{.00719}{.081507\,T}\right)\right]. \quad \ldots\ldots\ (8)$$

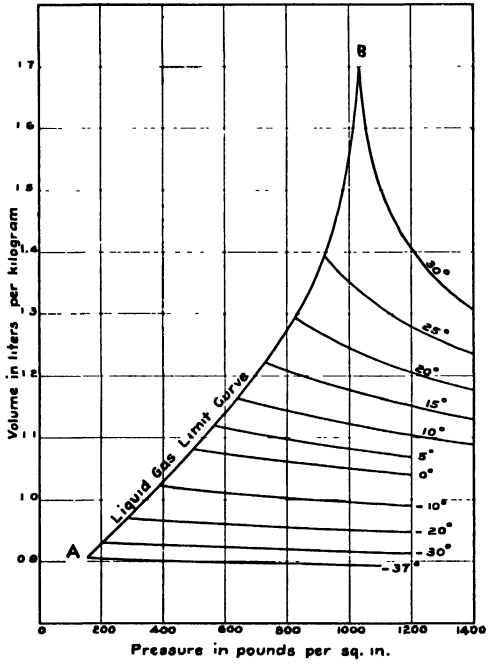

FIGURE 10.

Showing the Specific Volume of Carbon Dioxide at Various Temperatures and Pressures. The Compressibility Coefficient is the Slope of Each Isotherm.

In this equation P, V, and T are expressed in the same units as in the old van der Waals' equation given above.

Plank and Kuprianoff have derived an equation of state for calculating specific volumes of carbon dioxide which follows the experimental results quite well over a fairly wide pressure and temperature range. It also has the advantage of simplicity which is not a characteristic of most of these equations. The Plank and Kuprianoff equation is given in the following form:

$$V=\frac{RT}{P}-\left(\frac{0.0825+1.225\times 10^{-4}P}{\left(\frac{T}{100}\right)^{\frac{10}{3}}}\right) \quad \ldots\ldots\ (9)$$

[50] Kammerlingh-Onnes, H., *Communications Phys. Lab. Univ. Leiden*, **118 b** (1910).

The constants in this equation were computed when V was expressed in liters per kilogram, P in kilograms per square meter, T in degrees Kelvin and R had a value of 19.273. It will be observed that the expression

$$\left(\frac{0.0825 + 1.225 \times 10^{-7} P}{\left(\frac{T}{100}\right)^{10/3}}\right)$$

is a correction factor to the ideal gas equation $PV = RT$. When the above units are used this expression represents cubic meters per kilogram.

Without doubt the most accurate of all equations of state yet proposed is that of Beattie and Bridgeman.[51] This equation gives very accurate results for carbon dioxide over a temperature range from—252° C. to 400° C. and a pressure range up to 200 atmospheres. It has the disadvantage that the evaluation of P or V is a very laborious operation. The equation is given in the following form:

$$P = \frac{RT(1-\epsilon)}{v^2}(v - B) - \frac{A}{v^2} \quad \ldots\ldots\ldots\ldots \quad (10)$$

where $A = A_0(1 - a/v)$; $B = B_0(1 - b/v)$; and $\epsilon = c/vT^3$. The constants for carbon dioxide when the specific volume is expressed in cc. per gram, $T - t^0 + 273.13$ and the pressure in atmospheres, are as follows:

$$R = 1.865;\ B_0 = 2.381;\ b = 1.6443;\ A_0 = 2586;\ a = 1.621 \text{ and } c = 15.0 \times 10^6.$$

These authors have compared pressures calculated with this equation with those observed by Amagat and found an average deviation of only 0.08 per cent.

Many other equations of state will be found in the literature but none of them has any very outstanding advantage over the ones given here.

The Specific Volumes of Gaseous, Liquid and Solid Carbon Dioxide. While the volume occupied by a gram, kilogram or pound of carbon dioxide can readily be calculated from the data already given it is perhaps well to put these important values in a more usable form. The calculated results of Plank and Kuprianoff[52] are excellent averages of the existing experimental data and cover pretty much the whole field. In Table 13 these values are listed for the liquid and vapor together with experimental data of Maass and Barnes for the solid state.

The Triple Point. The existing data on the triple point of carbon dioxide are scanty but what we have are in such good agreement there can

[51] Beattie, J. A. and Bridgeman, O. C., *J. Am. Chem. Soc.*, **49**, 1665-7 (1927).

[52] Plank, R. and Kuprianoff, J., *Loc. cit.*

TABLE 13.—*Specific Volume of Carbon Dioxide in the Gaseous, Liquid and Solid State.*

Temperature			Saturated Vapor		Saturated Liquid		Solid	
° C.	° F.	° Kelvin	Liter / Kilogram	Cu. ft. / Pound	Liter / Kilogram	Cu. ft. / Pound	Liter / Kilogram	Cu. ft. / Pound
31	87.8	304.1	2.156	.03453	2.156	.03453		
30	86.0	303.1	2.990	.04789	1.6768	.02686		
25	77.0	298.1	4.167	.06675	1.4168	.02269		
20	68.0	293.1	5.258	.08422	1.2976	.02078		
15	59.0	288.1	6.329	.10138	1.2226	.01958		
10	50.0	283.1	7.519	.12044	1.1655	.01867		
5	41.0	278.1	8.850	.14176	1.1197	.01793		
0	32.0	273.1	10.383	.16632	1.0813	.01732		
− 5	23.0	268.1	12.141	.19448	1.048	.01678		
−10	14.0	263.1	14.194	.22792	1.019	.01632		
−15	5.0	258.1	16.609	.26606	0.994	.01592		
−20	− 4.0	253.1	19.466	.31188	0.971	.01555		
−25	−13.0	248.1	22.885	.36659	0.950	.01521		
−30	−22.0	243.1	27.001	.43251	0.931	.01491		
−35	−31.0	238.1	32.008	.51272	0.913	.01462		
−40	−40.0	233.1	38.164	.61132	0.897	.01437		
−45	−49.0	228.1	45.809	.73378	0.881	.01411		
−50	−58.0	223.1	55.407	.88752	0.867	.01388		
−55	−67.0	218.1	67.620	1.0832	0.853	.01366		
−56.6	−69.9	216.5	72.220	1.1568	0.849	.01360	0.661	.01059
−60	−76.0	213.1			0.840	.01345	0.657	.01052
−65	−85.0	208.1					0.652	.01044
−70	−94.0	203.1					0.647	.01036
−75	−103.0	198.1					0.643	.01030
−80	−112.0	193.1					0.639	.01023
−85	−121.0	188.1					0.635	.01017
−90	−130.0	183.1					0.632	.01012
−95	−139.0	178.1					0.629	.01007
−100	−148.0	173.1					0.627	.01004
−110	−166.0	163.1					0.623	.00998
−120	−184.0	153.1					0.619	.00992
−130	−202.0	143.1					0.615	.00985
−183	−297.4	90.1					0.599	.00960

be but little doubt as to the value of this constant. The results obtained by four investigations are as follows:

Triple Point	Vapor Pressure Atmosphere	Observer	Reference
− 56.7	5.1	Villard and Jarry	*Compt. rend.*, 120, 1413 (1895).
− 56.24	5.10	Kuenen and Robson	*Phil. Mag.* (6) 3, 622 (1902).
− 56.4	5.11	Zeleny and Smith	*Phys. Rev.* (1) 24, 42 (1907).
− 56.59	5.113	Meyers and Van Dusen	*Refrigerating Eng.* 13, 180 (1926).

Plank and Kuprianoff consider that −56.6 is the most reliable temperature value and this will be considered the triple point in all future calculations in this work.

The Critical Temperature. The critical temperature is often defined as that temperature above which a substance cannot exist in the liquid state (however, cf. page 60). At this temperature the value of the surface tension becomes zero and the densities of the liquid and its saturated vapor become equal. At the critical temperature there exists a complete mutual solubility of the liquid and the gas. The usual visual evidence of this change is the disappearence of the meniscus at the surface of the liquid. That this is not a clear cut point has been demonstrated by several researches. It is not surprising, therefore, that critical temperature measurements by different investigators do not always agree. Meyers and Van Dusen have collected and tabulated the data obtained by a large number of investigators. These values are given in Table 14.

TABLE 14.—*The Critical Temperature and Critical Pressure of Carbon Dioxide.*

t_c °C.	P_c Atmos.	Observer	Reference
30.92	73	Andrews	*Trans. Roy. Soc. (London),* **159,** II 575 (1869).
31.0		Hautefeuille and Cailletet	*Compt. rend.* **92,** 840 (1881).
31.9	77	Dewar	*Phil. Mag.* **18,** 210 (1884).
31.35	72.9	Amagat	*Compt. rend.,* **114,** 1093, 1322 (1892).
31.40		Chappuis	*Compt. rend.,* **118,** 976 (1894).
31.7		Villard	*J. Phys.* (3) 441 (1894).
31.0		Verschaffelt	*Verhandel Akad. Wetenschappen Amsterdam,* 94 (1896); *Communications Phys. Lab. Univ. Leiden,* **28.**
31.1	73.26	Kuenen	*Phil. Mag.,* (5) **44,** 179 (1897).
31.4		De Heen	*Bull. acad. roy. Belgique,* **31,** 147, 379 (1896).
30.95 to 31.7		Von Wesendonck	*Verhandel deut. physik. Ges.,* **5,** 238 (1903).
30.98	72.93	Keesom	*Verhandel Akad. Amst.* 321, 533, 616 (1903).
31.12		Brinkmann	Brinkmann Dissertation Amsterdam (1904).
30.985		Onnes and Fabius	*Verhandel Akad. Amst.* 44 (1907); *Communications Phys. Lab. Univ. Leiden,* **98,** (1907).
31.26		Bradley, Brown and Hale	*Phys. Rev.* **26,** 470 (1908).
31.10	73.00	Dorsman	Dorsman Dissertation Amsterdam (1908).
31.00	72.85	Cardoso and Bell	*J. chim. phys.* **10,** 500 (1912).
30.97		Hein	*Z. physik. Chem.* **86,** 385 (1913-14).
31.1	72.95	Meyers and Van Dusen	*Refrigerating Eng.* **13,** 180 (1926).
30.96		Kennedy	*J. Am. Chem. Soc.* **51,** 1360 (1929).

The most probable value for the critical temperature is 31.0° C. and for the critical pressure 72.80 atmospheres.[53]

The work of Bradley, Brown and Hale[54] has given us some interesting information on the effect of mechanical vibration on liquid carbon dioxide

[53] Meyers, C. H. and Van Dusen, M. S., *Bur. Standards J. Research,* **10,** 381-412 (1933).

[54] Bradley, W. P., Brown, A. W. and Hale, C. F., *Phys. Rev.,* **26,** 470-82 (1908); *ibid.,* **27,** 90-106 (1909).

near the critical temperature. When the liquid is within two degrees of its critical temperature it is exceptionally sensitive to a minute change in volume so that the vibrations produced by a tuning fork, under the proper conditions, are sufficient to give rise to the so-called fog effect. These investigators have also found evidence that liquid carbon dioxide can exist above the critical temperature. An excellent discussion of the critical state of carbon dioxide has been made by Hein.[55]

Melting Point. Below the triple point (−56.6° C.) solid carbon dioxide sublimes directly to a gas. The sublimation temperature is of course a function of the opposing pressure and at one atmosphere pressure the temperature of sublimation is −78.515° C. (−109.33° F.).[56] This temperature is so easily reached with solid carbon dioxide that it is often used as a reference point for standardization of low temperature thermometers. Temperatures below this point or even up to the triple point can easily be maintained by controlling the pressure of the gas above the solid carbon dioxide. With a vacuum produced by an ordinary water aspirator it is possible to reach temperatures well below −100° C. The relation between temperature and pressure can be determined by reference to the vapor pressure table of the solid.

The effect of pressure changes on the melting point of solid carbon dioxide was studied by Kuenen and Robson[57] who calculated that dp/dt was equal to 47.9 atmospheres per degree centigrade while Tammann[58] obtained a value of 50 atmospheres per degree. Bridgeman[59] very definitely located the freezing temperatures at pressures up as high as 11613 atmospheres. His results are shown in Table 15. The most interesting fact brought out by this table is that carbon dioxide can exist as a solid at temperatures above its critical point.

TABLE 15.—*Showing the Freezing Points of Carbon Dioxide at Various Pressures.*

(Data by Bridgeman)

Pressure		Temperature	Change in vol. ΔV
Kg/cm.²	Atmos.	° C.	Cm.³/gm.
1	5.11	−56.6	0.188
1000	967.8	−37.3	....
2000	1935.5	−20.5	....
3000	2903.2	− 5.5	.1071
4000	3871.1	+ 8.5	.0979
5000	4838.7	21.4	.0896
6000	5806.6	33.1	.0822
7000	6774.3	44.2	.0755
8000	7742.1	55.2	.0697
9000	8709.8	65.8	.0644
10000	9677.7	75.4	.0602
11000	10645.5	84.6	.0564
12000	11613.0	93.5	.0531

[55] Hein, Paul, *Z. physik. Chem.*, **86**, 385-426 (1913-14).
[56] Meyers, C. H., and Van Dusen, M. S., *Loc. cit.*
[57] Kuenen, J. P., and Robson, W. G., *Phil. Mag.*, (6) **3**, 622 (1902).
[58] Tammann, G., *Wied. Ann.*, **68**, 572 (1899).
[59] Bridgeman, P. W., *Phys. Rev.* (2) **3**, 158 (1914).

The decrease in volume as carbon dioxide changes from the liquid to the solid state is exceptionally large. The specific volume of the liquid, at the triple point, is 0.849, while for the solid it is 0.661 liters per kilogram. This decrease amounts to 28.5 per cent while water increases about 10 per cent on changing to the solid condition. It will be noticed that at higher temperatures this volume change on freezing becomes much less.

Vapor Pressure of Liquid Carbon Dioxide. Various parts of the liquid-vapor equilibrium curve have been studied by such investigators as Regnault, Cailletet, Amagat and Villard. The recent measurements of Meyers and Van Dusen, however, have covered the whole field from the triple point to the critical temperature. This work was so carefully and completely done that it inspires considerable confidence in the reliability of the results. The values obtained in this investigation are shown in Tables 16 and 17.

Plank and Kuprianoff found that Young's equation

$$p = a\left(\frac{T}{100} - b\right)^n \quad \ldots\ldots\ldots\ldots \quad (11)$$

fitted the vapor pressure curve of Meyers and Van Dusen very well. When p is expressed in kilograms per square centimeter the values for the constants are: $a = 7.856$, $b = 1.261$, $n = 3.917$.

Bridgeman[60] measured the vapor pressure of carbon dioxide at the water ice point with the view of obtaining a pressure system for the calibration of piston gages which would be less complicated than the mecury column. His value at 0° C. was 34.4009 ± 0.0013 atmospheres ($g = 980.665$) or 26144.7 ± 1.0 international mm. of mercury.

Vapor Pressure of Solid Carbon Dioxide. In order to determine the course of the equilibrium curve for the system $CO_{2(s)} \rightleftarrows CO_{2(g)}$ it is necessary to piece together the results of several research workers in this field. At very low temperatures, measurements have been made by Kammerlingh Onnes and Weber[61] who obtained the following results:

Temp. °C.	−183	−179.6	−175.37	−171.01	−168.83	−167.04
Pressure mm.	.000006	.0000195	.0000795	.000303	.000593	.000983

At −134° C. the vapor pressure of solid carbon dioxide is only slightly over 1 mm. and from this point up to the triple point, data is available for plotting the equilibrium curve with considerable accuracy. However, the course of this curve can perhaps be calculated better by using the empirical equation developed by Plank and Kuprianoff. This equation may be written

$$\log p = 58.361 - \frac{2206.455}{T} - 21.431 \log T + 0.02527\, T \quad \ldots\ldots \quad (12)$$

[60] Bridgeman, O. C., *J. Am. Chem. Soc.*, **49**, 1174-83 (1927).

[61] Kammerlingh Onnes, H., and Weber, S., *Verhandel. Akad. Wetenschappen Amsterdam*, **22**, 226-39.

TABLE 16.—*Vapor Pressure of Carbon Dioxide in mm.*

(Mercury at 0° C. and g=980.665)

(by Meyers and Van Dusen)

°C	0	1	2	3	4	5	6	7	8	9
−56.59	3885.7	Triple point								
−50	5127.3	4922.2	4723.3	4530.4	4343.4	4162.1	3986.7			
−40	7543.5	7270.2	7004.1	6745.4	6493.8	6249.3	6011.6	5780.6	5556.4	5338.6
−30	10715	10360	10014	9676.3	9347.2	9026.4	8714.1	8409.7	8113.2	7824.6
−20	14775	14325	13885	13455	13036	12625	12225	11833	11451	11078
−10	19864	19305	18757	18221	17696	17182	16680	16187	15706	15235
0	26132	25447	24776	24118	23473	22841	22221	21614	21018	20435
0	26132	26830	27541	28267	29006	29760	30529	31312	32110	32923
10	33752	34596	35457	36333	37226	38137	39064	40009	40972	41953
20	42953	43972	45010	46069	47148	48247	49369	50512	51678	52867
30	54080	55317								
31.1	55442	Critical point								

TABLE 17.—*Vapor Pressure of Carbon Dioxide in Atmospheres.*

(1 atmos.=760 mm. mercury)

(by Meyers and Van Dusen)

°C	0	1	2	3	4	5	6	7	8	9
−56.59	5.113	Triple point								
−50	6.746	6.477	6.215	5.961	5.715	5.477	5.246			
−40	9.926	9.566	9.216	8.876	8.544	8.223	7.910	7.606	7.311	7.025
−30	14.098	13.631	13.176	12.732	12.299	11.877	11.466	11.065	10.675	10.295
−20	19.441	18.849	18.270	17.704	17.152	16.612	16.085	15.570	15.068	14.577
−10	26.137	25.401	24.681	23.975	23.284	22.608	21.947	21.299	20.666	20.047
0	34.384	33.483	32.600	31.735	30.886	30.054	29.238	28.439	27.656	26.889
0	34.384	35.302	36.239	37.193	38.166	39.158	40.169	41.200	42.250	43.320
10	44.410	45.521	46.653	47.807	48.982	50.180	51.400	52.644	53.910	55.201
20	56.517	57.858	59.224	60.617	62.036	63.483	65.959	66.463	67.997	69.561
30	71.157	72.786								
31.1	72.950	Critical point								

Values obtained by means of this equation are shown in Table 18 together with data taken from the works of the various authors indicated.

TABLE 18.—*Vapor Pressure of Solid Carbon Dioxide in mm. of Mercury.*

t ° C.	T	Meyers and Van Dusen	Kuenen and Robson	Henning and Stock	v. Siemens	K. Onnes	Plank and Kuprianoff
— 56.6	216.5	3385.7					3884.0 Tr. Pt.
— 60	213.1		3017.2				3076.7
— 65	208.1		2107.8				2157.4
— 70	203.1		1428.8				1489.1
— 75	189.1		972.8				1010.1
— 78.52	194.58			760			760
— 80.05	193.05			669.9			669.5
— 87.91	185.19			338.5			338.0
— 95.92	177.18			158.7			158.3
—102.96	170.14			76.7			76.5
—109.74	163.36			35.7			35.7
—117.78	155.32				13.09		13.18
—127.21	145.89				3.50		3.52
—134.68	138.42					1.073	1.073

References

Meyers and Van Dusen, *Refrigerating Eng.*, **13**, 180 (1926).
Kuenen, J. P. and Robson, W. G., *Phil. Mag.* (6), **3**, 149 (1902).
Henning, F. and Stork, A., *Z. Physik.*, **4**, 226 (1921).
v. Siemens, H., Dissertation Berlin and *Ann. Phys.* (4) **42**, 871 (1913).
Kammerlingh Onnes, H. and Weber, S., *Communications Phys. Lab. Univ. Leiden*, 137 b and c (1913).

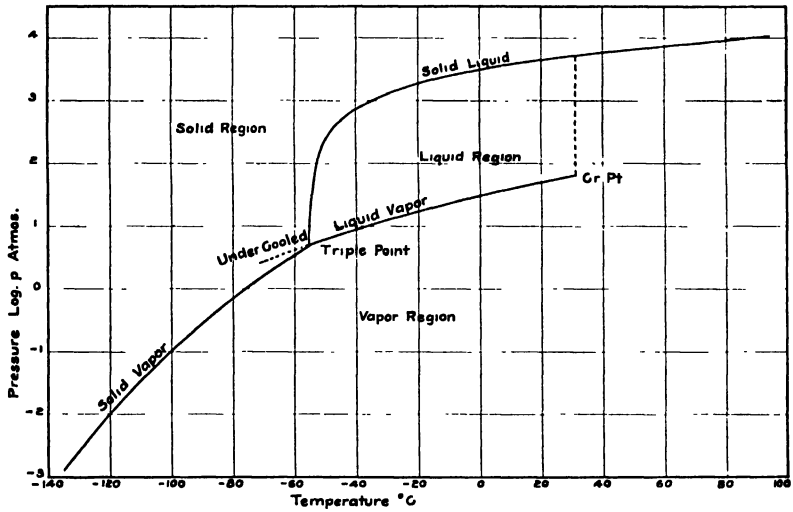

FIGURE 11. Equilibrium Curve for Carbon Dioxide.

The Equilibrium Diagram of Carbon Dioxide. The triple point diagram for carbon dioxide has been plotted in Figure 11.

Dissociation of Carbon Dioxide at High Temperatures. The degree of dissociation of carbon dioxide at elevated temperatures was first calcu-

lated by Löwenstein[62] from data obtained by the Victor Meyer-Nernst method of determining vapor pressures. At 1550° C. he calculated the per cent dissociation to be 0.4. Somewhat later Bjerrum[63] by means of the equation

$$\frac{a^3}{(1-a)^2(1+a/2)}=2RTK_c. \quad \ldots\ldots\ldots\ldots \quad (13)$$

where a = degree of dissociation and K_c is the dissociation constant, calculated the per cent dissociation of carbon dioxide over a wide range of temperatures and pressures. The results obtained by these calculations are shown in table 19.

TABLE 19.—*Per Cent Dissociation of Carbon Dioxide at Various Temperatures and Pressures.*

(Calculated by Bjerrum)

Temp. °K	Pressure .1 atmos.	1 atmos.	10 atmos.	100 atmos.
1000	.0000531	.0000247	.0000114	.00000531
1500	.104	.0483	.0224	.0104
2000	4.35	2.05	.960	.445
2500	33.5	17.6	8.63	4.09
3000	77.1	54.8	32.2	16.9
3500	93.7	83.2	63.4	39.8
4000	97.9	93.9	83.4	63.8
4500	99.2	97.4	92.4	80.3
5000	99.6	98.7	96.1	89.0

The Molecular Heat Capacity of Gaseous Carbon Dioxide. It is rather difficult to obtain from the literature, specific or molal heat data on carbon dioxide in which one may have absolute confidence. Many investigators have measured the specific heat of this compound and many others have calculated it, using mathematical expressions based on experimental results obtained by other workers. The earlier investigators often failed to specify the temperature under which their measurements were made. Others determined the ratio of specific heats of carbon dioxide at two different temperatures and some determined the ratio of the specific heat of carbon dioxide to the specific heat of some other gas at the same temperature. A very complete list of all these investigators is given by Mellor[64] and only the more recent work will be considered here.

For many years the most popular equation for calculating specific or molal heats has been that of Lewis and Randall[65] which is usually written for carbon dioxide in the following form:

$$C_p=7.0+0.0071\,T-0.00000186\,T^2. \quad \ldots\ldots\ldots \quad (14)$$

This equation is based on the experimental values of Holborn and Austin,[66]

[62] Löwenstein, Leo, *Z. physik. Chem.*, **54**, 707 (1906).

[63] Bjerrum, Niels, *Z. physik. Chem.*, **79**, 537-550 (1912).

[64] Mellor, J. W., "Comprehensive Treatise on Inorganic and Theoretical Chemistry," **6**, page 34, Longmans, Green and Co. (London).

[65] Lewis, G. N., and Randall, M., *J. Am. Chem. Soc.*, **34**, 1128 (1912).

[66] Holborn, L., and Austin, L., *Abhandl. physik. tech. Reichsanstalt*, **4**, 131 (1905).

Holborn and Henning,[67] and Pier.[68] Recent determinations seem to indicate that this equation gives values much too high especially at elevated temperatures. Leduc[69] has made a critical survey of the literature and has selected certain values for the molal heat capacity for carbon dioxide which he considers somewhat more reliable than those previously published. That Leduc was justified in his choice of values seems evident from the curves

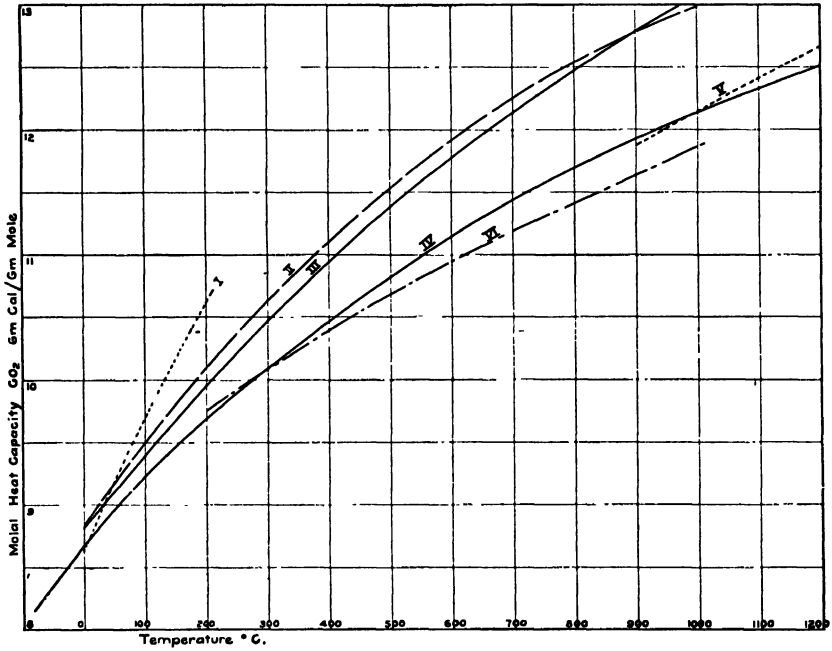

FIGURE 12. Experimental Data on the Molal Heat Capacity of Carbon Dioxide by Various Investigators.

Curve I by Eucken and Lüde	Experimental
Curve II by Holborn and Henning	Experimental
Curve III by Lewis and Randall	Calculated
Curve IV by Leduc	Calculated
Curve V by King and Partington	Experimental
Curve VI by Chopin	Experimental

plotted in Figure 12. The curve plotted by means of the Lewis and Randall equation agrees fairly well with that made from the experimental values of Holborn and Henning but the curve obtained with Leduc's values does not agree with either of them. This latter plot is supported to a certain extent by the recent experiments of Chopin[70] and those made by King and

[67] Holborn, L., and Henning, F., *Ann. Physik.*, **23**, 809-45 (1907).
[68] Pier, M., *Z. Elecktrochem.*, **15**, 536 (1909); **16**, 897 (1910).
[69] Leduc, A., "International Critical Tables," **5**, 83, McGraw-Hill Book Co., New York (1929).
[70] Chopin, Marcel, *Compt. rend.*, **188**, 1660-2 (1929).

Partington.[71] The results obtained by Eucken and Lüde[72] are hard to explain as they do not support any of the investigators just mentioned.

Table 20 has been constructed using Leduc's values above 0° C. and values calculated from the equation

$$C_p = 8.68 + .0066\,t - .0000022\,t^2 \quad \ldots\ldots\ldots\ldots \quad (15)$$

TABLE 20.—*The Molal Heat Capacity of Carbon Dioxide in Gram. Cal.*

t, °C.	t, °F.	C_v	C_p	C_p Calc. Eq. 16	$\frac{C_v}{C_p}$	C_p 0°—t
— 80	—112	6.085	8.166	8.176	1.342	
— 70	— 94	6.150	8.229		1.338	
— 60	— 76	6.216	8.292	8.280	1.334	
— 50	— 58	6.282	8.355		1.330	
— 40	— 40	6.349	8.419	8.397	1.326	
— 30	— 22	6.417	8.484		1.322	
— 20	— 4	6.485	8.548	8.506	1.318	
— 10	+ 14	6.555	8.614		1.314	
0	32	6.625	8.680	8.612	1.310	8.680
+100	212	7.197	9.220		1.281	8.927
200	392	7.656	9.670	9.585	1.263	9.138
300	572	8.081	10.077		1.247	9.338
400	752	8.476	10.468	10.402	1.235	9.537
500	932	8.822	10.808		1.225	9.737
600	1112	9.146	11.133	11.082	1.217	9.897
700	1292	9.449	11.433		1.210	10.098
800	1472	9.724	11.708	11.644	1.204	10.268
900	1652	9.956	11.947		1.200	10.437
1000	1832	10.173	12.157	12.106	1.195	10.569
1100	2012	10.357	12.346		1.192	10.698
1200	2192	10.528	12.518	12.488	1.189	10.808
1300	2372	10.680	12.666		1.186	10.925
1400	2552	10.817	12.807	12.810	1.184	11.047
1500	2732	10.964	12.949		1.181	11.168
1600	2912	11.092	13.077	13.088	1.179	11.277
1700	3092	11.220	13.206		1.177	11.407
1800	3272	11.351	13.338	13.347	1.175	11.527
1900	3452	11.472	13.457		1.173	11.648
2000	3632	11.612	13.598	13.597	1.171	11.768

below 0° C. The ratios of C_p to C_v below 0° C. were mechanically extrapolated from those given by Leduc above this temperature. It is believed that this extrapolation can be made with considerable confidence as it extends the curve only a relatively short distance. The molal heats at constant volume (C_v) were calculated from C_p by means of the ratio of these two values.

The whole range of values for C_p from −80° to 2000° C. may be calculated by means of the equation

$$C_p = 7.0 + 6.56\times10^{-3}T - 2.503\times10^{-6}T^2 + 3.932\times10^{-10}T^3 \quad \ldots\ldots \quad (16)$$

with an accuracy well within one per cent at any point. Many other empirical equations have been derived for the calculation of specific or molal

[71] King, F. E., and Partington, J. R., *Phil. Mag.*, (7) **9**, 1020-6 (1930).

[72] Eucken, A., and v. Lüde, K., *Z. physik. Chem.*, Abt. B **5**, 413-41 (1929).

heats of carbon dioxide and most of them take the same general form, i. e., $C_p = a + bt - ct^2 + dt^3$ in which a, b, c and d are constants. The value of these constants vary considerably with different investigators.

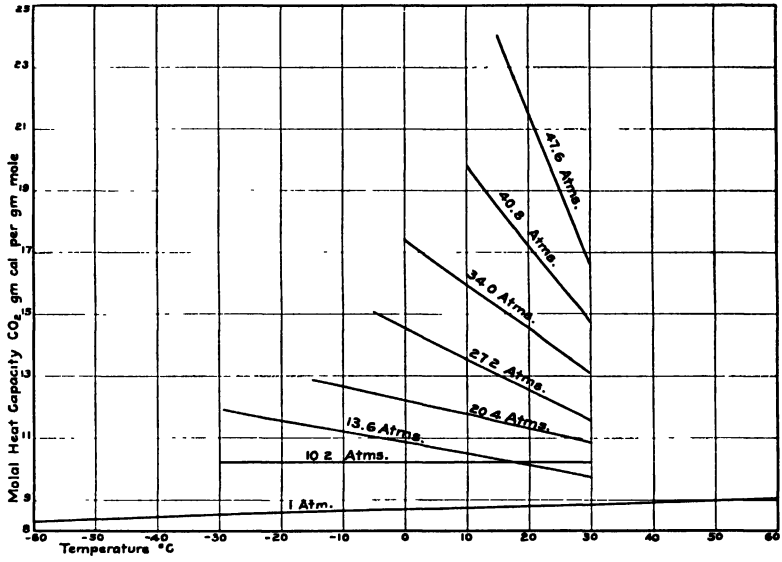

FIGURE 13. Molal Heat Capacity of Carbon Dioxide at Different Pressures and Temperatures.

That the specific heat of carbon dioxide changes with a change in pressure has been demonstrated by Jenkin and Pye[73] who have determined the heat capacities at a number of different temperatures and pressures. The

TABLE 21.—*The Molal Heat Capacity of Carbon Dioxide in Gram Cal. at Various Pressures and Temperatures.*
(Data from Jenkin and Pye.)

Pressure Atmos.	10.2	13.6	20.4	27.2	34.0	40.8	47.6
lbs./sq. in.	150	200	300	400	500	600	700
Temperature ° C.							
−30	10.186	11.88					
−25	10.186	11.70					
−20	10.186	11.53					
−15	10.186	11.35	12.85				
−10	10.186	11.13	12.63				
− 5	10.186	11.00	12.41	15.05			
0	10.186	10.82	12.19	14.52	17.42		
+ 5	10.186	10.65	11.97	14.04	16.72		
+10	10.186	10.47	11.75	13.55	16.02	19.80	
+15	10.186	10.30	11.48	13.02	15.27	18.52	24.07
+20	10.186	10.12	11.26	12.54	14.52	17.25	21.56
+25	10.186	9.94	11.04	12.06	13.81	15.97	19.10
+30	10.186	9.72	10.82	11.57	13.11	14.70	16.63

[73] Jenkin, C. F., and Pye, D. R., *Phil. Trans.*, **A 215**, 353 (1915).

results of their measurements are plotted in Figure 13. The curve representing the pressure of 1 atmosphere was based on the values of Leduc and this, with the other curves, shows very clearly how the slope changes with a change in pressure. The data from which these plots were made are given in Table 21.

The Molal Heat Capacity of Liquid Carbon Dioxide. Jenkin and Pye[74] have determined the specific heats of liquid carbon dioxide from −50° to +20° C. Their results are as follows:

t, °C.	−50	−40	−30	−20	−10	0	10	20
Sp. ht. (c_p)	.47	.49	.515	.54	.57	.60	.64	.68
Mol. ht. (C_p)	20.7	21.6	22.7	23.5	25.1	26.4	28.2	29.9

No other experimental determinations have been made in recent years, but Keyes and Kinney[75] have calculated the probable specific heat of the liquid as 0.543 at temperatures between 0° and −20° C. and 0.544 at −40° C.

The Molal Heat Capacity of Solid Carbon Dioxide. Without doubt the best experimental values for the molal heat capacity of solid carbon dioxide has been furnished by Maass and Barnes[76] who obtained an average of 12.496 gram cal. per gram mole between −115° and −183.1° C. The molal heat capacity of the solid between −56° and −110° C. can be calculated by means of the equation

$$C_p = 44(0.400 - 0.00283\,T + 0.0000125\,T^2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

Some of the values calculated from this equation expressed as gram cal. per gram mole are:

t, °C.	−56.6	−60	−70	−80	−90	−100	−110
C_p	16.41	16.06	15.00	14.08	13.24	12.54	11.92

The Latent Heat of Vaporization of Carbon Dioxide. The first measurement of the latent heat of vaporization of carbon dioxide was made by Regnault.[77] At 17° C. he obtained 40.0 cal. per gram. Somewhat later Chappuis[78] found a value of 56.25 cal. per gram at 0° C. Mathias[79] by means of a few direct measurements obtained

Temp. °C.	12.35	22.04	29.85	30.82
Lv in gram cal./gram	44.94	31.8	14.4	3.72

Indirect calorimetric determinations have been made by Jenkin and Pye between +20° and −30° C. and several investigators have published values calculated in various ways. No important direct measurements have been made below 0°.

[74] Jenkin, C. F., and Pye, D. R., *Phil. Trans.*, **A 213**, 67-117 (1914).
[75] Keyes, F. G., and Kinney, A. W., *Refrigerating Eng.*, **3**, Part 4, Jan. (1917).
[76] Maass, O., and Barnes, *Proc. Roy. Soc. (London)*, **A 111**, 224-44 (1926).
[77] Regnault, H. V., *Mém. acad.*, **26**, 335 (1862).
[78] Chappuis, J., *Ann. chim. phys.*, (6) **15**, 517 (1888).
[79] Mathias, E., Diss. Paris, No. 6807 (1890).

Plank and Kuprianoff have tabulated the most important experimental and calculated values for the latent heat of vaporization between the critical point and the triple point. These values may be calculated, with an accuracy which is sufficient for practically all purposes, by means of the equation of Thiesen,[80]

$$L_v = 15.2(304.1 - T)^{0.38} \quad \ldots\ldots\ldots\ldots \quad (18)$$

TABLE 22.—*Heat of Vaporization of CO_2 L_v in Gm. Cal/Gm.*

t °C.	t °F.	Mollier	Langen	Eichelberg	Jenkin and Pye	Keyes	Plank and Kuprianoff	B. t. u. per lb.
+31.0	+87.8	0.000	0.00	0.00			0.00	0.00
30.0	86.0	14.93	15.34	14.7		19.77	15.05	27.09
25.0	77.0	28.84	28.74	28.4			28.53	51.35
20.0	68.0	36.75	36.20	36.5	36.5	38.61	37.10	66.78
15.0	59.0	42.69	42.12	42.5	41.9		43.07	77.53
10.0	50.0	47.52	47.05	47.5	46.2	48.50	48.09	86.56
5.0	41.0	51.67	51.28	52.2	50.3		52.35	94.23
0.0	32.0	55.19	55.03	55.8	54.1	56.15	56.13	101.03
− 5.0	23.0	58.36	58.42	59.2	57.7		59.50	107.10
−10.0	14.0	61.18	61.54	62.4	60.9	62.67	62.51	112.52
−15.0	5.0	63.73	64.45	65.2	63.8		65.26	117.47
−20.0	− 4.0	66.04	67.20	67.8	66.5	68.45	67.79	122.02
−25.0	−13.0	68.15	69.82	70.5	69.0		70.14	126.25
−30.0	−22.0	70.07	72.32	72.9	71.3	73.72	72.37	130.27
−35.0	−31.0		74.76	75.1	73.6		74.51	134.12
−40.0	−40.0		77.16	77.4	75.7	78.59	76.58	137.84
−45.0	−49.0		79.52	79.7	77.8		78.59	141.46
−50.0	−58.0		81.88	81.8	79.9	83.16	80.56	145.01
−55.0	−67.0			83.9			82.50	148.50
−56.6	−69.9						83.12	149.62

Table 22 gives the results of the tabulation of Plank and Kuprianoff.

Heat of Sublimation of Carbon Dioxide. The latent heat of sublimation of carbon dioxide was first determined by Favre[81] who obtained a value of 138.7 gram cal. per gram at a pressure not stated but probably atmospheric. Behn[82] some years later found a value of 142.4 gram cal. per gram at −78° and 1 atmos. pressure. Kuenen and Robson by means of the Clausius-Clapeyron equation calculated a value of 129.9 gram cal. per gram at the triple point. Recently Andrews[83] obtained at atmospheric pressure 141.0 and Maass and Barnes[84] 136.9 gram cal. per gram. At lower temperatures and pressures we have the measurements of Eucken and Donath[85] who found 140.7 at −103.1° C. and 144.0 gram cal. per gram at −133.1° C.

The most recent calculations have been made by Plank and Kuprianoff who, by means of a modified form of the Clausius-Clapeyron equation, have computed a series of values which are in good agreement with experi-

[80] Thiesen, *Verhandel Phys. Ges. Berlin*, **16**, 80 (1897).
[81] Favre, P. A., *Compt. rend.*, **39**, 729 (1854); *Liebig's Ann.*, **92**, 194 (1854).
[82] Behn, U., *Ann. Physik.*, (4) **3**, 733 (1900).
[83] Andrews, J. W., *J. Am. Chem. Soc.*, **47**, 1597 (1925).
[84] Maass, O., and Barnes, *Proc. Roy. Soc. (London)*, **A 111**, 224 (1926).
[85] Eucken, A., and Donath, E., *Z. physik. Chem.*, **124**, 194 (1926).

mental results. The equation they used is somewhat complicated and is difficult to use unless one has access to their table of correction factors. A much more usable equation for calculating heats of sublimation is

$$L_s = L_0 - 0.2409\,T + 0.0014957\,T^2 - 0.00000431\,T^3 \quad \ldots\ldots \quad (19)$$

where L_0 is a constant which can be calculated from any experimental data. Plank and Kuprianoff used for L_0 a value of 158.96 which was calculated from the experimental data of Eucken and Donath.

The calculated data of Plank and Kuprianoff are given in Table 23.

TABLE 23.—*Heat of Sublimation L_s of Carbon Dioxide in Gram. Cal./Gram. and B. t. u./lb.*

t °C.	t °F.	P Atmos.	L_s g. cal./g.	L_s B. t. u./lb.
− 56.6	− 69.9	5.112	129.88	233.78
− 60.0	− 76.0	4.048	131.35	236.43
− 65.0	− 85.0	2.838	133.38	240.08
− 70.0	− 94.0	1.959	134.93	242.87
− 75.0	−103.0	1.329	136.13	245.07
− 78.9	−110.0	0.986	136.89	246.40
− 80.0	−112.0	0.885	137.08	246.74
− 85.0	−121.0	0.577	137.88	248.18
− 90.0	−130.0	0.367	138.57	249.43
− 95.0	−139.0	0.228	139.19	250.54
−100.0	−148.0	0.137	139.77	251.59

Heat of Fusion of Carbon Dioxide. It is evident that the heat of fusion L_f of carbon dioxide is equal to the heat of sublimation L_s minus the heat of vaporization L_v. From the numerical values already given for these at the triple point we find

$$L_f = L_s - L_v = 129.88 - 83.12 = 46.76 \text{ gram cal. per gram.}$$

Maass and Barnes have measured the heat of fusion at the triple point and found 45.3 gram cal. per gram. Kuenen and Robson also obtained 43.8 for

TABLE 24.—*Heat of Fusion L_f of Carbon Dioxide in gram. cal./gram and B.t.u./lb.*
(Data from P. W. Bridgeman)

t, °C.	t, °F.	P Atmos.	L_f gm. cal./gm.	L_f B. t. u./lb.
−56.6	− 69.9	5.11	46.7*	84.06*
− 5.5	+ 22.1	2903.2	46.7	84.06
+ 8.5	+ 47.3	3871.1	48.6	87.48
+21.4	+ 70.5	4838.7	50.1	90.18
+33.1	+ 91.6	5806.6	51.0	91.80
+44.2	+111.6	6774.3	51.0	91.80
+55.2	+131.4	7742.1	51.2	92.16
+65.8	+150.5	8709.8	51.3	92.34
+75.4	+167.7	9677.7	51.7	93.06
+84.6	+184.2	10645.5	52.2	93.96
+93.2	+199.8	11613.0	52.8	95.04

* From Plank and Kuprianoff.

this value. The values of L_f at different temperatures and pressures have been determined by Bridgeman[86] and his results are given in Table 24.

The Enthalpy of Carbon Dioxide. When a fluid is permitted to pass adiabatically through a small orifice or a porous plug in such a manner that its kinetic energy of flow on either side of the opening is too small to be of consequence then

$$u_1+p_1v_1=u_2+p_2v_2 \text{ or } u+pv=\text{a constant} \quad \ldots\ldots\ldots \quad (20)$$

where u_1 and u_2 are the specific intrinsic energies, v_1 and v_2 are the corresponding specific volumes at the respective pressures p_1 and p_2 before and after passing through the opening. The function $(u+pv)$ is known as the *enthalpy* of the fluid. In the following discussion we will designate this function as i.

Under isenthalpic conditions or with a constant enthalpic porous plug expansion, changes in both temperature and volume usually accompany the pressure drop across the plug. The limiting ratio of the temperature change Δt to the pressure change Δp as the latter approaches zero is variously known as the Joule-Thompson effect, the Joule-Kelvin effect or the throttling effect. This ratio designated by μ, is analytically defined by the relation

$$\mu=\left(\frac{\partial t}{\partial p}\right)_{(u+pv)} \quad \ldots\ldots\ldots\ldots \quad (21)$$

Kester[87] was perhaps the first to make any attempt to conduct throttling experiments on carbon dioxide over a wide pressure range. He applied his measurements to the equation

$$\left(\frac{\partial t}{\partial p}\right)_{(u+pv)}=a-bp \quad \ldots\ldots\ldots\ldots \quad (22)$$

in which a and b are constants.

Jenkin and Pye[88] conducted an extensive series of throttling experiments with liquid carbon dioxide over a temperature range between +15° and −55° C. The most interesting part of this work was the establishment of an inversion point at −25° C. Below this temperature the liquid is slightly heated after passing through a small orifice. The enthalpy of the liquid was also studied at 50 and 63 atmos. pressure and between −39° and +10° C. A little later another series of measurements was made by the same investigators[89] in which the research range was greatly extended. This work gave values for the enthalpy of the vapor from 10.5 to 50 atmos. pressure and for temperatures from −30° C. to the critical point. The liquid values were found between −33° and −50° C. while the superheated vapor was studied from 21 to 50 atmos. pressure and between +12° and +30° C.

[86] Bridgeman, P. W., *Phys. Rev.*, (2) **3**, 158 (1914).
[87] Kester, F. E., *Physik. Z.*, **6**, 44 (1905); *Phys. Rev.*, (1) **21**, 260 (1905).
[88] Jenkin, C. F., and Pye, D. R., *Trans. Roy. Soc. (London)*, **A 213**, 67 (1914).
[89] Jenkin, C. F., and Pye, D. R., *Trans. Roy. Soc. (London)*, **A 215**, 353 (1915).

Later Jenkin and Shorthose[90] measured the enthalpy of liquid and gaseous carbon dioxide at pressures from 63 to 127 atmos. and temperatures from +12° to +100° C. This work indicated that the earlier values of Jenkin and Pye were in error especially at high pressures. This error was in some cases as high as 7 per cent.

TABLE 25.—*Isenthalpic Values for Carbon Dioxide.*

(Data by Burnett)

Pressure in atmospheres; temperatures in ° K.; μ in ° K. per atmos.

P	0	1	20	40	60	72.9	80	100
				Vapor Isenthalps				
T	379.94	380.64	393.12	404.56	414.39	420.00	422.88	430.22
μ	0.7080	0.7029	0.6118	0.5284	0.4564	0.4154	0.3944	0.3407
T	356.30	357.10	370.92	383.40	394.00	400.00	403.05	410.74
μ	0.7924	0.7860	0.6748	0.5745	0.4892	0.4410	0.4165	0.3546
T	331.40	332.30	347.99	361.90	373.52	380.00	383.27	391.43
μ	0.9054	0.8974	0.6582	0.6348	0.5317	0.4742	0.4452	0.3728
T	304.30	305.35	323.77	339.76	352.85	360.00	363.57	372.35
μ	1.0760	1.0655	0.8816	0.7220	0.5914	0.5200	0.4844	0.3967
T	272.42	273.88	297.03	316.46	331.83	340.00	344.00	353.64
μ	1.3750	1.3590	1.0885	0.8620	0.6826	0.5872	0.5405	0.4280
T	226.91	229.09	263.56	290.42	310.15	320.00	324.63	335.27
μ	2.1272	2.0948	1.5620	1.1470	0.8422	0.6900	0.6184	0.4540
T	208.69	211.26	(252.26)	282.91	304.56	315.00	319.82	330.59
μ	2.5786	2.5338	(1.8181)	1.2826	0.9046	0.7223	0.6381	0.4501
T	181.28	(184.70	237.43	274.42)	298.85	310.00	314.97	325.60
μ	3.4295	(3.3588	2.2620	1.4928)	0.9850	0.7533	0.6500	0.4290
T	157.40	(161.24	226.49	269.35	295.97)	307.50	312.48	322.77
μ	4.343	(4.2514	2.6950	1.6727	1.0380)	0.7630	0.6442	0.3998
T	120.90	(126.80	212.44	264.32	293.71)	305.50	310.36	319.77
μ	6.000	(5.832	3.400	1.926	1.091)	0.7560	0.6179	0.3508
T	76.00	(81.40	198.40	260.85	292.77)	304.50	309.09	317.42
μ	8.396	(8.114	4.288	2.1915	1.1200)	0.7264	0.5724	0.2926
				Critical Isenthalps				
T	0.00	(13.38	182.77	260.56	293.70	304.10)	307.80	313.82
μ	13.580	(13.01	5.783	2.463	1.049	0.6050)	0.4470	0.1906
				Liquid Isenthalps				
T	(195.21	198.25	251.57	281.51	297.44)	303.50	305.92	310.43
μ	(3.7974	3.6800	2.0194	1.0744	0.5716)	0.3804	0.3041	0.1613
T	(245.42	247.07	271.83	287.94	297.79)	302.00	303.81	307.48
μ	(1.6720	1.6312	1.0210	0.6239	0.3812)	0.2774	0.2329	0.1423
T	(265.03	265.92	280.04	290.11	296 87)	300.00	301.41	304.45
μ	(0.9102	0.8924	0.6108	0.4099	0.2751)	0.2127	0.1846	0.1239
T	(275.86	275.93	277.16)	278.34	279.39	280.00	280.32	281.14
μ	(.06978	.06936	.06202)	.05514	.04901	.04543	.04357	.03873
T	(259.24	259.26	259.46)	259.67	259.88	260.00	260.07	260.26
μ	(.01096	.01094	.01064)	.01027	.00993	.00973	.00962	.00931
T	(240.54	240.53)	240.40	240.29	240.10	240.00	239.94	239.79
μ	(−.00704	−.00705)	−.00723	−.00742	−.00761	−.00773	−.00781	−.00801
T	(222.19	222.17)	221.66	221.08	220.44	220.00	219.74	218.98
μ	(−.02537	−.02548	−.02778	−.03040	−.03329	−.03528	−.03464	−.03989

Note: Values between parentheses () in the main part of this table indicate "mathematical" courses of the curves when both liquid and vapor phases are present. Physically and experimentally the temperatures and slopes observed are those of the saturation curve for the pressures corresponding to the values within the parentheses.

[90] Jenkin, C. F. and Shorthose, *Proc. Roy Soc. (London)*, **A 99**, 352 (1921).

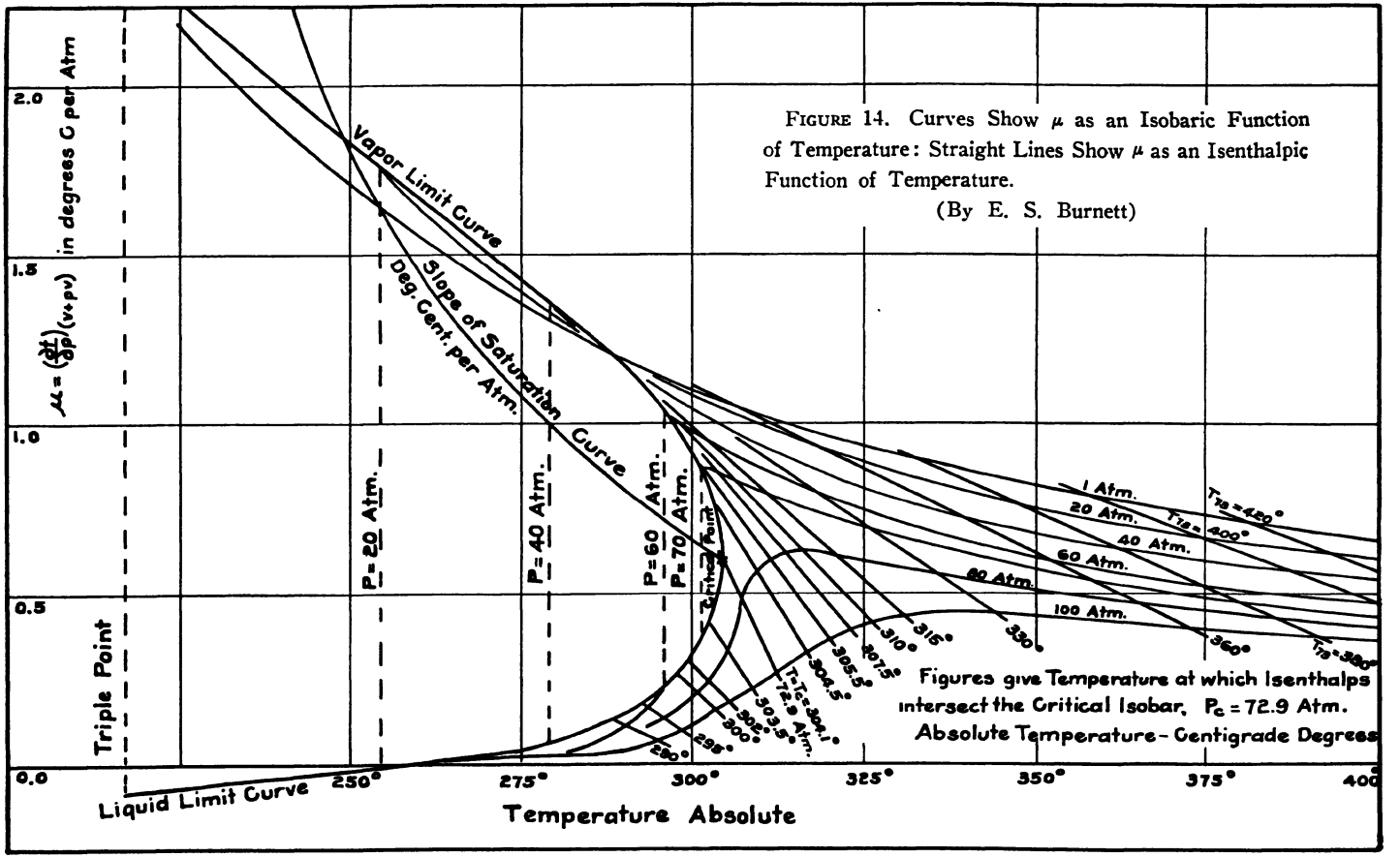

FIGURE 14. Curves Show μ as an Isobaric Function of Temperature: Straight Lines Show μ as an Isenthalpic Function of Temperature.

(By E. S. Burnett)

TABLE 26.—*Isothermal and isobaric values of μ expressed in ° C. per atmos.*
(Data by Burnett)

Temp. ° K.	Pressure in atmospheres 0	1	10	20	40	60	72.9	80	100
				Vapor phase above line					
400.0	0.6475	0.6440	0.6210	0.5950	0.5375	.4790	.4410	.4225	.3635
390.0	0.6755	0.6725	0.6485	0.6200	0.5595	.4965	.4560	.3850	.3235
380.0	0.7080	0.7045	0.6780	0.6475	0.5835	.5165	.4742	.4505	.3855
370.0	0.7415	0.7335	0.7100	0.6775	0.6160	.5405	.4952	.4705	.3995
360.0	0.7790	0.7750	0.7455	0.7110	0.6420	.5685	.5200	.4930	.4155
350.0	0.8195	0.8150	0.7850	0.7500	0.6780	.6020	.5500	.5210	.4340
340.0	0.8640	0.8595	0.8920	0.7950	0.7205	.5425	.5872	.5550	.4500
330.0	0.9140	0.9095	0.8795	0.8450	0.7720	.6925	.6331	.5945	.4490
325.0	0.9425	0.9375	0.9075	0.8745	0.8025	.7230	.6605	.6165	.4420
320.0	0.9710	0.9665	0.9380	0.9050	0.8360	.7570	.6900	.6380	.3570
315.0	1.0020	0.9985	0.9705	0.9395	0.8735	.7970	.7223	.6500	.2210
310.0	1.0360	1.0320	1.0055	0.9765	0.9160	.8435	.7554	.6100	.1585
305.0	1.0710	1.0675	1.0445	1.0155	0.9640	.9000	.7468	.2690	.1270
304.1	1.0775	1.0740	1.0505	1.0240	0.9735	.9100	.6050	.2420	.1215
300.0	1.1070	1.1045	1.0840	1.0600	1.0175	.9675	.2147	.1650	.1005
295.0	1.1480	1.1455	1.1270	1.1090	1.0805	.1990	.1324	.1134	.0794
290.0	1.1920	1.1900	1.1750	1.1635	1.1525	.1156	.9999	.0815	.0619
285.0	1.2395	1.2385	1.2280	1.2245	1.2400	.0761	.06355	.0586	.0478
280.0	1.2900	1.2900	1.2845	1.2915	1.3470	.0515	.0454	.0425	.0364
275.0	1.3455	1.3455	1.3470	1.3645	0.0414	.0355	.0324	.0309	.0275
270.0	1.4050	1.4060	1.4155	1.4455	0.0274	.0246	.0228	.0221	.0202
260.0	1.5375	1.5405	1.5735	1.6375	0.0106	.0101	.00973	.0096	.0090
250.0	1.6885	1.6954	1.7570	0.0^3735	0.0^3733	$.0^3731$	$.0^3730$	$.0^3729$	$.0^3727$
240.0	1.860	1.870	1.974	−0.00723	−0.00742	−.00761	−.00774	−.00781	−.00801
230.0	2.060	2.070	−0.0168	−0.0171	−0.0177	−.0183	−.0187	−.0190	−.0195
220.0	2.2855	2.3035	−0.0294	−0.0304	−0.0323	−.0341	−.0353	−.0359	−.0375

Liquid phase below line

Supplementary values at graphically determined intersections of isotherms and isobars of μ with the saturation curve.

p	1	5	10	15	20	30	40	50	60	65	70	72.9
T	(193.5)	216.2	233.4	245.05	254.1	268.15	279.0	288.0	295.7	299.15	302.35	304.1
μ_v	(3.055)	2.510	2.135	1.922	1.773	1.545	1.371	1.211	1.043	0.937	0.801	0.6050
μ_e	(?)	−0.0346	−0.0083	−0.0031	0.0046	0.0245	0.0575	0.1182	0.2225	0.2985	0.418	0.6050
T	216.9	220.0	230.0	240.0	250.0	260.0	270.0	280.0	285.0	290.0	295.0	300.0
p	5.15	5.95	8.8	12.65	17.6	23.9	31.55	41.0	41.0	52.55	59.0	61.3
μ_v	2.475	2.410	2.200	2.020	1.841	1.675	1.515	1.345	1.345	1.174	0.961	0.914
μ_e	−0.3375	−0.0290	−0.0167	−0.0074	+0.0007	+0.0115	0.0285	0.0625	0.0938	0.1386	0.2095	0.3235

Finally important throttling experiments with carbon dioxide were published by Burnett.[91] These experiments were conducted over a period of time from 1910 to 1923 and in general agree well with the measurements of Jenkin and Pye but comparisons with the results of Jenkin and Shorthose were not made. The measurements cover the liquid and vapor region inclusive of the critical state for pressures from 20 to 75 atmos.,

TABLE 27.—*Enthalpy of Dry Saturated Carbon Dioxide in Kg. Cal. per Kg.*
(From Plank and Kuprianoff)

Temp.	Mollier	Jenkin and Pye	Langen	Eichelberg	Plank and Kuprianoff	Extrapolated
Crit.	134.14	131.6	132.25	132.0		133.50
+ 30	141.32	139.1	140.56	140.1		140.95
25	147.28		146.71	146.2		147.33
20	150.20	149.1	149.92	149.6		151.10
15	152.14	151.4	151.83	151.7		153.17
10	153.50	152.55	153.24	153.3		154.59
5	154.49	153.45	154.30	155.0		155.45
0	155.19	154.1	155.03	155.8	156.13	156.13
− 5	155.68	154.7	155.48	156.6	156.41	
− 10	155.97	155.1	155.76	157.3	156.60	
− 15	156.10	155.2	155.93	157.7	156.70	
− 20	156.11	155.1	156.02	158.0	156.72	
− 25	156.00	154.8	156.03	158.5	156.67	
− 30	155.78	154.45	155.97	158.7	156.56	
− 35		154.1	155.84	158.9	156.39	
− 40		153.6	155.65	159.1	156.17	
− 45		153.3	155.40	159.2	155.89	
− 50		153.0	155.09	159.3	155.57	
− 55				159.4	155.22	
− 56.6					155.09	
− 60					155.06	
− 65					154.87	
− 70					154.52	
− 75					154.06	
− 80					153.49	
− 85					152.86	
− 90					152.16	
− 95					151.42	
−100					150.65	

and temperatures from −24° to +117° C. Unfortunately these experiments were made on a gas having air present in various amounts which sometimes fluctuated between 0.25 per cent and 1.5 per cent in a single experiment. Burnett corrected for this impurity but as Plank and Kuprianoff point out, this injects an uncertainty factor into his results which seriously impairs their value. However, these measurements seem to be the most complete of any recorded to date and the results for μ at constant enthalpy are listed in Table 25 while the isothermal and isobaric values are given in Table 26. On plotting these results the curves shown in Figure 14 were obtained. Burnett found the inversion point in the liquid state to be −24° C.

[91] Burnett, E. S., *Phys. Rev.*, (2) **22**, 590 (1923).

Plank and Kuprianoff developed an equation for calculating the enthalpy of carbon dioxide over quite a wide range of temperature and pressure. This equation may be written in the following form:

$$i = 169.34 + (0.1965 + 0.000115\,t)\,t - 8.3724\frac{p}{\left(\frac{T}{100}\right)^{4.8}}(1 + 0.007424\,p) \quad . \; . \; (23)$$

in which the value of i is obtained in kilogram calories per kilogram, when p is expressed in kg. per square cm., T in degrees Kelvin, and t in degrees centigrade. Values of i obtained by means of this equation are listed in Table 27 together with results obtained by various other investigators. The last column contains extrapolated values from 0° C. to the critical temperature. The extrapolation was very carefully done by these authors and the results, without doubt, represent values very close to the true ones.

TABLE 28.—*Enthalpy of Liquid Carbon Dioxide on the Limit-Curve in kcal./kg.*

t, °C.	Enthalpy
Crit. temp.	133.50
+30	125.90
25	118.80
20	114.00
15	110.10
10	106.50
5	103.10
0	100.00
− 5	96.91
−10	94.09
−15	91.44
−20	88.93
−25	86.53
−30	84.19
−35	81.88
−40	79.59
−45	77.30
−50	75.01
−55	72.72
−56.6	71.97

TABLE 29.—*Enthalpy of Solid Carbon-Dioxide in kcal./kg.*

t, °C.	Enthalpy
−56.6	25.21
−60	23.71
−65	21.49
−70	19.59
−75	17.93
−78.9	16.73
−80	16.41
−85	14.98
−90	13.59
−95	12.23
−100	10.88

The enthalpy of the liquid at any point on the limit-curve may easily be calculated by subtracting the latent heat of vaporization from the enthalpy of the vapor. In a like manner the enthalpy of the solid may be calculated by subtracting the latent heat of sublimation from the enthalpy of the vapor. Values calculated in this manner are given in Table 28 and Table 29. For a more detailed discussion of this subject one should refer to the original paper of Plank and Kuprianoff.

The Entropy of Carbon Dioxide. One may take as a fixed point for the entropy of carbon dioxide in the liquid state at 0° C. the value of 1.00000 k. cal. per kg., and therefore $S_l = 1.0000$ Clausius. Also one may

calculate the entropy of carbon dioxide in the vapor state by means of the expression given by Plank and Kuprianoff which may be stated as follows:

$$S_v = 0.591 + 0.307888 \log T + 0.00023\, T - 0.1039478 \log p$$

$$- 6.44028 \frac{p}{T\left(\frac{T}{100}\right)^{\frac{10}{3}}}(1 + 0.007424\, p) \quad \ldots\ldots\ldots \quad (24)$$

This equation serves to calculate the entropy of the vapor on the limit curve between 0° and −100° C. as well as in the superheated region at various temperatures and pressures up to 35 atmos. The entropy of the liquid may be calculated from the expression

$$S_l = S_v - L_v/T \quad \ldots\ldots\ldots\ldots\ldots \quad (25)$$

and for the solid

$$S_s = S_v - L_s/T \quad \ldots\ldots\ldots\ldots\ldots \quad (26)$$

The entropy and enthalpy values of the liquid at 0° C. are given in Table 30 at various pressures.

TABLE 30.—*Entropy and Enthalpy of Liquid Carbon Dioxide at 0° C.*

p kg./cm.²	S_0	i_0
35.54	1.0000	100.00
40.0	0.9991	99.90
50.0	0.9974	99.69
60.0	0.9957	99.52
70.0	0.9942	99.37
75.0	0.9935	99.30
80.0	0.9928	99.25
90.0	0.9915	99.14
100.0	0.9903	99.05
110.0	0.9892	98.95
120.0	0.9882	98.87

In Figure 15 is shown a temperature entropy diagram plotted from the data of Plank and Kuprianoff. This is a most useful arrangement of data especially from the point of view of compressor design or refrigerating engineering. F. B. Hunt of The Liquid Carbonic Corporation, has transposed the data into English engineering units and constructed a similar diagram. Another diagram similar to this has been constructed by Goosmann and Ambro.[92]

The Surface Tension of Liquid Carbon Dioxide. The capillary constant and surface tension of liquid carbon dioxide was measured by Verschaffelt[93] in 1895. Recently a more extensive series of determinations was made by Quinn.[94] Values are given in Table 31 which were taken from a large scale diagram on which curves were drawn from the data

[92] Goosmann, J. C., *Ice and Refrigeration*, 207-14 (1930).
[93] Verschaffelt, J. E., *Verhandel. Akad. Wetenschappen Amsterdam*. 4, 74 (1895).
[94] Quinn, E. L., *J. Am. Chem. Soc.*, 49, 2704 (1927).

FIGURE 15. Entropy Diagram of Plank and Kuprianoff.

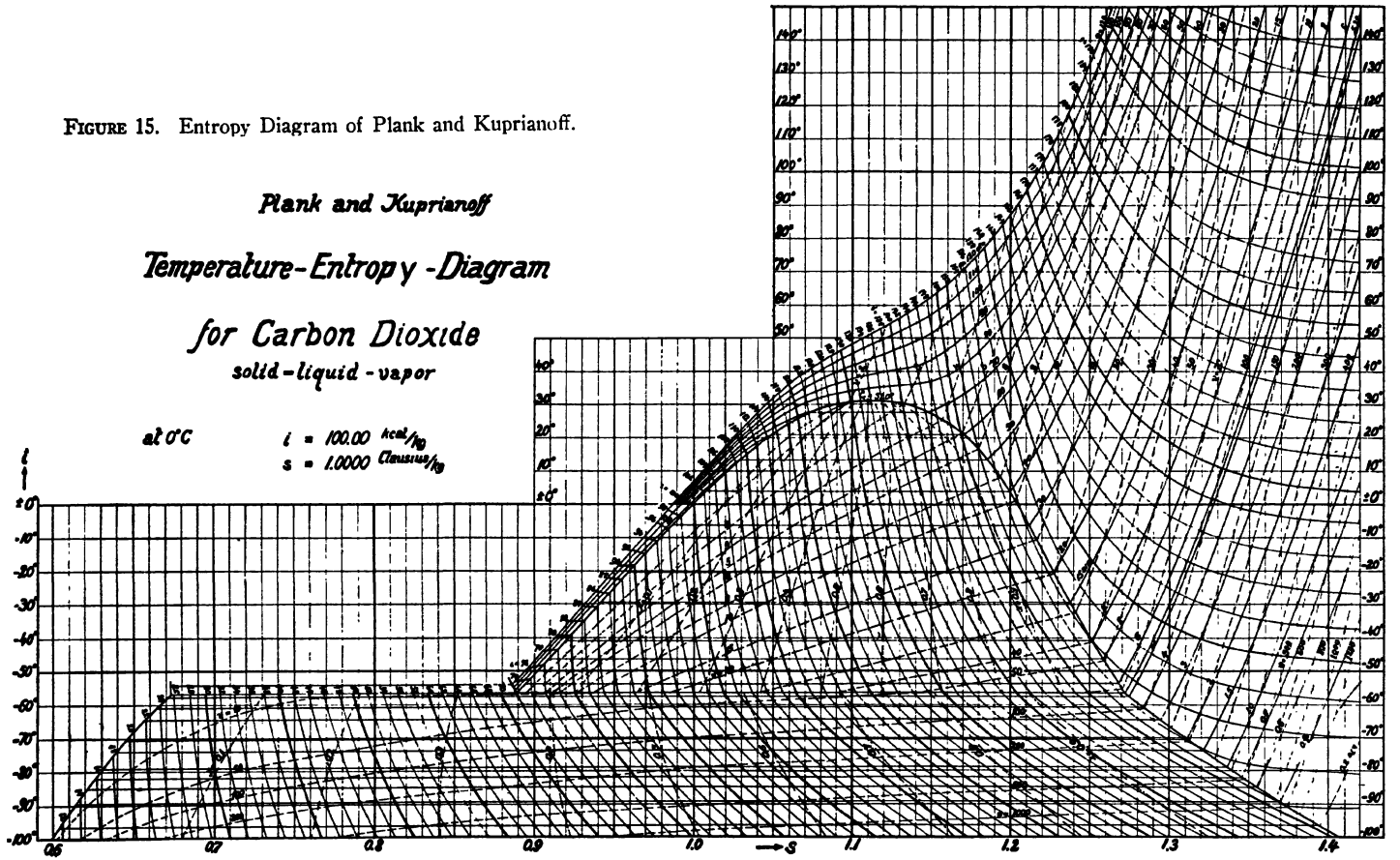

TABLE 31.—*Surface Tension of Liquid Carbon Dioxide.*

Temp. °C.	γ in dynes/cm. According to Verschaffelt	γ in dynes/cm. According to Quinn
31		0.00 Cr. Pt.
30		0.10*
25		0.69
20	1.13	1.45
15	1.87	2.12
10	2.71	2.91
5		3.75
0		4.65
− 5		5.59
−10		6.56
−15		7.57
−20	8.36	8.64
−25		9.71
−30		10.79
−35		11.93
−40		13.17
−45		14.55
−50		15.93
−56.6		17.82* Tr. Pt.

* Extrapolated

of both Verschaffelt and Quinn. The equation for the surface tension curve as given by Quinn is

$$\gamma = 0.0653(31.35 - t)^{1.24} \quad \ldots\ldots\ldots\ldots \quad (27)$$

where γ is the surface tension in dynes per centimeter.

The Dielectric Constant. About the first measurements of the dielectric constant ε for carbon dioxide were made by Linde[95] who found for gaseous carbon dioxide, $\epsilon = 1.060$ at 15° C. and and 39 atmospheres; 1.015 at 19.9 atmospheres and 1.009 at 9.4 atmospheres pressure. For the liquid he found $\epsilon = 1.608$ at −5° C.; 1.583 at 0° C.; 1.540 at 10° C. and 1.526 at 15° C. Riegger[96] found the constant for the liquid at −73° C. to be 1.001392 and Herz[97] obtained 1.50 at 10° C. and 1.27 at the critical temperature. The most recent determinations have been made by Keyes and Kirkwood[98] who measured the dielectric constant of the gas at 35°, 70° and 100° C. at a number of different pressures. They also measured the change in the dielectric constant of the liquid with change in pressure at a temperature of 0° C. Their results for the liquid are as follows:

P, atm.	50	75	100	125	150	175	200
ε	1.6016	1.6187	1.6321	1.6425	1.6526	1.6603	1.6674

The values obtained for the gas are given in Table 32.

The Crystal Form. Gaseous carbon dioxide may be frozen into small snow-like crystals or into large transparent masses according to the method used for producing them. When the solid is produced by the usual method

[95] Linde, F., *Wied. Ann.*, **56**, 546 (1895).
[96] Riegger, H., *Ann. Phys.* (4) **59**, 753 (1919).
[97] Herz, W., *Z. physik. Chem.*, **103**, 269 (1922).
[98] Keyes, F. G., and Kirkwood, J. G., *Phys. Rev.*, **36**, 754-61 (1930).

TABLE 32.—*The Dielectric Constant for Carbon Dioxide Gas.*
(Data by Keyes and Kirkwood)

Pressure Atmos.	Temperature °C.		
	35	70	100
10	1.00971	1.00831	1.00753
20	1.02021	1.01717	1.01549
30	1.03228	1.02693	1.02404
40	1.04649	1.03748	1.03333
50	1.06461	1.04950	1.04306
60	1.08838	1.06305	1.05269
70	1.1309	1.07810	1.06447
80	1.3146	1.09616	1.07707
90	1.4206	1.1159	1.09005
100	1.4559	1.1396	1.1041
126		1.2165	1.1456
151		1.3072	1.1912

of expanding the liquid from a cylinder, the result is a snow-like substance often spoken of as carbon dioxide snow. When, however, liquid carbon dioxide is slowly cooled below the freezing point the result is a transparent mass. This ice-like material becomes opaque very quickly as the temperature increases because the high coefficient of expansion of the solid produces numerous cracks in the block. Liversidge[99] noted that the crystals belong to the cubic system and that they much resembled solid ammonium chloride. Behnken[100] made an exhaustive study of the subject and succeeded in making some excellent photographs of the crystals. He formed the crystals by admitting limited quantities of carbon dioxide to a glass plate cooled by means of liquid air. It was found that by admitting the gas in very small puffs the crystals could be grown to any size. These crystals were undoubtedly isometric and their forms were combinations of cubes and octahedra. Behnken noted a strange phenomenon in that crystals appeared to explode spontaneously. This happened in most cases to the sharpest and best-formed crystals and he supposed it to be due to contraction strains set up in the crystal on cooling. Wahl[101] also studied crystals of carbon dioxide and found them isotropic and in the form of small cubes. X-ray studies made by Mark and Pohland[102] showed an elementary cube with a side of 5.62 Å.

The Index of Refraction. The indices of refraction of various wave lengths of light through carbon dioxide at 0° and 760 mm. pressure have been measured by a considerable number of investigators. A list of these workers with their results is given in Table 33.

The variation of the index of refraction with temperature and pressure for sodium light is expressed by Walker by means of the equation

$$\mu-1=1+\frac{.0004510}{(1+.00380\,t)}\frac{p}{76} \quad \ldots\ldots\ldots\ldots \quad (28)$$

[99] Liversidge, A., *Chem. News*, **71**, 152 (1895); **77**, 216 (1898)
[100] Behnken, H. E., *Phys. Rev.*, **35**, 66 (1912).
[101] Wahl, W., *Proc. Roy. Soc. (London)*, **89 A**, 327 (1914).
[102] Mark, H., and Pohland, E., *Z. Krist.*, **61**, 293 (1925).

TABLE 33.—*Refractive Index of Carbon Dioxide at 0° C. and 760 mm. Pressure.*

Wave length of light	Refractive Index	Observer	Reference
White	1.0004497	Biot and Arago	*Mém. acad.*, **7**, 301 (1806)
White	1.0004495	Dulong	*Ann. chim. phys.*, (2) **31**, 154 (1826)
White	1.0004500	Jamine	*Ann. chim. phys.*, (3) **49**, 282 (1857)
0.5352 N	1.0004507	Kettler	"Farbenzerstreuung der Gase," Bonn, (1865)
0.6708 N	1.0004477	"	"Farbenzerstreuung der Gase," Bonn, (1865)
0.4290 N	1.0004960	Croullebois	*Ann. chim. phys.*, (4) **20**, 136 (1870)
0.5260 N	1.0004560	"	" " " " " "
0.6560 N	1.0003950	"	" " " " " " "
White	1.0004400	"	" " " " " " "
0.4800 N	1.0004587	Mascart	*Compt. rend.*, **78**, 617 (1874)
0.6438 N	1.0004532	"	" " " "
White	1.0004494	"	" " " " "
0.4677 N	1.0004550	Perreau	*Ann. chim. phys.*, (7) **7**, 289 (1896)
0.6438 N	1.0004487	"	" " " " " " "
0.5890 N	1.0004510	Walker	*Phil. Trans.*, **201 A**, 435 (1903)
0.4359 N	1.0004563	Koch	*Ann. Physik.*, (4) **17**, 658 (1905)
0.8678 N	1.0004579	"	" " " " "
0.3342 N	1.0004668	Rentschler	*Astrophys. J.*, **28**, 435 (1908)
0.5771 N	1.0004487	"	" " " " "
0.4359 N	1.0004589	Stuckert	"Ueber die Lichtbrechnung der Gase
0.6708 N	1.0004466	"	und ihre Verwendung in analytischen Zweeken." Karlsruhe (1910)
0.4472 N	1.0004568	Gruschke	"Die Brechung und Dispersion des
0.6678 N	1.0004475	"	Lichtes in einigen Gasen," Breslau, (1910)

where μ is the index of refraction, and p is expressed in cm. of Hg. Chappuis and Rivière[103] suggested the equation

$$\mu-1=.000540\,p(1+.0076\,p+.0000050\,p^2). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

as an expression which showed the change in μ with change in pressure. The constants were calculated with values obtained at 21° C. Posejpal[104] found the equations

$$\frac{(\mu-1)}{D}=\text{constant}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

and

$$\frac{(\mu^2-1)}{(\mu^2+2)D}=\text{constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

hold with a fair degree of accuracy for pressures up to 19 atmos.

The index of refraction of liquid carbon dioxide was found by Bleekrode[105] to be 1.999 at 12.5° C.; 1.192 at 15.5° C.; 1.186 at 18.5° C. and 1.173 at 24° C.

Adsorption. Most of the earlier investigations on the adsorption of carbon dioxide on the surface of solid bodies were directed towards its action on minerals and glass. Scheermesser[106] made an investigation of the

[103] Chappuis, J., and Rivière, C., *Compt. rend.*, **103**, 37 (1886).
[104] Posejpal, V., *J. phys. radium*, **2**, 85 (1921); **4**, 451 (1923).
[105] Bleekrode, L., *Proc. Roy. Soc. (London)*, **37**, 339 (1884).
[106] Scheermesser, F., *Vierteljahrsschr. prakt. Pharm.*, **20**, 570 (1871).

adsorption of carbon dioxide by sand and clay and noted an increase in the adsorption when the mixture was wet, also that carbon dioxide was given off in the sunlight and readsorbed in the shade. Hannay[107] observed that carbon dioxide under pressure was adsorbed by glassy silicates, borates, and phosphates. Bunsen[108] studied the adsorption of carbon dioxide on glass and made some very interesting observations on the rate and the probable mechanism of the reaction. In the light of our present knowledge, however, these observations are of no special importance. Matignon and Marchal[109]

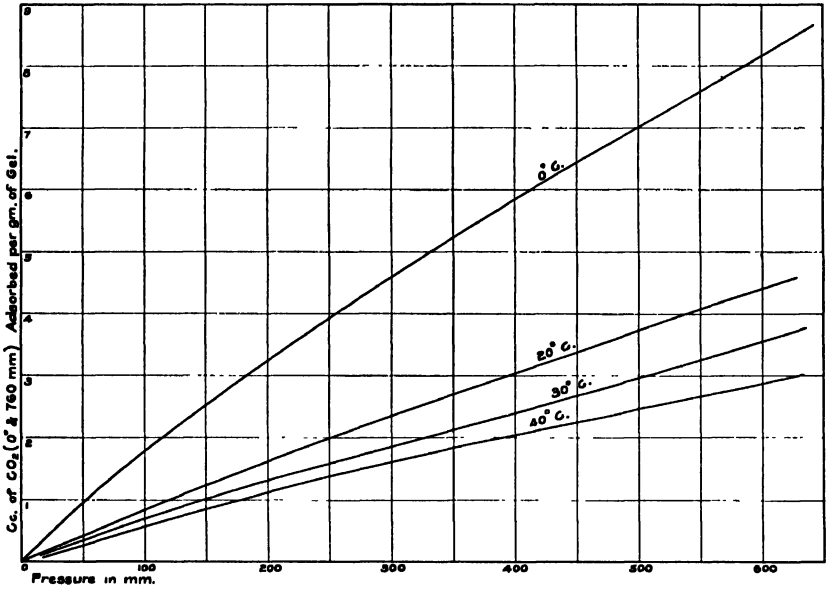

FIGURE 16. Adsorption of Carbon Dioxide by Silica Gel.
(Data by Patrick, Preston and Owens)

determined the nature of the action of carbon dioxide under 10 atmospheres pressure on *quartz, mica, dioptase, wallastonite, talc, asbestos* and *glass.*

At present most of the interest in the adsorption of carbon dioxide on solids seems to be directed towards silica gel and activated carbon as the adsorbents. This condition has developed because of the practical use of these substances for the purification of carbon dioxide in the manufacturing plant and also because of certain theoretical ideas that recently have been advanced. The action of carbon dioxide on silica gel has been studied by Patrick, Preston and Owens[110] and the isotherms shown in Figure 16

[107] Hannay, J. B., *Proc. Roy. Soc. (London)*, **32**, 407 (1881).

[108] Bunsen, R., *Wied. Ann.*, **20**, 545 (1883); **22**, 145 (1884); **24**, 321 (1885); **29**, 161 (1886); *Phil. Mag.* (5) **22**, 530 (1886).

[109] Matignon, C., and Marchal, G., *Compt. rend.*, **170**, 1184 (1920).

[110] Patrick, W. A., Preston, W. C., and Owens, A. E., *J. Phys. Chem.*, **29**, 421-34 (1925).

were constructed from their data. From these curves it becomes evident at once that the degree of adsorption is a function of the temperature as well as of the pressure and, as will be shown later, of the previous history of the sample of adsorbing material. Use is made of these facts in the process of de-gassing adsorbing substances by submitting them to very high temperatures and to very low pressures. Perhaps the most important theoretical idea advanced by Patrick and his co-workers is that the adsorbed gas exists as a liquid in the pores of the solid. Thus the surface tension of the liquefied gas would play an important part in the process of adsorption. How this surface action of the liquid enters into the problem is indicated by the equation which has been developed by Patrick and his associates. This equation may be put into the form

$$V=K\left(\frac{P\gamma}{P_0}\right)^{\frac{1}{n}} \quad \ldots\ldots\ldots\ldots\ldots \quad (32)$$

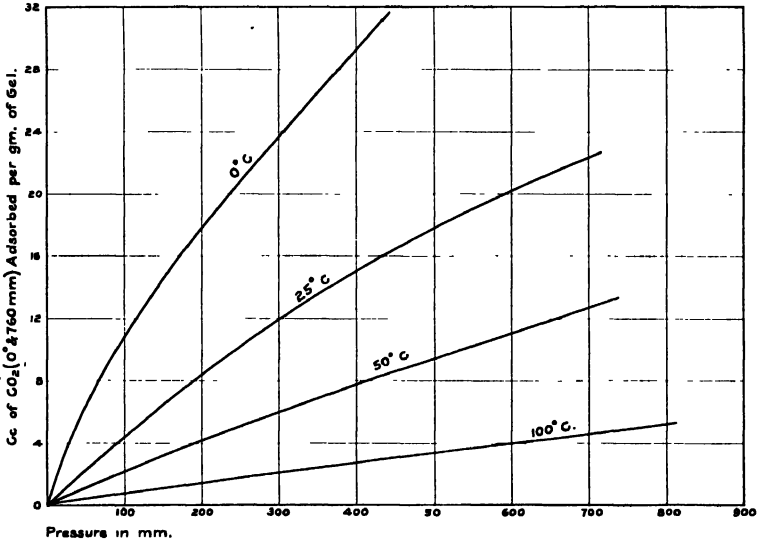

FIGURE 17. Adsorption of Carbon Dioxide by Silica Gel.
(Data by Magnus and Kieffer)

where V is the volume of liquefied gas adsorbed per gram of gel, P is the equilibrium pressure, P_0 is the ordinary saturation pressure at the temperature at which the surface tension is measured, γ the surface tension of the liquefied gas, and K and $\frac{1}{n}$ are constants dependent entirely upon the structure of the gel. The constants for carbon dioxide at 0° C. have been calculated as $\frac{1}{n}=0.866$ and $K=0.145$ while at 20° C. the corresponding values for these constants are 0.898 and 0.558. This equation is of little

importance from a practical point of view at present but is of considerable theoretical interest.

How the history of the adsorbent affects its action as an adsorbing agent is easily seen by comparing the isotherms just given in Figure 16 and those of Magnus and Kieffer[111] which are shown in Figure 17. The silica gel used in the first investigation by these authors was made by treating sodium silicate with C. P. hydrochloric acid. The resulting gel was

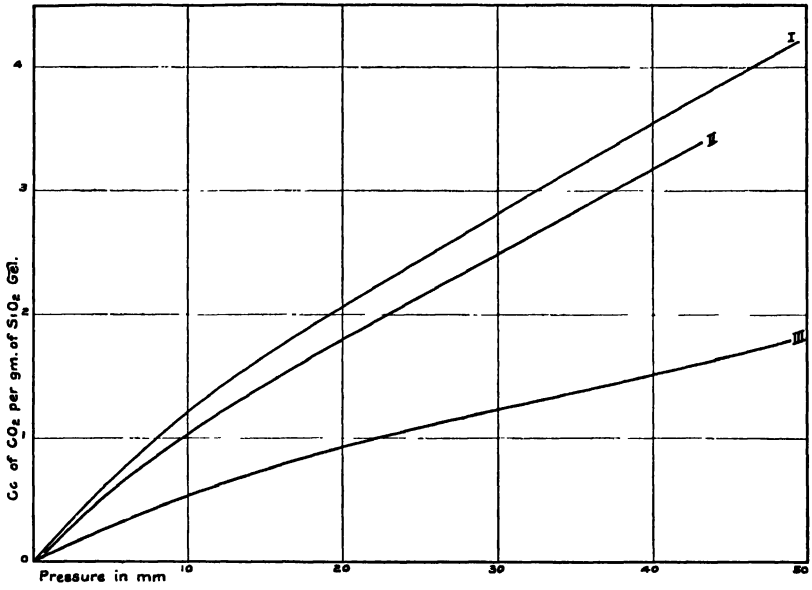

FIGURE 18. The Adsorption of Carbon Dioxide on Silica Gel at 0° C.

washed for two weeks with running water, air dried for eleven days and refluxed with aqua regia for fifteen hours. It was again washed with distilled water for ten days, air dried and heated in an electric furnace in an atmosphere of dry air to a maximum temperature of 400° C. and after grinding and sizing it was reheated to 550° C. for twelve hours. It then showed a water content of 3.64 per cent. A second sample was heated two weeks longer at a temperature of 700° to 750° C. and then showed a water content of 1.28 per cent. The gel used by Magnus and Kieffer was also made from sodium silicate and purified with aqua regia but the de-gassing was accomplished in a vacuum oven at 300° C. and a continuous pressure of 0.003 mm. After this treatment the sample showed a water content of 5.4 per cent.

Kälberer and Mark[112] found that the initial portion of the adsorption isotherms for carbon dioxide on many silica gels are linear for a considerable distance which indicates adsorption on a plane surface. For other

[111] Magnus, A., and Kieffer, R., *Z. anorg. allgem. Chem.*, **179**, 215-32 (1929).
[112] Kälberer, W., and Mark, H., *Z. physik. Chem.*, Abt. A **139**, 151-62 (1928).

gels the initial portion of the isotherms exhibits a much faster increase in the amount adsorbed than in the succeeding linear region of the curve which indicates active areas in the gel. Later Kälberer and Schuster[113] observed that some isotherms have convex curvatures in the initial portion which indicates capillary condensation of carbon dioxide to a liquid in the gel. All these effects may be superimposed on each other. Comparison of isotherms of these investigators made with different samples of silica gel, and plotted in Figure 18, again shows how the history of the sample affects not only the degree of adsorption but also the shape of the curve. The data from which Curve I was plotted resulted from a gel de-gassed at 200° C., Curve II from a gel de-gassed at 350° C. and Curve III from a gel de-gassed at dark red heat for about one hour. Figure 19 shows the same isotherms at higher pressure and it is of interest to note the change in the relative order of these three curves. Isotherms for carbon dioxide on silica gel were also constructed from the data by Magnus and Kälberer and they check closely the values of Magnus and Kieffer.

Some later measurements on the adsorption of gases on silica gel have been made by Sameshima[114] who determined the velocity and amount of

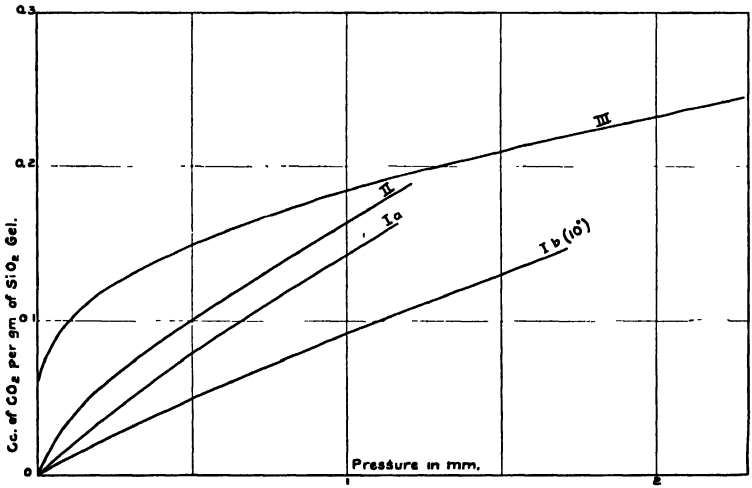

FIGURE 19. The Adsorption of Carbon Dioxide on Silica Gel at 0° C. (Curve Ib at 10° C.)

adsorption of gases by dehydrated silica gel at 25° C. and one atmosphere pressure. Under these conditions 1 gram of gel adsorbed 46.53 cc. of ammonia, 6.4 cc. of carbon dioxide and 4.5 cc. of ethylene.

The most active adsorbing agent for carbon dioxide seems to be charcoal. As in the case of gels the history of the adsorbing agent exerts a considerable influence on the quantity of carbon dioxide it is capable of

[113] Kalberer, W., and Schuster, C., *Z. physik. Chem.*, Abt. A **141**, 270-96 (1929).
[114] Sameshima, J., *Bull. Chem. Soc.*, (Japan), **7**, 133-5 (1932).

taking up. Yet when the isotherms of the various investigators are plotted together the similarity of the curves is quite remarkable. Such plots have been made on a large scale graph for the purpose of comparing the results of several investigators, and these curves gave the values shown in Table 34.

TABLE 34.—*Showing the Volume of Carbon Dioxide (cc. at 0°C. and 760 mm. per gram) Adsorbed on Charcoal According to Various Investigators.*

Temperature = 0° C.

Equil. pressure in mm.	Magnus and Kälberer	Richardson	Homfray	Richardson and Woodhouse	Titoff	Magnus and Kratz
50	19.7	20.0	18.6	16.1	21.7	19.7
100	27.4	28.5	28.2	25.7	30.6	30.1
150	32.7	34.3	35.0	32.7	37.3	38.2
200	36.3	39.0	40.3	38.6	42.5	45.1
250	39.0	42.6		43.7	46.3	51.8
300	41.2	45.3		48.2	49.3	
350	43.4	47.4		52.0	52.0	
400	45.5	49.2		55.4	54.4	
450	47.6	50.8		58.6	56.4	
500	49.7	52.3		61.7	58.2	
550		53.8		64.6	59.9	
600		55.4		67.5	61.6	
650				70.0	63.1	
700				72.3	64.5	

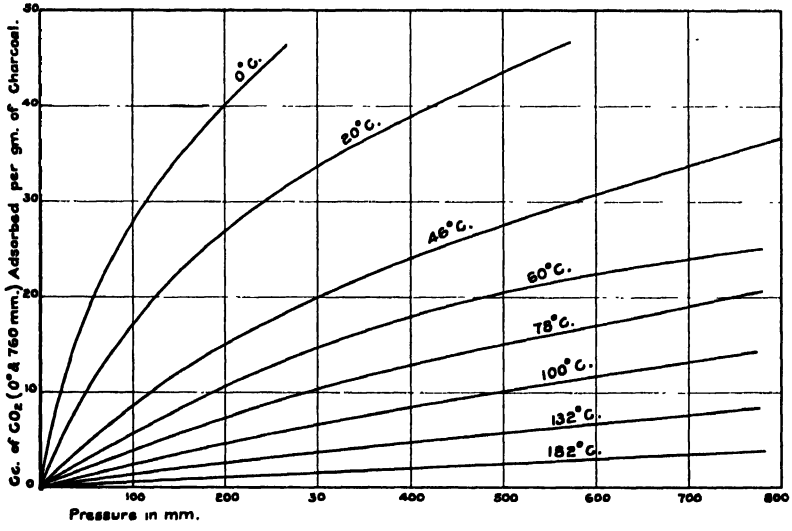

FIGURE 20. Adsorption of Carbon Dioxide by Charcoal.
(Data by Homfray)

The adsorbing material used by Miss Homfray[115] was made by heating cocoanut shell fragments in an oven for about five hours. The granules,

which were about 10 cu. mm. in size, were then boiled with nitric acid to remove the mineral matter and after washing with distilled water were dried by strong heating under reduced pressure. The eight isotherms shown in Figure 20 were plotted from data obtained by Miss Homfray.

Titoff[116] *made his charcoal by distilling cocoanut shells under sand. The product was then heated to about 550° C. in a long combustion tube under*

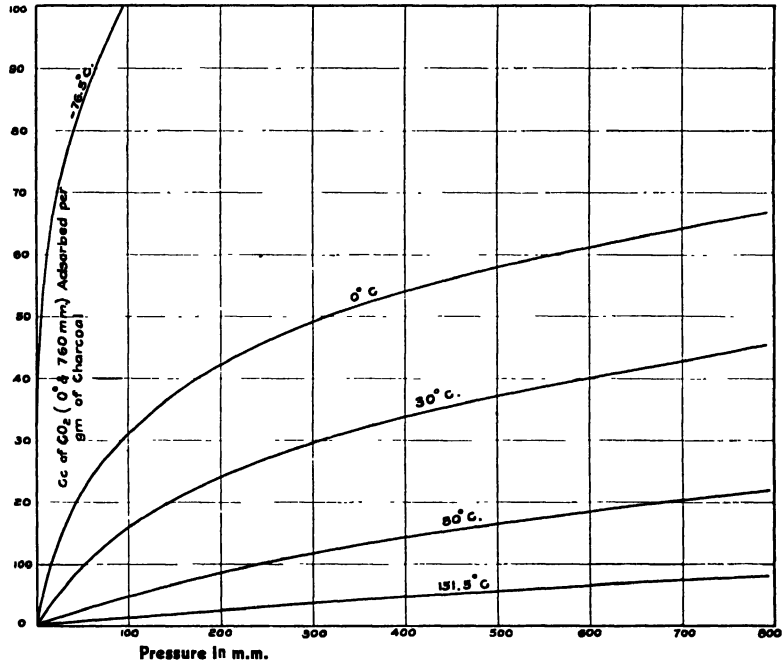

FIGURE 21. Adsorption of Carbon Dioxide by Charcoal.
(Data by Titoff)

the simultaneous action of a water pump. The grains of charcoal were then sized so they varied from 200 to 20 mg. with an average of 77 mg. The mineral matter was removed with acid and after drying the charcoal was de-gassed in the reaction flask at 400° C. under a pressure of 0.001 to 0.003 mm. of mercury. The isotherms obtained by this investigator are shown in Figure 21.

Richardson's[117] results were obtained with an adsorbent made by heating fragments of cocoanut shells in an iron tube immersed in a bath of molten antimony. The temperature was kept near 630° C. for about one hour.

[116] Titoff, Alexander, *Z. physik. Chem.*, 74, 641-78 (1910).

[117] Richardson, L. B., and Woodhouse, J. C., *J. Am. Chem. Soc.*, 45, 2638-53 (1923).

The results listed under Richardson and Woodhouse were obtained on a steam-activated charcoal, obtained from the Barneby Cheney Engineering Company. The de-gassing was accomplished at 425° for four hours under a vacuum of less than 1 mm.

Unfortunately details concerning the manufacture of the charcoal used by Magnus and Kälberer[118] are lacking. The de-gassing took place at a temperature of 600° C.

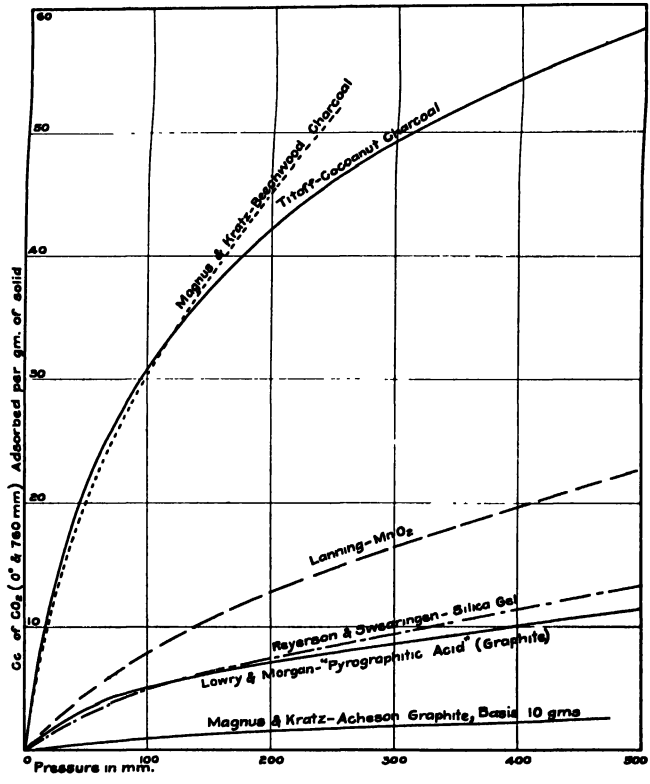

FIGURE 22. Adsorption of Carbon Dioxide by Various Solid Substances at 0° C.

Magnus and Kratz[119] made their charcoal by the destructive distillation of beechwood at 540° C. and a pressure of about 0.15 mm. of mercury. The ash content was 1.69 per cent based on the dry material. The charcoal was finally de-gassed for 5 days at a temperature of 320° to 340° C. during which a vacuum of less than 0.001 mm. was maintained on the system.

Hirano[120] found that cane sugar charcoal increased its efficiency as an adsorbent for carbon dioxide with temperatures of carbonation up to 800°

[118] Magnus, A., and Kalberer, W., *Z. anorg. allgem. Chem.*, **164**, 345-56 (1927).
[119] Magnus, A., and Kratz, H., *Z. anorg. allgem. Chem.* **184**, 241-71 (1929).
[120] Hirano, H., *J. Chem. Soc. Japan*, **50**, 439-40 (1929).

but at 900° C. the adsorbing effect was slightly decreased. Allmand and Chaplin[121] determined the isotherms for nine samples of charcoal at 25° C. and a pressure range from 0.01 to 0.15 mm. Burrage[122] studied the adsorption isothermal of carbon dioxide by a static method over a pressure range from 0.04 to 81 mm. while Magnus and Giebenhain[123] made adsorption determinations of carbon dioxide on six different charcoals at very low pressures. Remy and Hene[124] made a comparison between the dynamic and static methods for determining adsorption isotherms for carbon dioxide and found that the dynamic method gave the lower values.

According to the researches of Lanning[125] manganese dioxide ranks in about the same class as silica gel as an adsorbent for carbon dioxide. He prepared his manganese dioxide according to the method proposed by Frèmy.[126] Granules of about 6 to 10 mesh were selected and the adhering water separated by means of a suction filter after which they were subjected to a pressure of several tons per square inch for 48 hours. The compressed cakes were then dried in an air bath for three hours at a temperature of 110° C. Four other samples were used for the adsorption tests but the final treatment of these was slightly different from the one just described. The results obtained with this adsorbing material are shown by a curve in Figure 22. The other isotherms differed only slightly from this one. Foote and Dixon[127] showed that the presence of water on the manganese dioxide decreased the adsorbing capacity considerably.

The effect of catalytic adsorption of carbon dioxide on metallized silica gels was studied by Reyerson and Swearingen.[128] The effect on such substances would in general be that of silica gel plus any specific adsorption which might be due to the metals deposited as films on the surface of the gel. The results obtained in this investigation are shown in Table 35.

TABLE 35.—*The Adsorption of Carbon Dioxide by Metallized Silica Gels at 0° C.*

The values in the table are cc. of carbon dioxide (0° and 760 mm.) adsorbed by one gram of adsorbent.

(Data by Reyerson and Swearingen)

Pressure in mm. of Hg. .	100	200	300	400	500	600	700
Silica gel	4.98	7.15	9.25	11.45	13.65	15.70	17.80
Silverized gel	4.25	7.30	9.80	12.20	14.55	16.80	19.20
Platinized gel	4.65	8.00	10.75	13.00	14.80	16.60	18.45
Palladized gel	7.20	12.30	15.90	19.30	23.00	26.20	29.60
Copperized gel	5.30	8.50	11.20	13.90	16.50	19.20	21.85

The uncertainty regarding the chemical nature of activated charcoals has led to researches in which graphite was used as the adsorbing agent.

[121] Allmand, A. J., and Chaplin, R., *Proc. Roy. Soc. (London)*, **A 132**, 460-79 (1931)
[122] Burrage, L. J., *J. Phys. Chem.*, **36**, 2272-83 (1932).
[123] Magnus, A., and Giebenhain, H., *Z. physik. Chem.*, A **164**, 209-22 (1933).
[124] Remy, H., and Hene, W., *Kolloid- Z.*, **62**, 154-7 (1933).
[125] Lanning, C. E., *J. Am. Chem. Soc.*, **52**, 2411-15 (1930).
[126] Frèmy, *Compt. rend.*, **82**, 1231 (1879).
[127] Foote, H. W., and Dixon, J. K., *J. Am. Chem. Soc.*, **52**, 2411 (1930).
[128] Reyerson, L. H., and Swearingen, L. E., *J. Phys. Chem.*, **31**, 88-101 (1927).

Magnus and Kratz[129] conducted an investigation on the adsorption of Ceylon graphite and Acheson graphite. In the former investigation the pressures were not carried high enough to make a good isotherm on the scale we have used, but their results on Acheson graphite are shown for 0° C. in Figure 22. In order to separate the curve from the pressure axis the volumes of gas are based on 10 grams of graphite instead of 1 gram as in the case of all other isotherms. Lowry and Morgan[130] made an adsorbing material from graphite having an adsorbing capacity for carbon dioxide practically the same as silica gel. They treated powdered Ceylon graphite with H_2F_2 and after washing and drying, digested with fuming nitric acid. The product which is often called "graphitic acid" was exploded in a vacuum producing "pyrographitic acid". This substance has been shown to be simply finely divided graphite. Blocks made by compression of this material had an adsorptive capacity of about one-third to one-fourth that of the best charcoal. Of the several isotherms they constructed, one has been selected for reproduction in Figure 22.

In order to set some idea of the relative adsorptive capacities of charcoals, gels etc., representative curves for each class of substances have been plotted in Figure 22. Perhaps the most interesting thing shown by this diagram is the high adsorptive capacity of beechwood charcoal. Apparently this is the best adsorbent yet found for carbon dioxide, at least under the pressures indicated by the upper portion of this curve.

Various other substances have been investigated more or less extensively for their adsorptive action on carbon dioxide. Munro and Johnson[131] found alumina a good adsorbing agent. Nikitin and Jurjew[132] studied the action of carbon dioxide on gels of TiO_2 and SnO_2, with the following results:

Substance	Drying temp. °C.	Water content in %	Pressure of CO_2 in mm.	Adsorption temp. °C.	Adsorption in cc.
SnO_2	400	0 9	738.4	12 7	21.2
TiO_2	250	4.8	741.0	14.0	127.8
TiO_2	175	7.8	754.2	15.3	123.3

The weight of the gel in each case was 4.2717 grams and the amount of gas adsorbed and indicated in the last column was calculated to standard conditions. Kälberer and Mark[133] determined the adsorptive action of aluminum foil for carbon dioxide and from their results calculated the thickness of the layer of adsorbed carbon dioxide on the foil, at 0°, 45° and 65° C., to be of the order of 1.5×10^{-8} cm. Adsorption of carbon dioxide on bare and oxygen covered surfaces of silver has been investigated by Drake and Benton.[134] Bare silver showed only an instantaneous physical adsorption for carbon dioxide at −78° and 0° C. with a heat of adsorp-

[129] Magnus, A., and Kratz, H., *Z. anorg. allgem. Chem.*, **184**, 241-72 (1929).
[130] Lowry, H. H., and Morgan, S. O., *J. Phys. Chem.*, **29**, 1105 (1925).
[131] Munro, L. A., and Johnson, F. M. G., *Ind. Eng. Chem.*, **17**, 88 (1925).
[132] Nikitin, N. J., and Jurjew, W. J., *Z. anorg. allgem. Chem.*, **171**, 281-4 (1928).
[133] Kälberer, W., and Mark, H., *Z. physik. Chem.*, Abt. A **139**, 151-62 (1928).
[134] Drake, L. C., and Benton, A. F., *J. Am. Chem. Soc.*, **56**, 506-11 (1934).

tion of about 5 kg.-cal. On silver surfaces occupied by adsorbed oxygen, activated adsorption of carbon dioxide occurred between 0° and 200° C. Silver surfaces occupied by silver oxide reacted with carbon dioxide to form silver carbonate at temperatures as low as 56° C. Isotherms for the adsorption of carbon dioxide on finely divided gold were constructed by Magnus and Klar[135] for 0°, 20° and 40° C. and pressures up to 520 mm. of mercury. It was found that at low pressures the adsorption does not follow Henry's law, the adsorption being always greater than that corresponding with the law. Somewhat later Magnus and Klar[136] studied the adsorption isotherms of carbon dioxide at the same temperatures on pyrophoric iron and gold powder. The adsorption of carbon dioxide on palladium oxide has been studied by McKinney.[137] Bosworth[138] found that mercury drops, falling through a mixture of sulfur dioxide, carbon dioxide and water vapor, selectively adsorbed these gases on the surface of the mercury as monomolecular layers.

Interesting experiments were made by Bangham and Fakhoury[139] in which they measured the expansion of charcoal on adsorption of gases and vapors. They found the expansion directly proportional to the square of the amount of gas adsorbed. The expansion caused by the adsorption of carbon dioxide amounted roughly to 0.101 per cent at 30° C. and one atmosphere pressure. In some later experiments[140] these investigators derived the quantative expression

$$x=K\frac{s}{S-s} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (33)$$

to represent the linear expansion x of a charcoal rod during the adsorption of gases. In this equation s is the weight of the gas taken up per unit weight of adsorbent while K and S are constants.

Drucker[141] made a study of the effect of adsorption on the coefficient of friction of a binary mixture of gases passing through a glass tube. He calculated the thickness of the adsorbed layers of carbon dioxide on the surface of the glass to be 1.0×10^{-8} cm. and that of water to be 5.5×10^{-8} cm. The coefficient of friction is not a linear function of the gas composition and he explains this as being due to the selective adsorption of the various components. The adsorption of carbon dioxide and nitrous oxide on charcoal has been determined by Richardson and Woodhouse as single gases and also in mixtures of varying composition. The replacement of one gas already adsorbed on charcoal by another, is rather an interesting reaction. The replacement takes place rapidly at first but the speed gradually becomes slower and slower and complete replacement never takes place.

[135] Magnus, A., and Klar, R., Siebert Festschr. **1931**, 235-9.
[136] Magnus, A., and Klar, R., *Z. physik. Chem.*, A **161**, 241-54 (1932).
[137] McKinney, P. V., *J. Am. Chem. Soc.*, **55**, 3626-32 (1933).
[138] Bosworth, R. C., *Trans. Faraday Soc.*, **28**, 896-902 (1932).
[139] Bangham, D. H., and Fakhoury, N., *Nature*, **122**, 681-2 (1928).
[140] Bangham, D. H., and Fakhoury, N., *Proc. Roy. Soc. (London)*, A **130**, 81-9 (1930).
[141] Drucker, Carl, *Z. Elektrochem.*, **35**, 640-4 (1929).

That is to say, the amount of the second gas adsorbed never becomes equal to that which would have been adsorbed from a mixture of the same composition thoroughly mixed before being admitted to the charcoal. The adsorption of carbon dioxide on activated charcoal in the presence of carbon tetrachloride and hydrogen cyanide was determined by Chaplin[142] on several charcoals at 25° C. His results show that adsorbed singly they impede but do not change the nature of the adsorption process for carbon dioxide. When adsorbed together, however, they suppress the irreversible adsorption of carbon dioxide completely and allow only superimposed simple adsorption. A theoretical treatment of this subject from a thermodynamic standpoint has been made by Krichevskiĭ[143] who deals with the kinetics of the oxygen-carbon dioxide system on silica gel in terms of adsorption of the two phases.

The Heat of Adsorption. Because of its theoretical importance the heat of adsorption of vapors and gases have assumed special importance in recent researches. In general it may be said that the heat of adsorption is not only a function of the temperature at which the adsorption takes place but also of the equilibrium pressure of the system. In the region where Henry's law holds, i. e. at very low pressures, the degree of adsorption is in many cases practically a linear function of the pressure. This region has been studied extensively not only for the degree of adsorption but the heat of adsorption as well. In some cases the ratio of adsorption to the

TABLE 36.—*Heat of Adsorption of Carbon Dioxide on Various Adsorbing Agents in the Region of Validity of Henry's Law.*

Adsorbent	$\frac{A}{p}$ 25°	Q in gram cal. per mole of gas adsorbed 12.5°	25°	37.5°
Charcoal 1	15.9	7900	about 7700	
Charcoal 2	15.4		7720	
Charcoal 1	14.1	7790	7570	7320
Charcoal 1	12.2	7550	7320	7040
Charcoal 2	11.6	7520	about 7300	
Charcoal 1	8.2	7250	7030	6800
Silica gel	2.37		6958	
Silica gel	2.44	7065	6830	6600
Graphite A	0.0603	7730	7540	7320
Graphite C	0.0214	7700	7460	7230
Graphite C	0.0182	7490	7250	7020

Charcoal samples marked 1 were made from beechwood, those marked 2 were made from cocoanut shells. Graphite A was Acheson graphite and graphite C was Ceylon graphite. A is the adsorption coefficient of carbon dioxide in micromoles ($=10^{-6}$ mole), p is the equilibrium pressure expressed in mm. of Hg.

pressure remains quite constant up to a pressure of about 10 mm. but in others it shows a tendency to change after a pressure of 2 to 3 mm. has been reached. The work of Magnus and Kratz[144] is interesting as it compares the heat of adsorption of several samples of charcoal and other

[142] Chaplin, R., *Trans. Faraday Soc.*, **30**, 249-60 (1934).

[143] Krichevskiĭ, I. R., *J. Phys. Chem. (U. S. S. R.)*, **5**, 742-9 (1934).

[144] Magnus, A., and Kratz, H., *Z. anorg. allgem. Chem.*, **184**, 241-71 (1929).

adsorbents in the region where Henry's law is valid. These data are given here as Table 36.

Magnus and Giebenhain also measured the heat of adsorption on a purified charcoal at 0° and at 25° C. Tables 37, 38, 39 and 40 give their results.

TABLE 37

Adsorption Temp. 0° C.

p in mm.	Q in gm.-cal./mole
0.92	8467
2.00	8247
3.54	8184
6.90	8091
10.00	7917
56.40	7506
211.10	7283
505.70	6739

TABLE 38

Adsorption Temp. 0° C.

p in mm.	Q in gm.-cal./mole
0.0765	12462
0.484	10496
0.89	9597
4.89	8542
18.30	7910
26.90	7680
58.20	7384
70.10	7268
150.30	7194
278.80	7062
521.10	7006

TABLE 39

Adsorption Temp. 0° C.

p in mm.	Q in gm.-cal./mole
0.232	8254
0.413	8194
0.742	8126
1.641	7977
2.329	7925
6.800	7732

TABLE 40

Adsorption Temp. 25° C.

p in mm.	Q in gm.-cal./mole
0.517	7710
0.867	7766
1.905	7735
4.015	7558
6.300	7517
13.300	7434

The heats of adsorption of carbon dioxide on silica gel are in general somewhat lower than on charcoal at the same equilibrium pressures. Several investigators have calculated the heat of adsorption by means of the Clausius-Clapeyron equation but recently a number of direct measurements

TABLE 41

Adsorption of Carbon Dioxide on Silica Gel at 0° C.

p in mm.	Q in gm.-cal./mole
0.630	7371
0.800	7343
1.010	7290
1.300	7398
1.498	7343
1.609	7362
2.235	7300
5.50	7270
8.70	7290
18.20	7150
36.40	7104
63.45	7033
92.50	6997

TABLE 42

Adsorption of Carbon Dioxide on Silica Gel at 25° C.

p in mm.	Q in gm.-cal./mole
1.350	6958
2.430	6936
3.250	6942
4.746	6950
5.18	6942
9.15	6925
15.20	6882
19.15	6800
24.40	6800
31.00	6795
41.75	6773
55.90	6712
78.90	6700
122.10	6670

[165] Kälberer, W., and Mark, H., *Z. physik. Chem.*, Abt. A. **139**, 151-62 (1928).

have been made. Kälberer and Mark[145] obtained a value of 6200 gram-cal. per mole of carbon dioxide adsorbed, by calculation from the data obtained in the linear portion of their isotherm, while from the steeper portion of the isotherm they obtained an average value of 7500 calories. Magnus and Kälberer also studied the heat of adsorption on silica gel and give an elaborate theoretical discussion concerning it. In Tables 41 and 42 are given the results obtained by Magnus and Giebenhain by the use of this adsorbent.

Solubility. The usual methods of expressing the solubility of a gas in a liquid are: (1) *The Bunsen Absorption Coefficient* α. This is the volume of gas reduced to standard conditions which at the temperature of the experiment, is dissolved by one volume of the solvent, the partial pressure of the gas being 760 mm. This may be calculated at various temperatures by means of the equation

$$\alpha = \frac{v}{V(1+0.00367\,t)} \qquad (34)$$

where α is the absorption coefficient, v the volume of the solute and V the volume of the solvent. (2) *The Ostwald Solubility Expression* l. This is the ratio of the concentration of the gas in the liquid to its concentration in the gas phase or $l = v/V$. This expression differs from the Bunsen Absorption Coefficient in that the volume v of the dissolved gas is not reduced to standard conditions.

Other methods of expressing gas solubilities are also used, for example, the *Kuenen Absorption Coefficient* and the *Raoult Absorption Coefficient,* but an attempt will be made in this work to confine all data to the first two methods of expression.

The Effect of Temperature on Solubility. The most extensive data we have on the solubility of carbon dioxide in water at different tempera-

TABLE 43.—*The Solubility of Carbon Dioxide in Water at Various Temperatures.*

Temp. °C.	α	$10^{-6}\times K$	Temp. °C.	α	$10^{-6}\times K$	Temp. °C.	α	$10^{-6}\times K$
0	1.713	0.552	13	1.083	0.873	26	0.738	1.27
1	1.646	0.575	14	1.050	0.901	27	0.718	1.30
2	1.584	0.597	15	1.019	0.929	28	0.699	1.34
3	1.527	0.619	16	0.985	0.958	29	0.682	1.37
4	1.473	0.642	17	0.956	0.987	30	0.665	1.41
5	1.424	0.666	18	0.928	1.018	35	0.592	1.58
6	1.377	0.689	19	0.902	1.049	40	0.530	1.77
7	1.331	0.713	20	0.878	1.079	45	0.479	1.95
8	1.282	0.738	21	0.854	1.110	50	0.436	2.15
9	1.237	0.764	22	0.829	1.140	55	0.394	
10	1.194	0.791	23	0.804	1.170	60	0.359	2.57
11	1.154	0.819	24	0.781	1.209			
12	1.117	0.845	25	0.759	1.247			

tures are found in the works of Bohr.[146] The temperature range covered by his works extend from 0° to 60° C. and it is interesting to note the close agreement of his results with many determined more recently. Table 43 gives these data together with the values of K (Henry's law constant) calculated by Loomis.[147] These values for K were obtained by means of the expression

$$K = p_A/x_A \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (35)$$

where p_A is the partial pressure of A and x_A is the mole fraction of A in the solution.

The Effect of Pressure on Solubility. The relation between the solubility of carbon dioxide in water and its pressure above the solution was worked out very early (1882) by Wroblewski[148] and his results are still considered of great value. When his data are plotted on a large scale graph the smoothness of the curves gives one considerable confidence in the accuracy of the results. In the present case these large scale plots were

TABLE 44.—*Solubility of Carbon Dioxide in Water at Pressures above 1 Atmosphere.*
(Data by Wroblewski)

P in atmos.	α 0°	α 12.4°	P in atmos.	α 0°	α 12.4°
1	1.797	1.086*	16	23.00	14.32
2	3.56	2.15	17	24.00	15.05
3	5.32	3.20	18	24.92	15.78
4	7.02	4.22	19	25.84	16.48
5	8.65	5.15*	20	26.65	17.11*
6	10.28	6.10	21	27.50	17.84
7	11.78	7.00	22	28.30	18.48
8	13.20	7.88	23	29.10	19.23
9	14.65	8.75	24	29.87	19.75
10	16.03	9.65*	25	30.55	20.31*
11	17.25	10.45	26	31.25	20.95
12	18.50	11.25	27	31.90	21.54
13	19.70	12.04	28	32.55	22.14
14	20 85	12.80	29	33.16	22.72
15	21.95	13.55	30	33.74	23.25*

Values marked * are original data.

made for the two temperatures at which data are available and readings made from these curves furnished the values shown in Table 44. Wroblewski called the results he obtained, the coefficient of saturation but this is, without doubt, the Bunsen Absorption Coefficient.

[146] Bohr, C., *Ann. Physik.*, **68**, 500 (1899).

[147] Loomis, A. L., "International Critical Tables," **3**, 260, 265, McGraw-Hill Publishing Co., New York.

[148] Wroblewski, S., *Compt. rend.*, **94**, 1335 (1882).

Solubility measurements at very high pressures have been made by Sander.[149] His results were obtained by means of the well-known Cailletet apparatus using in one case 0.210 cc. of water and in a second set of determinations 0.102 cc. of solvent. The water was measured into the Cailletet tube and the decrease in the quantity of gas after solution at each pressure was determined. It is at once evident that this method of determining solubilities is subject to considerable error and this fact is more forcefully impressed on one by attempting to plot isotherms from the reported data. The points are so widely scattered that one has considerable difficulty in even guessing the probable location of the curve. The data perhaps have some value, however, on account of the very high pressures to which they were extended and the isotherms give one some idea of the conditions under which Henry's law becomes valid. These isotherms have been constructed by the authors, on a large scale and the probable location of the curve in each case has been determined. Readings from these curves are recorded in Table 45.

TABLE 45.—*Solubility of Carbon Dioxide in Water at High Pressures.*
(Data by Sander)

Temp. ° C.	Pressure in kg./sq. cm.	Cc. of CO_2 Reduced to 1kg./sq.cm. dissolved by 1 cc. of H_2O	Temp. ° C.	Pressure in kg./sq. cm.	Cc. of CO_2 Reduced to 1kg./sq.cm. dissolved by 1 cc. of H_2O
20	25	17.8	60	90	23.1
"	30	19.5	"	100	26.2
"	40	23.3	"	110	29.6
"	50	27.5	"	120	33.2
"	55	30.1	100	60	8.9
35	30	11.8	"	70	9.9
"	40	15.0	"	80	11.0
"	50	18.6	"	90	12.2
"	60	22.7	"	100	13.5
"	70	27.5	"	110	14.8
"	80	32.9	"	120	16.1
60	40	10.4	"	130	17.5
"	50	12.4	"	140	18.9
"	60	14.7	"	150	20.3
"	70	17.3	"	160	21.9
"	80	20.1	"	170	23.4

The Effect of Temperature and Pressure Changes Expressed in Pounds per Square Inch and in Degrees Fahrenheit. A very useful solubility table has been calculated by Heath[150] in which the data are expressed in English engineering units. These data are especially useful to the bottling industry and they are here reproduced as Table 46.

[149] Sander, W., *Z. physik. Chem.*, **78**, 513-49 (1912).
[150] Heath, W. P., Privately Printed, Atlanta, Ga., (1915).

Solubility of Carbon Dioxide in Water Solutions of Inorganic Compounds. Because of the large amount of data reported it is somewhat difficult for one to see at a glance what effect the presence of inorganic compounds may have on the solubility of carbon dioxide in water. In the tables following an attempt has been made to rearrange these results and in many cases to recalculate them to a common unit. In cases where the

TABLE 46.—*The Solubility of Carbon Dioxide in Water at Various Temperatures in ° F. and Various Pressures in lbs. per sq. in. Gage.*

Table shows the volume of carbon dioxide measured at 32° F. and 14.7 lbs./sq. in. which dissolves in one volume of water at the temperature and pressure indicated.

(Calculated by Heath)

P lbs./	Temperature °C.												
sq. in.	32	36	40	44	48	55	60	65	70	75	80	85	90
15	3.46	3.19	2.93	2.70	2.50	2.20	2.02	1.86	1.71	1.58	1.84	1.35	1.27
20	4.04	3.73	3.42	3.15	2.92	2.57	2.36	2.17	2.00	1.84	1.69	1.58	1.48
25	4.58	4.27	3.92	3.61	3.35	2.04	2.69	2.48	2.29	2.10	1.93	1.80	1.70
30	5.21	4.81	4.41	4.06	3.77	3.31	3.03	2.80	2.58	2.37	2.18	2.03	1.91
35	5.80	5.35	4.91	4.52	4.19	3.69	3.37	3.11	2.86	2.63	2.42	2.26	2.13
40	6.37	5.89	5.39	4.97	4.61	4.05	3.71	3.42	3.15	2.89	2.67	2.49	2.34
45	6.95	6.43	5.88	5.43	5.03	4.43	4.06	3.74	3.44	3.16	2.91	2.72	2.56
50	7.53	6.95	6.36	5.89	5.45	4.80	4.40	4.05	3.73	3.42	3.16	2.94	2.77
55	8.11	7.48	6.86	6.34	5.87	5.17	4.74	4.37	4.02	3.69	3.40	3.17	2.99
60	8.71	8.02	7.35	6.79	6.29	5.53	5.08	4.68	4.31	3.95	3.64	3.39	3.20
70	9.86	9.09	8.33	7.70	7.13	6.27	5.76	5.30	4.89	4.49	4.14	3.86	3.63
80	11.02	10.17	9.31	8.61	7.98	7.00	6.43	5.92	5.46	5.02	4.62	4.31	4.06
90	12.18	11.25	10.30	9.52	8.82	7.74	7.11	6.54	6.04	5.55	5.12	4.77	4.49
100	13.34	12.33	11.29	10.43	9.66	8.40	7.79	7.18	6.62	6.08	5.60	5.22	4.91

densities of the solutions were not reported in the original papers, an attempt has been made to supply them. In most cases such densities were obtained from the density tables of Hodgman and Lange.[151] The Bunsen absorption coefficient has been selected as the most useful unit for expressing the solubility of the gas, while the concentration of the salt is, in general, given as moles per liter of solution. Exceptions to this have been made in a few cases, notably the data of Christoff who expresses his concentrations in terms of normality. In some cases there is much uncertainty as to how he calculated this normality. In the data of Setschenow the absorption coefficient is based on the number of cc. of carbon dioxide measured at 0° C. and 760 mm. pressure which dissolved in one cc. of a saturated solution of carbon dioxide. It will be noted that this coefficient may deviate slightly from the Bunsen coefficient which is based on one cc. of the solvent. There are reasons to believe, however, that this slight difference is much less than the error of measurements and these values have been listed as Bunsen absorption coefficients. These data have been tabulated in Table 47.

[151] Hodgman, C. D., and Lange, N. A., "Handbook of Chemistry and Physics." Chemical Rubber Publishing Co., Cleveland (1929).

TABLE 47.—*Solubility of Carbon Dioxide in Water Solutions of Inorganic Compounds.*

Compound	Temp. ° C.	Moles of comp. per liter sol.	Density at t ° C.*		Absorption coeff. a	Observer
HCl	15.0	0.500	1.007+	20	0.989	Geffcken
"	"	1.000	1.016+	"	0.975	"
"	"	2.000	1.033+	"	0.948	"
"	25.0	0.500	1.007+	"	0.738	"
"	"	1.000	1.016+	"	0.732	"
"	"	2.000	1.033+	"	0.728	"
HNO_3	15.0	0.500	1.015+	"	1.022	"
"	"	1.000	1.032+	"	1.029	"
"	"	2.000	1.066+	"	1.042	"
"	25.0	0.500	1.015+	"	0.769	"
"	"	1.000	1.032+	"	0.781	"
"	"	2.000	1.066+	"	0.803	"
H_2SO_4	15.0	0.250	1.015+	"	0.965	"
"	"	0.500	1.030+	"	0.927	"
"	"	1.000	1.061+	"	0.869	"
"	"	1.500	1.091+	"	0.662	"
"	"	2.000	1.120+	"	0.632	"
"	15.5	0.258	1.015+	"	0.865	"
"	"	0.526	1.032+	"	0.728	"
"	"	1.087	1.066+	"	0.562	"
"	"	2.323	1.139+	"	0.509	"
"	"	3.727	1.218+	"	0.507	"
"	"	5.313	1.303+	"	0.481	"
"	"	6.182	1.348+	"	0.489	"
"	"	11.49	1.610+	"	0.619	"
"	"	16.65	1.814+	"	0.967	"
"	20.0	4.672	1.267+	"	0.607	"
"	"	9.521	1.516+	"	0.670	"
"	"	17.88	1.835+	"	0.925	"
"	"	17.96	1.836+	"	0.926	Bohr
LiCl	15.2	0.394	.....	..	1.035	Setschenow
"	"	1.182	.....	..	0.808	"
"	"	2.957	.....	..	0.596	"
"	"	5.915	.....	..	0.497	"
"	"	11.82	.....	..	0.120	"
"	15.5	1.000	.....	..	0.733	Christoff
NH_4Cl	8.0	1.233	1.021	15	1.023	Mackenzie
"	"	1.707	1.047	"	1.000	"
"	"	2.505	1.053	"	0.922	"
"	10.0	4.856	1.072	"	0.813	"
"	15.0	1.233	1.021	"	0.825	Mackenzie
"	"	1.707	1.047	"	0.791	"
"	"	2.505	1.053	"	0.798	"
"	"	4.856	1.072	"	0.738	"
"	15.2	0.019	1.000+	20	1.013	Setschenow
"	"	0.187	1.001+	"	0.985	"
"	"	0.965	1.014+	"	0.941	"
"	"	3.216	1.047+	"	0.819	"
"	"	4.822	1.068+	"	0.770	"
"	22.0	1.233	1.021	15	0.718	Mackenzie
"	"	1.707	1.047	"	0.702	"
"	"	2.505	1.053	"	0.684	"
"	"	4.856	1.072	"	0.600	"
"	25.0	0.439	1.005	25	0.724	Findlay and Shen
"	"	0.966	1.013	"	0.691	" "
"	"	1.873	1.022	"	0.670	" "
"	"	3.194	1.045	"	0.609	" "

TABLE 47.—*(Continued)*

Compound	Temp. ° C.	Moles of comp. per liter sol.	Density at t ° C.*		Absorption coeff. α	Observer
NH_4NO_3	15.2	0.035	1.001+	17.5	1.013	Setschenow
"	"	0.140	1.005+	"	1.002	"
"	"	0.687	1.023+	"	0.989	"
"	"	1.261	1.041+	"	0.962	"
"	"	2.525	1.080+	"	0.911	"
"	"	5.051	1.155+	"	0.807	"
"	"	10.123	1.297+	"	0.612	"
$(NH_4)_2SO_4$	15.2	0.546	1.034+	20	0.712	"
"	"	1.092	1.077+	"	0.575	"
"	15.5	0.500	1.032+	"	0.737	Christoff
$FeSO_4(NH_4)_2$ $SO_4 \cdot 6H_2O$	25	0.242	1.052	25	0.587	Findlay and Shen
"	"	0.261	1.057	"	0.576	" "
"	"	0.572	1.124	"	0.421	" "
$(NH_4)_2$ $Fe_2(SO_4)_4$ $24\ H_2O$	15.5	1.000 (N)	.....	....	0.668	Christoff
$NH_4HB_2O_4$	15.5	0.25 (N)	.....	....	5.18 (?)	"
NaCl	0.0	1.170	1.0554	13.3	1.234	Bohr
"	"	3.407	1.1308	12.3	0.678	"
"	5.0	1.170	1.0554	13.3	1.024	"
"	"	3.407	1.1308	12.3	0.577	"
"	6.4	1.253	1.038	15.0	0.899	Mackenzie
"	"	2.400	1.080	"	0.633	"
"	"	3.344	1.123	"	0.518	"
"	"	5.312	1.195	"	0.347	"
"	10.0	1.170	1.0554	13.3	0.875	Bohr
"	"	3.407	1.1308	12.3	0.503	"
"	15.0	1.170	1.0554	13.3	0.755	"
"	"	1.253	1.038	15.0	0.735	Mackenzie
"	"	2.400	1.080	"	0.557	"
"	"	3.344	1.123	"	0.431	"
"	"	3.407	1.1308	12.3	0.442	Bohr
"	"	5.312	1.195	15.0	0.297	Mackenzie
"	15.2	0.220	.....	....	0.978	Setschenow
"	"	1.094	.....	....	0.760	"
"	"	2.188	.....	....	0.580	"
"	"	3.282	.....	....	0.466	"
"	15.5	1.000	.....	....	0.708	Christoff
"	20.0	1.170	1.0554	13.3	0.664	Bohr
"	"	3.407	1.1308	12.3	0.393	"
"	22.0	2.400	1.080	15.0	0.482	Mackenzie
"	"	3.344	1.123	"	0.389	"
"	"	5.312	1.195	"	0.263	"
"	25.0	1.170	1.0554	13.3	0.583	Bohr
"	"	3.407	1.1308	12.3	0.352	"
"	30.0	1.170	1.0554	13.3	0.517	"
"	"	3.407	1.1308	12.3	0.319	"
"	35.0	1.170	1.0554	13.3	0.460	"
"	"	3.407	1.1308	12.3	0.288	"
"	40.0	1.170	1.0554	13.3	0.414	"
"	"	3.407	1.1308	12.3	0.268	"
"	45.0	1.170	1.0554	13.3	0.370	"
"	"	3.407	1.1308	12.3	0.235	"
"	50.0	1.170	1.0554	13.3	0.335	"
"	"	3.407	1.1308	12.3	0.215	"
"	55.0	1.170	1.0554	13.3	0.305	"
"	"	3.407	1.1308	12.3	0.198	"
"	60.0	"	"	"	0.183	"

TABLE 47.—*(Continued)*

Compound	Temp. ° C.	Moles of comp. per liter sol.	Density at t ° C.*		Absorption coeff. a	Observer
NaBr	15.2	1.118	1.086+	20.0	0.775	Setschenow
"	"	4.473	1.338+	20.0	0.362	"
"	"	6.709	.....	....	0.221	"
$NaNO_3$	15.2	1.102	1.056+	20.0	0.835	"
"	"	1.543	1.079+	"	0.762	"
"	"	2.572	1.130+	"	0.621	"
"	"	5.145	1.254+	"	0.385	"
"	"	7.717	.....	....	0.244	"
$NaClO_3$	15.2	2.192	.....	....	0.625	"
"	"	3.288	.....	....	0.506	"
"	"	6.576	.....	....	0.257	"
Na_2SO_4	15.2	0.100	1.011+	20	0.950	"
"	"	0.668	1.080+	"	0.620	"
"	"	2.000	1.225+	"	0.234	"
$Na_4B_4O_7$	15.5	0.025 (N)	.....	....	1.487	Christoff
"	"	0.125 (N)	.....	....	3.586	"
"	"	0.250 (N)	.....	....	5.741	"
"	"	Sat. sol.	.....	....	12.33	"
"	"	" " +cryst.	.....	....	21.75	"
$NaBO_2$	15.5	0.250	.....	....	5.478	"
$Na_3PO_4 \cdot 12H_2O$	15.5	1.000 (N)	.....	....	3.932	"
$Na_4P_2O_7 \cdot 10H_2O$	15.5	1.000 (N)	.....	....	5.709	"
$Na_4P_4O_{12}$	15.5	1.000 (N)	.....	....	0.472	"
KCl	8.0	0.828	1.021	15	0.988	Mackenzie
"	"	1.220	1.053	"	0.918	"
"	"	1.732	1.080	"	0.864	"
"	"	4.674	1.549	"	0.688	"
"	15.0	0.500	.....	....	0.925	Geffcken
"	"	0.828	1.021	15	0.777	Mackenzie
"	"	1.000	.....	....	0.850	Geffcken
"	"	1.220	1.053	15	0.777	Mackenzie
"	"	1.732	1.080	"	0.720	"
"	"	4.674	1.549	"	0.571	"
"	15.5	1.000	.....	....	0.818	Christoff
"	22.0	0.828	1.021	15	0.670	Mackenzie
"	"	1.220	1.053	"	0.649	"
"	"	1.732	1.080	"	0.597	"
"	"	4.674	1.549	"	0.480	"
"	25.0	0.500	.....	....	0.695	Geffcken
"	"	0.614	1.026	25	0.686	Findlay and Shen
"	"	1.000	1.044	"	0.642	" "
"	"	1.000	1.044+	"	0.641	Geffcken
KBr	15.0	0.500	1.040+	20	0.935	"
"	"	1.000	1.082+	"	0.866	"
"	15.2	0.705	1.058+	"	0.908	Setschenow
"	"	1.409	1.116+	"	0.819	"
"	"	2.113	1.173+	"	0.748	"
"	"	4.227	1.343+	"	0.579	"
"	15.5	1.000	1.082+	"	0.863	Christoff
"	25.0	0.500	1.040+	"	0.703	Geffcken
"	"	1.000	1.082	"	0.653	"
KI	15.0	0.500	1.045+	20	0.940	"
"	"	1.000	1.118+	"	0.875	"
"	15.2	1.922	1.227+	"	0.777	Setschenow
"	"	2.883	1.340+	"	0.688	"
"	"	5.767	.....	....	0.506	"
"	15.5	1.000	1.118+	20	0.812	Christoff
"	25.0	0.500	1.045+	"	0.710	Geffcken

TABLE 47.—*(Continued)*

Compound	Temp. ° C.	Moles of comp. per liter sol.	Density at t ° C.*	Absorption coeff. α	Observer
KI	25.0	1.000	1.118+ 20	0.660	Geffcken
KNO_3	15.0	0.500	1.029+ "	0.953	"
"	"	1.000	1.050+ "	0.897	"
"	15.2	0.582	1.034+ "	0.959	Setschenow
"	"	1.162	1.069+ "	0.890	"
"	"	2.325	1.137+ "	0.781	"
"	15.5	1.000	1.050+ "	0.830	Christoff
"	25.0	0.500	1.029+ "	0.718	Geffcken
"	"	1.000	1.050+ "	0.686	"
$KHSO_4$	15.5	0.66 (N)	....	0.688	Christoff
"	"	2.00 (N)	....	0.675	"
K_2SO_4	15.5	0.66 (N)	....	0.769	"
"	"	1.00 (N)	....	0.676	"
$K_2Al_2(SO_4)_4 \cdot 24H_2O$	15.5	1.00 (N)	....	0.711	"
K_2HAsO_4	15.5	0.500 (N)	....	0.749	"
$KH_2As_3O_4$	15.5	1.00 (N)	....	0.548	"
KH_2PO_4	15.5	1.00 (N)	....	0.580	"
$K_4P_4O_{12}$	15.5	1.00 (N)	....	0.830	"
KSCN	15.2	3.356	....	0.691	Setschenow
"	"	5.032	....	0.590	"
"	"	10.06	....	0.387	"
$MgSO_4$	15.2	0.220	1.024+ 20	0.901	"
"	"	0.660	1.075+ "	0.669	"
"	"	1.320	1.148+ "	0.441	"
"	"	2.641	1.280+ "	0.188	"
"	15.5	0.250	1.028+ "	0.816	Christoff
"	"	0.500	1.057+ "	0.688	"
"	"	1.000	1.112+ "	0.447	"
"	"	2.000	1.217+ "	0.355	"
$CaCl_2$	8.0	0.407	1.036 15	0.942	Mackenzie
"	"	0.542	1.049 15	0.855	"
"	"	0.774	1.068 "	0.838	"
"	"	1.620	1.139 "	0.632	"
"	16.25	0.407	1.036 "	0.759	"
"	"	0.542	1.049 "	0.726	"
"	"	0.774	1.068 "	0.674	"
"	"	1.620	1.139 "	0.520	"
"	22.0	0.407	1.036 "	0.673	"
"	"	0.542	1.049 "	0.616	"
"	"	0.774	1.068 "	0.581	"
"	"	1.620	1.139 "	0.471	"
"	30.0	0.407	1.036 "	0.596	"
"	"	0.542	1.049 "	0.527	"
"	"	0.774	1.068 "	0.500	"
"	"	1.620	1.139 "	0.400	"
$Ca(NO_3)_2$	15.2	0.241	....	0.923	Setschenow
$CuSO_4$	15.5	1.000	....	0.507	Christoff
$ZnSO_4$	15.2	0.237	1.023+ 15	0.903	Setschenow
"	"	0.475	1.043+ "	0.783	"
"	"	1.424	1.126+ "	0.474	"
"	"	2.850	1.246+ "	0.209	"
"	15.5	1.000	1.090+ "	0.486	Christoff
RbCl	15.0	0.500	....	0.937	Geffcken
"	"	1.000	....	0.873	"
"	25.0	0.500	....	0.701	"
"	"	1.000	....	0.722	"
$SrCl_2$	8.0	0.652	1.087 15	0.779	Mackenzie
"	"	0.868	1.116 "	0.737	"

TABLE 47.—*(Continued)*

Compound	Temp. ° C.	Moles of comp. per liter sol.	Density at t ° C.*		Absorption coeff. α	Observer
$SrCl_2$	8.0	1.310	1.173	15	0.606	Mackenzie
"	"	2.642	1.343	"	0.285	"
"	16.25	0.652	1.087	"	0.663	"
"	"	0.868	1.116	"	0.586	"
"	"	1.310	1.173	"	0.473	"
"	"	2.642	1.343	"	0.245	"
"	22.0	0.652	1.087	"	0.581	"
"	"	0.868	1.116	"	0.507	"
"	"	1.310	1.173	"	0.444	"
"	"	2.642	1.343	"	0.247	"
"	30.0	0.652	1.087	"	0.508	"
"	"	0.868	1.116	"	0.539	"
"	"	1.310	1.173	"	0.367	"
"	"	2.642	1.343	"	0.223	"
CsCl	15.0	0.500	.....	....	0.954	Geffcken
"	25.0	0.500	.....	....	0.715	"
$BaCl_2$	8.0	0.375	1.068	15	0.969	Mackenzie
"	"	0.511	1.092	"	1.021	"
"	"	1.540	1.273	"	0.495	"
"	16.25	0.375	1.068	"	0.744	"
"	"	0.511	1.092	"	0.645	"
"	"	0.766	1.137	"	0.618	"
"	"	1.540	1.273	"	0.618	"
"	22.0	0.375	1.068	"	0.680	"
"	"	0.511	1.092	"	0.607	"
"	"	0.766	1.137	"	0.524	"
"	"	1.540	1.273	"	0.383	"
"	25.0	0.115	1.018	25	0.723	Findlay and Sher
"	"	0.238	1.040	"	0.679	" "
"	"	0.334	1.054	"	0.650	" "
"	"	0.408	1.070	"	0.619	" "
"	30.0	0.375	1.068	15	0.566	Mackenzie
"	"	0.511	1.092	"	0.543	"
"	"	0.766	1.137	"	0.467	"
"	"	1.540	1.273	"	0.315	"
$Ba(NO_3)_2$	15.2	0.240	.....	....	0.922	Setschenow

* Density values marked + were calculated from data given by Hodgman and Lange "Handbook of Physics and Chemistry" (1929).

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Listed in the order in which they appear in Table 47.
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Solubility of Carbon Dioxide in Water Solutions of Carbon Compounds. Table 48 represents the data collected from various sources showing the solubility of carbon dioxide in solutions of carbon compounds. The method of listing these data is essentially the same as that used in Table 47. So much data are available on the solubility of carbon dioxide in alcohol solutions that they have been collected here as Table 49. It is of special interest to note the minimum solubility of carbon dioxide in solu-

TABLE 48.—*Solubility of Carbon Dioxide in Water Solutions of Carbon Compounds.*

Compound	Temp. °C.	Gm. moles per liter		Density at t° C.		Absorption coeff. α	Observer
Acetamide	20.0	0.500		1.0005	20	0.879	Usher
Acetic acid	"	0.500		1.0026	"	0.868	"
Antipyrine	"	0.500		1.0134	"	0.859	"
Carbamide	"	0.500		1.0072	"	0.864	"
Catechol	"	0.500		1.0107	"	0.868	"
Citric acid	15.2	0.0624		1.004 +	"	1.007	Setschenow
" "	"	0.255		1.018 +	"	0.975	"
" "	"	0.515		1.038 +	"	0.950	"
" "	"	1.030		1.074 +	"	0.893	"
" "	"	1.551		1.110 +	"	0.841	"
" "	"	3.097		1.215 +	"	0.719	"
Chloral hydrate	15.0	1.161	17.7%	1.0851+	15	0.885	von Hammel
" "	"	2.222	31.6	1.1631+	"	0.803	"
" "	"	2.795	38.3	1.2044+	"	0.781	"
" "	"	3.857	49.8	1.2808+	"	0.760	"
" "	"	4.603	57.1	1.3333+	"	0.765	"
" "	"	5.923	68.8	1.4238+	"	0.797	"
" "	"	7.263	79.4	1.5132+	"	0.903	"
" "	25.0	0.307		1.019	25	0.815	Findlay and Shen
" "	"	0.612		1.041	"	0.795	" "
Dextrose	20.0	0.500		1.0328	20	0.792	Usher
Glycerol	15.0	3.013	26.11%	1.0625+	"	0.785	von Hammel
"	"	5.149	43.72	1.1094+	"	0.639	"
"	"	7.824	62.14	1.1591+	"	0.511	"
"	"	10.15	77.75	1.2018+	"	0.454	"
"	"	12.18	90.74	1.2367+	"	0.404	"
"	"	13.57	99.26	1.2590+	"	0.410	"
Glycine	20.0	0.500		1.0141	"	0.843	Usher
Mannitol	20.0	0.500		1.0303	"	0.782	"
n Propyl alcohol	20.0	0.500		0.9939	"	0.869	"
Pyrogallol	20.0	0.500		1.0172	"	0.853	"
Quinol	20.0	0.500		1.0095	"	0.887	"
Resorcinol	20.0	0.500		1.0096	"	0.901	"
Sucrose	15.5	0.100				0.826	Christoff
"	"	0.500				0.735	"
"	"	1.000				0.628	"
"	20.0	0.125		1.0152	20	0.846	Usher
"	"	0.250		1.0313	"	0.815	"
"	"	0.500		1.0637	"	0.756	"
"	"	1.000		1.1281	"	0.649	"
"	25.0	0.077		1.009	25	0.745	Findlay and Shen
"	"	0.151		1.018	"	0.731	" "
"	"	0.283		1.038	"	0.702	" "
"	"	0.360		1.051	"	0.681	" "
Thiocarbamide	20.0	0.500		1.0092	20	0.859	Usher
Urethane	20.0	0.500		1.0037	"	0.869	"

Note.—Density values for chloral hydrate were calculated by means of the equation found in the International Critical Tables which may be put in the following form:

$$d = .99913 + .004455\, p_R + .00002198\, p_R^2 + .00000004366\, p_R^3$$

where p_R is the per cent of chlorol hydrate in the solution. Other density values marked + were calculated from data given by Hodgman and Lange "Handbook of Physics and Chemistry." (1929).

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Findlay, A. and Shen, B., *J. Chem. Soc.*, **101**, 1459-68 (1912).

tions containing about 28 per cent of alcohol. This phenomenon has also been observed by other investigators, for example Lubarsch.[152]

The Solubility of Carbon Dioxide in Organic Solvents. In Table 50 are given the solubility data of Just[153] showing the solubility of carbon

TABLE 49.—*Solubility of Carbon Dioxide in Ethyl Alcohol Solutions.*

Temp. ° C.	Pressure of CO_2 mm. of Hg.	Density	at ° temp. C.	% Alcohol by wt.	Absorption coeff. α	Observer
−78	50	0.872	−78/4	....	93.30	Stern
"	100	"	"	....	97.53	"
"	200	"	"	....	100.9	"
"	400	"	"	....	107.9	"
"	700	"	"	....	120.8	"
−65	760	....	....	99.0	38.41	Bohr
"	"	....	....	98.7	39.89	"
−59	100	0.856	−59/4	....	34.97	Stern
"	200	"	"	....	35.09	"
"	400	"	"	....	36.25	"
"	700	"	"	....	37.79	"
−20	"	....	....	99.0	7.51	Bohr
"	"	....	....	98.7	7.25	"
−10	"	....	....	99.0	5.75	"
"	"	....	....	98.7	5.43	"
0	"	....	....	99.0	4.44	"
"	"	....	....	98.7	4.35	"
+10	"	....	....	99.0	3.57	"
20	"	....	....	99.0	2.98	"
"	"	0.998	20	1.07	0.861	Müller
"	"	0.969	"	22.76	0.841	"
22.4	"	0.960	"	28.46	0.792	"
20	"	0.956	20	31.17	0.801	"
17	"	0.935	17	42.15	0.877	"
19.1	760	0.922	19.1	49.0	0.982	"
18.8	"	0.870	18.8	71.1	1.293	"
16.0	"	0.835	16	85.3	1.974	"
19.0	"	0.795	19	99.7	2.719	"
25	"	....	....	99.0	2.76	Bohr
"	737	0.9931	25/15	2.97	0.721	Findlay and Shen
"	745	0.9929	"	3.03	0.731	" " "
"	747	0.9834	"	8.98	0.708	" " "
"	836	0.9931	"	2.97	0.819	" " "
"	937	0.9929	"	3.03	0.921	" " "
"	942	0.9834	"	8.98	0.890	" " "
"	1073	0.9931	"	2.97	1.049	" " "
"	1083	0.9929	"	3.03	1.061	" " "
"	1090	0.9834	"	8.98	1.031	" " "
"	1338	0.9931	"	2.97	1.308	" " "
"	1357	0.9929	"	3.03	1.328	" " "
"	1360	0.9834	"	8.98	1.292	" " "
40	"	....	....	99.0	2.57	Bohr
45	"	....	....	99.0	2.20	"
30	760	....	....	99.0	2.01	"

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Müller, O., *Wied. Ann. Physik.* (3), **37**, 24-43 (1889).
Findlay, A., and Shen, B., *J. Chem. Soc., (London)*, **99**, 1313 (1911).

[152] Lubarsch, *Ann. Physik.* (2), **37**, 525 (1889).
[153] Just, G., *Z. physik. Chem.*, **37**, 342-67 (1901)).

TABLE 50.—*Solubility of Carbon Dioxide in Certain Organic Solvents.*
Solubility expressed in terms of the Ostwald solubility coefficient *l*.
(Data by Just)

Solvent	l_{25}	l_{20}	l_{15}	Solvent	l_{25}	l_{20}	l_{15}
Water	0.8256	.....	.....	Benzene	2.425	2.540	2.710
Glycerol	0.0302	.....	.....	Amylbromide	2.455	2.638	2.803
Carbon disulfide	0.8699	0.8888	0.9446	Nitrobenzene	2.456	2.655	2.845
Iodobenzene	1.301	1.371	1.440	Propyl Alcohol	2.498	.....	.....
Aniline	1.324	1.434	1.531	Carvol	2.498	2.690	2.914
o-Toluidine	1.381	1.473	1.539	Ethyl Alcohol (97%)	2.706	2.923	3.130
m-Toluidine	1.436	1.581	1.730	Benzaldehyde	2.841	3.057	3.304
Eugenol	1.539	1.653	1.762	Amylchloride	2.910	3.127	3.363
Benzene Trichloride	1.643	.....	.....	Isobutylchloride	3.105	3.388	3.659
Cumol	1.782	1.879	1.978	Chloroform	3.430	3.681	3.956
Carven	1.802	1.921	2.030	Butyric Acid	3.478	3.767	4.084
Dichlorhydrine	1.810	1.917	2.034	Ethylene Chloride	3.525	3.795	4.061
Amyl Alcohol	1.831	1.941	2.058	Pyridine	3.656	3.862	4.291
Bromobenzene	1.842	1.964	2.092	Methyl Alcohol	3.837	4.205	4.606
Isobutyl Alcohol	1.849	1.964	2.088	Amylformate	4.026	4.329	4.646
Benzylchloride	1.938	2.072	2.180	Propionic Acid	4.078	4.407	4.787
Metoxylol	2.090	2.216	2.346	Amyl Acetate	4.119	4.411	4.850
Ethylenebromide	2.157	2.294	2.424	Acetic Acid (glacial)	4.679	5.129	5.614
Chlorobenzene	2.265	2.420	2.581	Isobutyl Acetate	4.691	4.968	.....
Carbontetrachloride	2.294	2.502	2.603	Acetic Anhydride	5.206	5.720	6.218
Propylenebromide	2.301	2.453	2.586	Acetone	6.295	6.921	.....
Toluene	2.305	2.426	2.557	Methyl Acetate	6.494	.....	.....

dioxide in various organic solvents at three different temperatures. For many years these were the only data available for such solubility measurements and much theoretical discussion has hinged on them. More recently Kunerth[154] has extended this field with some carefully worked out experiments covering a greater temperature range. The results of these determinations are listed in Table 51. Table 52 shows the results of Stern[155]

TABLE 51.—*The Solubility of Carbon Dioxide in Certain Organic Solvents.*
Solubility expressed in terms of the Ostwald solubility coefficient *l*.
(Data by Kunerth)

Compound	Temperature ° C.									
	18	20	22	24	26	28	30	32	34	36
Water	....	0.900	0.872	0.836	0.800	0.765	0.729	0.693	0.656	....
Acetone	....	6.98	6.76	6.55	6.22	5.88	5.49	5.08	4.66	....
Acetic Acid	5.40	5.23	5.07	4.91	4.73	4.57	4.41	4.25	4.12	4.00
Pyridine	3.95	3.85	3.75	3.63	3.53	3.45	3.33	3.25	3.13	3.03
Methyl Alcohol	3.63	3.57	3.51	3.44	3.37	3.28	3.19	3.09	2.97	....
Ethyl Alcohol	2.95	2.87	2.80	2.73	2.66	2.58	2.48	2.41	2.31	....
Benzaldehyde	3.06	2.99	2.90	2.80	2.73	2.66	2.58	2.52	2.46	2.39
Aniline	....	1.38	1.35	1.32	1.29	1.25	1.22	1.21	1.19	1.17
Amyl Acetate	4.79	4.65	4.55	4.44	4.35	4.24	4.14	4.10	4.02	....
Ethylene Bromide	2.32	2.27	2.22	2.16	2.12	2.07	2.03	1.97	1.92	1.86
Isoamyl Alcohol	....	1.91	1.88	1.85	1.81	1.76	1.72	1.69	1.67	....
Chloroform	3.83	3.71	3.60	3.50	3.39	3.26	3.11	2.94	2.81	2.68

[154] Kunerth, William, *Phys. Rev.*, **19**, 512-24 (1922).
[155] Stern, Otto, *Z. physik. Chem.*, **81**, 468 (1912-13).

TABLE 52.—*Solubility of Carbon Dioxide in Organic Solvents at Low Temperatures and Pressures.*

Expressed in terms of the Ostwald solubility expression *l*.

(Data by Stern)

Temp. °C.	Pressure in mm. of Hg.	Solvents			
		Methyl alcohol	Acetone	Ethyl acetate	Methyl acetate
−78	50	120.5	196.6	177.5	224.1
"	100	119.6	198.1	177.1	224.3
"	200	120.1	201.5	179.2	223.1
"	400	122.2	208.8	183.2	225.6
"	700	126.8	.....	.....	.....
−59	100	42.5	67.2	65.6	75.8
"	200	42.7	68.0	65.3	77.1
"	400	43.1	72.8	66.7	77.6
"	700	43.35	72.8	69.7	79.0
Densities at −78/4		0.884	0.900	1.017	1.056
Densities at −59/4		0.866	0.879	0.994	1.032

at very low temperatures. Sander[156] has also determined the solubility of carbon dioxide in various organic solvents to pressures as high as 130 kg. per sq. cm. Inasmuch as these solubility data were made with such very small volumes of solvent (0.08 cc. in one case) not much confidence can be placed on them.

Supersaturation of Carbon Dioxide in Liquids. This phenomenon so common to solutions of solids in liquids is also displayed to a certain extent in solutions of gases in liquids. To the bottling industry the supersaturation of carbon dioxide in beverages is of special importance and a gas which fails to do this properly is said to be "wild". The bottler well knows that "wildness" is due to impurities, usually air, in the carbon dioxide used for carbonating the beverage. As will be shown later there are other causes than gaseous impurities for the failure of a gas to produce a properly supersaturated solution.

In agitated solutions of gases the rate of desaturation follows the well known logarithmic law and this rate is therefore proportional to the concentration of the gas in the solution.[157] It is also true that this logarithmic law applies equally well to the process of absorption of gases in liquids. Furthermore Bohr[158] has shown that the ratio of the volume of gas which passes into solution through unit area in unit time (invasion coefficient) to the volume of gas which similarly passes out of solution (evasion coefficient) is constant, and equal to the absorption coefficient.

In the case of certain unagitated solutions, however, the rate of gas evolution may be very irregular. Findlay and King[159] observed that on reducing the pressure of carbon dioxide gas above a solution to atmospheric conditions, a period of quiescence ensues, during which no gas escapes from

[156] Sander, W., *Z. physik. Chem.*, **78**, 513-49 (1911).
[157] Carlson, T., *J. chim. phys.*, **9**, 235 (1911).
[158] Bohr, C., *Ann. Physik.* (3), **68**, 500 (1899).
[159] Findlay, A., and King, G., *J. Chem. Soc.*, **103**, 1170-93 (1913).

the supersaturated solution. In this condition the solution is very sensitive to mechanical disturbance and even a slight jar is sufficient to cause a rapid evolution of gas. It was also found that particles of solid in the solution as well as grease or dirt on the walls of the vessel prevented this period of quiescence. Moreover, it was discovered that this period did not endure indefinitely, after a certain time the evolution of gas started spontaneously and a rapid evolution of gas took place which gradually diminished to a certain point, when another rapid evolution took place and this phenomenon continued until equilibrium was finally established. Solutions of dextrin and solutions of gelatin showed a well marked period of quiescence while solutions of peptone and ferric hydroxide liberated the carbon dioxide immediately on reduction of pressure.

In an attempt to find some basis of comparison for the degree of supersaturation of carbon dioxide in various types of water solutions these investigators developed the following equation:

$$k=\frac{2.30}{t}\cdot\log_{10}\left(1-\frac{v}{V}\right) \quad \ldots\ldots\ldots\ldots \quad (36)$$

where k is a constant, t is time in seconds and v the volume of gas evolved in t seconds while V is the total volume evolved. While this equation is of no special importance from a theoretical point of view the average values of k do show to a certain extent the relative rates of desaturation of the various solutions. As far as the authors are aware no better method of

TABLE 53.—*The Supersaturation of Carbon Dioxide in Water Solutions of Various Substances.*

(Data by Findlay and King)

Solvent	Solute	Conc. of solute in gms./liter	$-k$ (Average)
Water	.....	.....	0.0665
"	Potassium chloride	60.000	.0546
"	Gelatin	0.242	.0904
"	"	0.281	.1245
"	"	0.502	.1504
"	"	30.010	.2335
"	Dextrine	10.010	.0657
"	"	30.000	.0572
"	"	125.100	.0672
"	Starch	30.000	.0367
"	Peptone	7.580	.0157
"	Ferric hydroxide	3.767	.0615
"	" "	13.530	.0671

expression has been devised up to the present time and therefore values of k have been listed in Table 53 showing the various solutions studied by Findlay and King. It should be noted that the values of k are averages taken from tables in which they are far from constant.

In a later research Findlay and King[160] studied in more detail the supersaturation of carbon dioxide in water solutions of gelatin and starch and

[160] Findlay, A., and King, G., *J. Chem. Soc.*, 105, 1297-1303 (1914).

concerned themselves primarily with the changes that took place with different methods of treating the solution. More recently, Findlay and Howell,[161] studied the rate of evolution of carbon dioxide from water solutions in the presence of colloids. In the case of starch and dextrin the velocity coefficient was greater than for pure water solutions of carbon dioxide and in the case of ferric hydroxide and gelatin the coefficient was smaller.

Metschl[162] investigated the supersaturation of carbon dioxide in water and alcohol solutions and found that within the pressure limits of 1 to 5 atmospheres of saturation pressure the degree of supersaturation was proportional to the saturation pressure. He found that V/P for water solutions of carbon dioxide was 0.0541 (average) and for alcohol solutions (98 per cent ethyl alcohol) it was 0.157. V is the volume of carbon dioxide measured under standard conditions, shaken out of the solution after the pressure had been reduced from P (measured in mm. of Hg) to one atmosphere.

Kenrick, Wismer and Wyatt[163] in the same year published results obtained in a series of researches on supersaturation. Pressures used by these investigators for the saturation of water with carbon dioxide were as high as 35 atmos. and it was found that even with these high pressures the solution could be reduced to one atmosphere without the formation of gas bubbles. It was also noted that an increase in the temperature of the solution favored the formation of gas bubbles but that a long heating of the tube containing the solution at a high pressure favored supersaturation.

Liquid Carbon Dioxide as a Solvent. The behavior of liquid carbon dioxide as a solvent was first investigated by Gore.[164] His work was necessarily qualitative in nature and was carried out by the simple process of allowing the solute to remain in contact with the liquid carbon dioxide in a tube over night at room temperature. He observed that naphthalene and camphor showed the greatest solubility, that yellow phosphorus and iodine showed only slight solubility, whereas other compounds (organic and inorganic salts) seemed to have no solubility. The beautifully colored solution of iodine in liquid carbon dioxide attracted the attention of several other investigators some of whom reported the results of solubility studies.[165] Hannay[166] found that silicates, phosphates and borates became dissolved to a certain extent in liquid carbon dioxide at high temperatures and pressures. Finally Dolter[167] reported that silicates were soluble in liquid carbon dioxide in the presence of water.

A study of binary mixtures of carbon dioxide with liquids and gases has been made by Dewar[168] who investigated carbon disulfide, chloroform

[161] Findlay, A., and Howell, O. R., *J. Chem. Soc.*, **121**, 1046 (1922).
[162] Metschl, John, *J. Phys. Chem.*, **28**, 417-38 (1924).
[163] Kenrick, F. B., Wismer, K. L., and Wyatt, K. S., *J. Phys. Chem.*, **28**, 1308-15 (1924).
[164] Gore, G., *Proc. Roy. Soc. (London)*, **11**, 85 (1861); *Chem. News*, **3**, 2990 (1861); *Phil. Mag.* (4), **22**, 485 (1861).
[165] Bacquerel, *Compt. rend.*, **75**, 1271 (1872). Cailletet, L. P., *Compt. rend.*, **92**, 840 (1881); **108**, 1280 (1889). Villard, P., *Ann. chim. phys.* (7), **10**, 387 (1897).
[166] Hannay, J. B., *Proc. Roy. Soc. (London)*, **32**, 407 (1881).
[167] Dolter, C., "Neues Jahrbuch f. Mineralogie, Geologie und Paläontologie," **I**, 118 (1890).
[168] Dewar, J., *Proc. Roy. Soc. (London)*, **30**, 538 (1880).

and benzene and Kuenen[169] who studied the critical phenomenon of mixing of acetylene, ethane, and methyl chloride.

Somewhat later Büchner made a rather exhaustive phase study of liquid carbon dioxide and various compounds mostly of the organic type. His summary of the information obtained up to that time is interesting. The classes of substances which had been found to be insoluble were:

Halogen salts:	$CaCl_2$, $HgCl_2$, HgI_2, NaCl, KBr, KI.
Sulfates:	$CuSO_4$, $FeSO_4$.
Nitrates:	$AgNO_3$.
Carbonates:	$CaCO_3$, Na_2CO_3.
Elements:	C, Si, Al, S, K, Na.
Additional:	As_2O_3, SiO_2, K_2SiF_6, Ca_3P_2, HPO_3, $Hg(CN)_2$, phosphorus sulfide and sodium phosphide.

Those substances having a slight solubility were: PCl_5, $AsBr_3$, $SbBr_3$, P (yellow), I and Br. Büchner conducted an elaborate research in which he investigated the phase relations in a large number of systems containing liquid carbon dioxide and various organic compounds. The results of this study are summarized in three classes: First those substances which were completely miscible in the liquid state such as p-dichlorbenzene, camphor, carbon disulfide, ether, pentane, amylene, acetone, benzene and xylene. Second, those having a very limited solubility such as naphthalene, phenanthrene, iodoform, p-dibrombenzene, borneol, substituted phenols such as nitrophenol, p-chlornitrobenzene, 1.2.3. and 1.3.2. dichloronitrobenzene, succinic acid anhydride, uric acid, benzamide, etc. Third, those having a limited solubility of liquids such as propyl-, butyl-, and isobutyl alcohols and bromoform which produce miscible solutions on warming.

The only strictly quantitative measurements of the solubility of solid solutes in liquid carbon dioxide were made by Quinn[171] who made a series of determinations using naphthalene and iodine as solutes. The results reported in terms of mole per cent of the solute at different temperatures for naphthalene are as follows:

Temp. °C.	25	20	10	0	−21
Mole % $C_{10}H_8$	0.698	0.662	0.511	0.372	0.180

and the results obtained when iodine was used as solute are:

Temp. °C.	25	20	10	0	−11.4	−21
Mole % I_2	0.0361	0.0305	0.0207	0.0136	0.00753	0.00405

Another investigation made by the same author[172] was designed to determine the solubility of lubricating oil in liquid carbon dioxide. These determinations were of importance from the point of view of compressor lubrication and especially in refrigeration systems where carbon dioxide was used as the refrigerant. The results obtained were as follows:

Temp. °C.	25	20	10	0	−20
Gms. oil per 100 gms. CO_2	0.718	0.843	0.904	0.800	0.388

[169] v. Kuenen, *Phil. Mag.* (5), **44**, 174 (1897).
[170] Büchner, E. H., *Z. physik. Chem.*, **54**, 665-88 (1905-6).
[171] Quinn, E. L., *J. Am. Chem. Soc.*, **50**, 672 (1928).
[172] Quinn, E. L., *Ind. Eng. Chem.*, **20**, 735-40 (1928).

One of the most interesting things concerning these data is the way the solubility of the oil reaches a maximum in the neighborhood of 10° C. This fact is shown more clearly in Figure 23 where the solubility curve has been plotted together with the density curves of the solvent and the solute. As is easily seen the maximum solubility takes place at the point where the densities of the components of the mixture are equal to each other. It should also be noted that at this temperature if liquid carbon dioxide and oil are sealed in a glass tube the position of the two non-miscible liquids change, that is to say, while at ordinary temperatures liquid carbon dioxide floats on the surface of the oil when the temperature is brought below 10° C. the oil rises to the top of the mixture. This change in position is most interesting to watch while the temperature of the tube is slowly lowered.

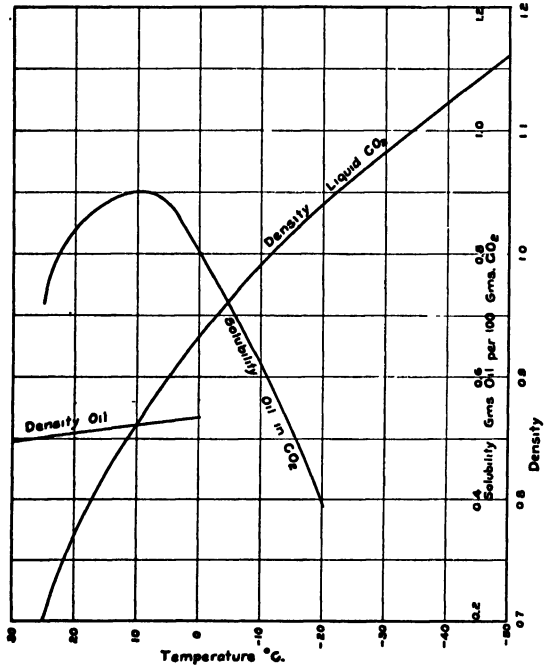


FIGURE 23.

Solubility of Lubricating Oil in Liquid Carbon Dioxide.

The solubility of glycerol in liquid carbon dioxide was also treated in the investigation mentioned above. It was found that the solubility of glycerol was so small (less than 0.05 per cent) that no quantitative measurements were possible under the conditions of the investigation.

The solubility of water in liquid carbon dioxide was investigated by Lowry and Erickson[173] who found the solubility less than 0.05 weight per cent over a temperature range from −5.8° C. to 22.9° C.

A very complete and carefully worked out investigation of the solubility relations between liquid carbon dioxide and various liquids was made by

[173] Lowry, H. H., and Erickson, W. R., *J. Am. Chem. Soc.*, **49**, 2729-34 (1927).

Thiel and Schulte.[174] The binary system ethyl ether-carbon dioxide was considered in detail and the results obtained by an analysis of the liquid and gaseous phases after equilibrium had been established were as follows:

Temp. °C.	−78.6	−63.7	−23.8	0.0	+15.2
Liquid Phase { Mole % ether	52.6	72.9	93.3	97.7	98.6
Liquid Phase { Mole % CO_2	47.4	27.1	6.7	2.3	1.4
Gaseous Phase { Mole % ether	.065	.25	6.1	23.8	45.4
Gaseous Phase { Mole % Co_2	99.935	99.75	93.9	76.2	54.6

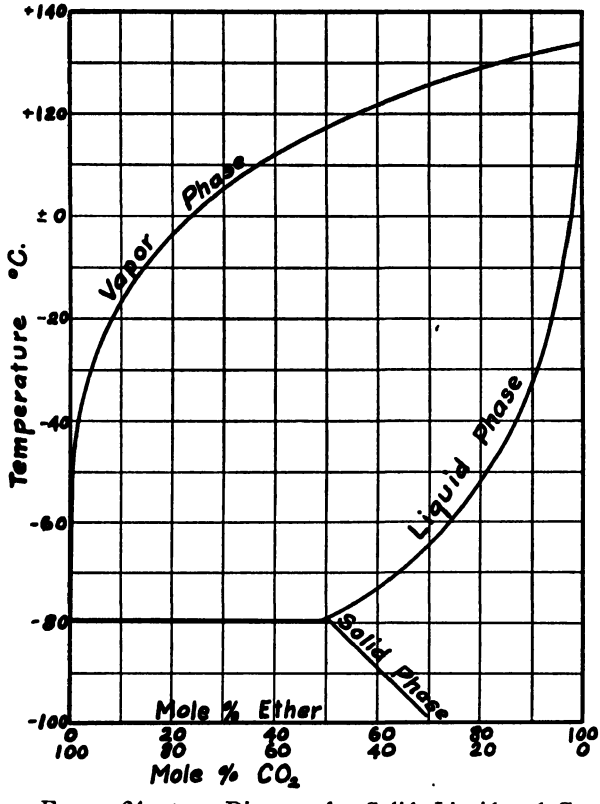


FIGURE 24. t—x Diagram for Solid, Liquid and Gas in the Carbon Dioxide-Ether System.

In order to make a rather complete *t-x* diagram these investigators also determined the solubility of solid carbon dioxide in ether with the results shown below:

Temp. °C.	−83.5	−92.5	−98.0
Mole % ether	54.6	63.4	69.4
Mole % CO_2	45.4	36.6	30.6

[174] Thiel, A., and Schulte, E., *Z. physik. Chem.*, **96**, 328 (1920).

From these data a most interesting t-x diagram can be constructed and such a diagram is given as Figure 24 where the total pressure of the system is 750 mm.

TABLE 54.—*Equilibrium Systems of Solid Carbon Dioxide with Various Solvents (at 750 mm.).*

(Data by Thiel and Schulte)

	System	Equilibrium temperature	Vapor phase	Liquid phase
1	Ethyl ether	−78.6 °	0.065 mole %	52.6 mole %
	Carbon dioxide		99.935 mole %	47.4 mole %
2	Ethyl chloride	−78.65°	0.30 mole %	67.8 mole %
	Carbon dioxide		99.70 mole %	32.2 mole %
3	Sulfur dioxide	−78.64°	0.28 mole %	66.4 mole %
	Carbon dioxide		99.72 mole %	33.6 mole %
4	Methyl ether	−78.78°	1.35 mole %	39.8 mole %
	Carbon dioxide		98.65 mole %	60.2 mole %
5	Chlorine	−79.44°	6.8 mole %	17.5 mole %
	Carbon dioxide		93.2 mole %	82.5 mole %
6	Hydrogen sulfide	−82.11°	24.7 mole %	74.6 mole %
	Carbon dioxide		75.3 mole %	25.4 mole %

In Table 54 have been tabulated the results obtained by Thiel and Schulte on six equilibrium systems in which solid carbon dioxide was used.

Of interest at this point is the process of Auerbach[175] for fractionating oils in which liquid carbon dioxide is used as a solvent for certain fractions of oil. No commercial applications of the process are made at present.

[175] Auerbach, E. B., U. S. Patent 1,805,751, May 19 (1931).

Chapter IV

Chemical Properties of Carbon Dioxide

Chemically carbon dioxide is not an active compound and reactions between dry carbon dioxide and other compounds and elements can, in general, be promoted only at high temperatures. In water solutions, however, the situation is quite different. Because of the acid properties of the solution many reactions take place spontaneously and some of them are of considerable geological importance. It will be the purpose of this chapter to consider many of these acid reactions and to deal also with some reactions taking place with the dry gas.

Action of Carbon Dioxide on Water. The formation of a definite hydrate of carbon dioxide, having the composition $CO_2.8H_2O$ was first observed by Wroblewsky.[1] He obtained the hydrate as an unstable solid on the side of a tube in which carbon dioxide under pressure of 45 atmospheres had been kept in contact with water at 0° C. and after the pressure of the gas was decreased to 12.3 atmospheres. The solid so obtained was stable only when the temperature was kept low and the gas pressure high. Villard[2] confirmed the formation of this hydrate but his method of analysis seemed to indicate that its composition was $CO_2.6H_2O$. The decomposition pressure of the hydrate was determined by both Villard and Wroblewsky and their results check in a most remarkable manner as will be seen in the following:

Temp. °C.	−6	0	0.48	2.7	3.6	5.3	6.1	6.3	6.9	10.0
P in atm. Wroblewsky ..		12.3		16.7	17.9	21.8		23.3	26.1	
P in atm. Villard	6.5	12.2	12.7	16.7	17.9	21.8	23.3		26.1	44.3

Later Hempel and Seidel[3] sealed a weighed quantity of solid carbon dioxide and water in a tube, and found that after the solid had melted, two liquid layers were formed. On cooling this system, crystals were produced which had a melting point of 8° C. An analysis of these crystals showed them to have a composition of either $CO_2.8H_2O$ or $CO_2.9H_2O$. The former degree of hydration checks the results obtained by Wroblewsky and it may be safely assumed that the correct formula is $CO_2.8H_2O$.

The density of the octohydrate of carbon dioxide is not known but Wroblewsky noticed that it was greater than the density of water saturated with CO_2. The heat of formation of $CO_2.8H_2O$ was found by Villard to be 14.9 calories.

[1] v. Wroblewsky, S., *Wied. Ann.*, **17**, 103 (1892); *Compt. rend.*, **94**, 212 (1882).
[2] Villard, P., *Compt. rend.*, **119**, 368 (1894); *Ann. chim. phys.* (7), **11**, 355 (1897).
[3] Hempel, W., and Seidel, J., *Ber.*, **31**, 2997 (1898).

Carbonic Acid. The hydrate $CO_2.H_2O$ or more correctly H_2CO_3 is now quite generally recognized as a well-defined compound although it has never been isolated in the free state. Under ordinary conditions this compound, called metacarbonic acid, has weak acid properties. It may, however, be considered a hydroxy derivative of formic acid and because of this it is to be expected it would have fairly strong acid properties. Recently numerous studies of the system carbon dioxide and water have shown this to be the case, at least from the point of view that carbonic acid is a highly dissociated compound in water solutions.

It is also reasonable to expect the occurrence of the ortho form of carbonic acid, having the formula $CO_2.2H_2O$ or H_4CO_4. Wilke[4] pointed out its probable existence but practically all the evidence we have for this lies in the fact that certain orthocarbonates, for example, ethyl orthocarbonate $C(OC_2H_5)_4$, are well known to students of organic chemistry.

When carbon dioxide dissolves in water an interesting equilibrium is set up between the various molecules and the ions produced from them. One may write as one of the equations for this reaction the following:

$$CO_2\ (\text{dissolved}) + H_2O \leftrightarrows H_2CO_3 \leftrightarrows H^+ + HCO_3^- \leftrightarrows 2H^+ + CO_3^{--}.$$

The carbon dioxide in solution is also in equilibrium with the undissolved carbon dioxide in the gaseous phase of the system, therefore another factor enters into the reaction. The conditions necessary to force this reaction either to the right or to the left are at once apparent and it might be mentioned that when sufficient pressure of carbon dioxide is maintained over the solution it is possible to increase the hydrogen-ion concentration to a point where carbonic acid may take part in certain industrial operations.

It may be profitable now for one to consider the above reaction step by step and to bring to light at least a few of the numerous researches concerning it.

The first factor, that is, the solution of carbon dioxide in water, has been treated quite fully under the subjects of absorption and solubility. It might be mentioned again, however, that solutions of carbon dioxide obey Henry's law quite satisfactorily at moderate temperatures and low pressures. Morgan and Maass[5] have determined the value of Henry's law

$$K_H = \frac{\text{partial pressure of } CO_2 \text{ in mm. of Hg}}{\text{mole fraction of } CO_2}$$

constant K_H where to be 0.797 at 10°, 1.039 at 18° and 1.255 at 25° C. These constants are in good agreement with the values determined by Bohr.

The second step, in the general equation given above, or the hydration of the carbon dioxide may take place in two ways, viz.:

$$CO_2 + H_2O = H_2CO_3$$

or

$$CO_2 + OH^- = HCO_3^-$$

[4] Wilke, E., *Chem.-Ztg.*, **39**, 309 (1915); *Z. anorg. allgem. Chem.*, **119**, 365-79 (1922).
[5] Morgan, O. M., and Maass, O., *Can. J. Research*, **5**, 162-99 (1931).

It is probable that both of these reactions take place simultaneously but that one of them may predominate depending on the pH of the liquid medium in which they take place.

In 1912 McBain[6] called attention to the interesting fact that when an alkaline solution, containing phenolphthalein, was mixed with a large excess of water saturated with carbon dioxide, the solution was not decolorized immediately but required from 5 to 20 seconds, depending upon conditions, for the color to fade. This time lag must, of course, be due to the hydration reactions or the ion formation which depends upon them. Ways and means were then sought for determining the rate of this hydration and the amount of carbonic acid existing in solution under equilibrium conditions. A number of capable investigators[7] worked on the problem and from the conclusions arrived at from their labors, it is now generally conceded that solutions of carbon dioxide contain very small amounts of the rather strong metacarbonic acid. If a base is added to such a solution only a fraction, equivalent to the amount of H_2CO_3 present, is neutralized at once; the rest of the carbon dioxide enters into combination by the time-reaction having the velocity of the reaction $CO_2+OH^-=HCO_3^-$. Attempts have been made to slow up the hydration reaction long enough to determine the amount of H_2CO_3 present in the solution at any one time. Strohecker found that phenol, pyrocatechol, resorcinol and hydroquinone retarded it a sufficient time for one to measure the acidity of the solution. The result of an investigation in which resorcinol was used as the retarding agent showed that in a 0.038 per cent solution of carbon dioxide at 4° C. only 0.56 per cent of the total carbon dioxide in the solution was in the form of H_2CO_3 and that this small fraction only was ionized.

Eucken and Grützner[8] recently studied, by conductivity measurements, the velocity of hydration of carbon dioxide. According to these investigators, the time-reaction observed when an aqueous solution of carbon dioxide is neutralized, is due to an instantaneous conversion of the alkali to carbonate, which is then slowly converted to bicarbonate, by the excess carbon dioxide. They also calculated that at equilibrium 0.2 per cent of the total carbon dioxide in the solution is in the form of carbonic acid.

Faurholt attempted to determine the rate of hydration and dehydration of carbon dioxide and while the probable error of his experiments was large (about 50 per cent) his conclusions and method of calculation are worth considering here. The rate of change in concentration of carbon dioxide in the reaction $CO_2+H_2O \rightarrow H_2CO_3$ is

$$\frac{d[CO_2]}{dt} = -k_1[CO_2] \quad \ldots\ldots\ldots\ldots \quad (37)$$

[6] McBain, J. W., *J. Chem. Soc.*, **101**, 814 (1912)

[7] Thiel, A., *Ber.*, **46**, 241, 867 (1913); *Z. Elektrochem.*, **22**, 423 (1916); *Z. allgem. Chem.*, **121**, 211 (1922). Strohecker, E. R., *Z. Nahr. Genussm.*, **31**, 121-60 (1916). Thiel, A., and Strohecker, E. R., *Ber.*, **47**, 945, 1061 (1914). Pusch, L., *Z. Elektrochem.*, **22**, 206, 293 (1916). Faurholt, C., *Z. anorg. allgem. Chem.*, **120**, 85 (1922); *J. chim. phys.*, **21**, 400-55 (1924).

[8] Eucken, A., and Grützner, H. G., *Z. physik. Chem.*, **125**, 363-93 (1927).

and for the reaction $CO_2+OH^- \rightarrow HCO_3^-$ is

$$\frac{d[CO_2]}{dt} = -k_2[OH^-][CO_2]. \quad \ldots\ldots\ldots\ldots \quad (38)$$

He found the numerical values of k_1 to be 0.0013 at 0° C. and 0.0011 at 18° C. while k_2 equals $10^{42.61}$ at 0° and $10^{43.24}$ at 18° C. As both reactions take place simultaneously the hydration can be represented by the equation

$$\frac{d[CO_2]}{dt} = -(k_1+k_2[OH^-])[CO_2] \quad \ldots\ldots\ldots \quad (39)$$

in which the brackets indicate concentration. In solutions where the OH^- concentration is constant it is evident that hydration of the carbon dioxide is a monomolecular reaction. When the pH of the liquid medium in which the hydration takes place is less than 8 then the OH^- concentration is so small the reaction is practically $CO_2+H_2O \rightarrow H_2CO_3$ but when the pH of the solution becomes greater than 10 it is the reaction $CO_2+OH^- \rightarrow HCO_3^-$ that predominates. Between these two pH values of course both reactions are important.

The dehydration reaction, according to Faurholt, may take place by the reversal of the two equations given above thus:

$$H_2CO_3 \rightarrow H_2O+CO_2 \text{ and } HCO_3^- \rightarrow CO_2+OH^-.$$

The rate of change of the first reaction is

$$\frac{d[H_2CO_3]}{dt} = -k_3[H_2CO_3]. \quad \ldots\ldots\ldots\ldots \quad (40)$$

and of the second

$$\frac{d[HCO_3^-]}{dt} = -k_4[HCO_3^-] \quad \ldots\ldots\ldots\ldots \quad (41)$$

and the values for k_3 are given as $\pm 1.$ at 0°, 7.1 at 18° and for k_4, $10^{-5.59}$ at 0° and $10^{-4.52}$ at 18° C.

As in the case of hydration, between pH 8 and pH 10 the velocities of both dehydration reactions are quite similar. Below pH 8 the reaction becomes $H_2CO_3 \rightarrow H_2O+CO_2$ while in more alkaline solutions than pH 10 the bicarbonate decomposition prevails.

The Dissociation Constant of Carbonic Acid. The principal dissociation reaction of carbonic acid is that of a monobasic acid, producing thereby hydrogen ions and bicarbonate ions. Equilibrium calculations involving the production of these ions may, of course, be based on the actual amount of carbonic acid present or on the apparent amount estimated from the total carbon dioxide dissolved in the solution. It is therefore evident that there may be two sets of data on the dissociation constants of this acid depending on the method of calculation used. The apparent dissociation constant may be calculated from the relationship

$$K_a = \frac{[H^+][HCO_3^-]}{[H_2CO_3]+[CO_2]} \quad \ldots\ldots\ldots\ldots \quad (42)$$

and the real dissociation constant from

$$K_r = \frac{[H^+]\,[HCO_3^-]}{[H_2CO_3]} \quad \ldots\ldots\ldots\ldots\ldots (43)$$

The experimental difficulty of determining the actual concentration of H_2CO_3 in solution makes the values of K_r somewhat less accurate than the values of K_a. Strohecker[9] found 4.4×10^{-4} for the value of K_r at 4° C. and he points out the fact that carbonic acid is more strongly dissociated than formic acid ($K=2.14\times10^{-4}$) of which it may be considered the hydroxy derivative. Haehnel[10] obtained a value of 4.4×10^{-4} for K_r at 15° C. and his calculations indicated that 91 per cent of the carbonic acid present in the solution is dissociated into ions. Buytendyke, Brinkman and Mook[11] made twelve experiments in the temperature range from 14° to 18° C. and always found values of K_r between 1.5×10^{-4} and 4.0×10^{-4}.

The dissociation of H_2CO_3 under high pressures has been investigated by Müller and Luber.[12] They calculated that the concentration of true H_2CO_3 at room temperature and 50 atmospheres pressure is 6.36×10^{-3} mole (=0.386 gram) per liter. By the use of graded indicators the H^+ concentration was found to be 1.25×10^{-3} or pH=2.9. From this value the degree of dissociation was calculated to be 0.196 per cent. The primary dissociation constant[13] of H_2CO_3 under 50 atmospheres pressure of carbon

TABLE 55.—*Experimental and Theoretical Data for the System Carbon Dioxide-Water.* (Data from Morgan and Maass)

CO_2 %	$[CO_2]$ moles/liter	Partial Press. CO_2 mm. of Hg	$[H^+]$	pH	$K_a\times10^8$
At 0° C.					
0.0202	0.00458	57.0	0.000028	4.55	17.44
0.0661	0.01503	160.0	0.000055	4.26	20.18
0.1412	0.03208	352.7	0.000082	4.09	20.93
0.2143	0.04870	530.2	0.000101	4.00	21.23
0.2929	0.06656	681.3	0.000119	3.92	21.65
0.3676	0.08354	853.0	0.000135	3.87	21.85
At 10° C.					
0.0240	0.00545	81.7	0.000038	4.42	26.87
0.0611	0.01389	206.1	0.000062	4.21	28.30
0.1297	0.02947	424.1	0.000092	4.04	29.22
0.1975	0.04488	644.8	0.000115	3.94	29.39
0.2475	0.05624	835.6	0.000128	3.89	29.27
At 18° C.					
0.0216	0.00491	92.3	0.000039	4.41	32.48
0.0580	0.01318	229.8	0.000066	4.18	33.35
0.1140	0.02590	491.4	0.000094	4.03	34.23
0.1740	0.03954	744.5	0.000116	3.94	34.44
At 25° C.					
0.0200	0.00454	98.9	0.000040	4.40	35.22
0.0502	0.01141	253.2	0.000064	4.19	36.46
0.1025	0.02329	540.0	0.000093	4.03	37.84
0.1559	0.03542	822.2	0.000116	3.94	38.04

[9] Strohecker, E. R., *Z. Nahr.-Genussm.*, **31**, 121-60 (1916).
[10] Haehnel, O., *Centr. Mineral Geol.*, **1920**, 25-32.
[11] Buytendyke, F. J. J., Brinkman, R., and Mook, H. W., *Biochem. J.*, **21**, 576-84 (1927).
[12] Müller, E., and Luber, A., *Z. anorg. allgem. Chem.*, **187**, 209-30 (1930).
[13] Müller, E., and Luber, A., *Z. anorg. allgem. Chem.*, **190**, 427 (1930).

dioxide was found to be

$$\frac{[H^+]\,[HCO_3^-]}{[H_2CO_3]} = 3.06 \times 10^{-4}$$

The apparent dissociation constant has been more frequently and perhaps more accurately determined. Of the recorded data[14] it may suffice to mention here those obtained by Kendall and also those of Morgan and Maass. Kendall made conductivity measurements on water solutions of carbon dioxide under a partial pressure of carbon dioxide as it is found in ordinary atmospheric air. His results were: $K_a = 2.24 \times 10^{-7}$ at 0°, 3.12×10^{-7} at 18° and 3.50×10^{-7} at 25° C. The results obtained by Morgan and Maass are, without doubt, the most valuable of any yet obtained and these have been tabulated in Table 55. The variation of K_a at various concentrations of carbon dioxide is well illustrated by the isotherms in Figure

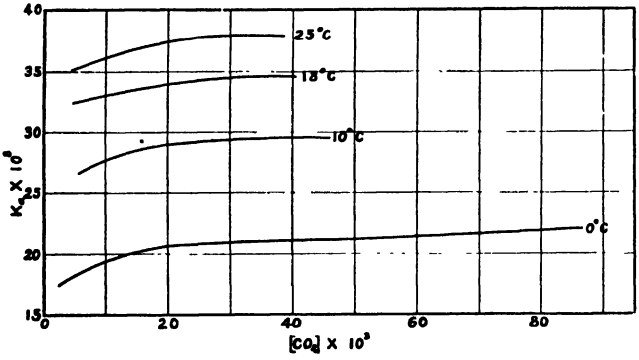


FIGURE 25. Relation of K_a to Concentration in the System CO_2-H_2O. (Data from Morgan and Maass.)

25. MacInnes and Belcher,[15] using a method involving galvanic cells and glass electrodes, obtained a value of 4.54×10^{-7} for the first dissociation constant at 25° C.[16] In a very recent work, however, measurements made by Kauko and Carlberg[17] support the older values of 3.50×10^{-7} at 25° C. and 3.12×10^{-7} at 18° C.

The second stage of ionization is relatively of small importance due to the slight extent to which it takes place. In many calculations it may be left out of consideration altogether without seriously affecting the accuracy of the results. This stage of dissociation may be represented by the equation $HCO_3^- \longrightarrow H^+ + CO_3^{--}$ and therefore the dissociation constant $K_2 = [H^+]\,[CO_2^{--}]/[HCO_3^-]$. The value of K_2 was calculated by Bod-

[14] Pfeiffer, E., *Ann. phys.*, 23, 625-650 (1884). Knox, *Ann. phys.*, 55, 44 (1895). Walker, J. and Cormak, W., *J. Chem. Soc.*, 77, 5-21 (1900). Kendall, J., *J. Am. Chem. Soc.*, 38, 1480-97 (1916). Morgan, O. M., and Maass, O., *Can. J. Research*, 5, 162-99 (1931).

[15] MacInnes, D. A., and Belcher, D., *J. Am. Chem. Soc.*, 55, 2630-46 (1933).

[16] See also Carlberg, J., *Acta Chem. Fennica*, 8 B, 4 (1935).

[17] Kauko, Y., and Carlberg, J., *Z. physik. Chem.*, A 173, 141-9 (1935).

länder[18] and found to be 1.259×10^{-11}. Prideau[19] obtained 6.0×10^{-11} while somewhat later Menzel[20] found it to be 6.2×10^{-11} at 18° C. MacInnes and Belcher in some recent measurements found the constant to be 5.61×10^{-11} at 25° C.[21]

The carbon dioxide equilibrium in sea water, is a subject of considerable interest to those studying sea life and a number of investigations have been made on this subject. An interesting study was made by Kändler[22] of the relations between hydrogen-ion concentration, free carbon dioxide and the alkalinity of sea water. This relationship was expressed in the following form:

$$[H^+]=\left(\frac{K_1\times[CO_2]}{[\text{Alky.}]}\right)^{0.92}$$

where K_1 is the first dissociation constant of H_2CO_3. The first and second apparent dissociation constants of carbonic acid in sea water at different salt contents have been determined by Buch[23] and his co-workers.

The first dissociation constant of carbonic acid in hemoglobin solutions has been measured by Margaria and Green.[24]

The pH of Water Solutions of Carbon Dioxide. While the dissociation data of carbonic acid is of great fundamental importance, from a practical point of view the true acidity expressed in terms of pH units is more useful. Byke[25] has calculated the pH values for solutions of carbon dioxide in pure water. The range covered in his calculations extends from a partial pressure of carbon dioxide of one atmosphere to zero. The equations for carbonic acid equilibria and the values of the constants used are as follows:

(1)	$[H^+]\,[OH^-]=K=0.54\times10^{-14}$	(20° C.)
(2)	$[H^+]\,[HCO_3^-]/H_2CO_3=k_1=3.18\times10^{-7}$	(20° C.)
(3)	$[H^+]\,[CO_3^{--}]/[HCO_3^-]=k_2=3.54\times10^{-11}$	(20° C.)
(4)	$[H_2CO_3]=ncP \quad nc=3.093$	(20° C.)
(5)	$[H^+]=2\,[CO_3^{--}]+[HCO_3^-]+[OH^-]$	

The value of the hydrogen-ion concentration can therefore be calculated from the equation

$$(6)\qquad [H^+]=\frac{2\,k_1\,k_2\,ncP}{[H^+]^2}+\frac{k_1\,ncP}{[H^+]}+\frac{k_w}{[H^+]}$$

by substituting various values for P, the partial pressure of carbon dioxide with which the pure water is in equilibrium. The results of Byck's calcu-

[18] Bodländer, G., *Z. physik. Chem.*, **35**, 23 (1900).

[19] Prideau, E. B. R., *Proc. Roy. Soc. (London)*, **91**, A 535 (1915).

[20] Menzel, H., *Z. physik. Chem.*, **100**, 276 (1922).

[21] See also Kauko, Y., *Acta. Chem. Fennica*, **5B**, 53 (1932).

[22] Kändler, R., *Intern. Rev. ges. Hydrobiol. Hydrog.*, **24**, 177 (1930).

[23] Buch, K., *Finska Kemistsamfundets Medd.*, **40**, 55-62 (1931). Buch, K., Wattenberg, H., and Harvey, H. W., *Nature*, 128. 4011-2 (1931). Buch, K., Harvey, H. W., and Wattenberg, H., *Naturwissenschaften*, **19**, 773 (1931).

[24] Margaria, R., and Green, A. A., *J. Biol. Chem.*, **102**, 611-34 (1933).

[25] Byke, H. T., *Science*, **75**, 224 (1932).

lations are given graphically in Figure 26. It should be kept in mind that such a calculation carries with it a certain error. Morgan and Maass have already shown that the dissociation constant depends upon the carbon dioxide concentration and is not constant as is assumed in these calculations.

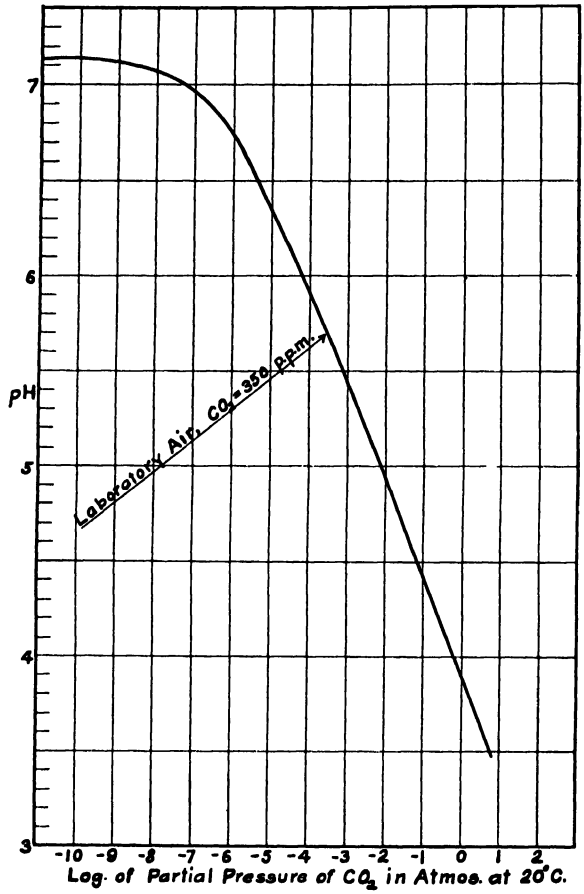


FIGURE 26. pH Values of Carbonic Acid Solutions at Different Pressures of Carbon Dioxide.

Values for pH of solutions of carbon dioxide in water at pressures above 1 atmos. have been determined colorimetrically by Moore and Buchanan.[26] These measurements given in Table 56 were made in an attempt to explain the action of carbon dioxide in carbonated beverages in inhibiting the growth of bacteria. The maximum acidity was reached with a pH of 3.3 at a pressure of 9.5 atmos., the conclusion was therefore

[26] Moore, M. B., with Buchanan, J. H., *Iowa State College, J. Sci.*, 4, 431-40 (1930).

reached that the action of carbon dioxide solutions on bacteria was due, in part at least, to some factor other than the increase of H—ion concentration of the solution.

TABLE 56.—*pH of Carbon Dioxide Solutions.*
(Colorimetric measurements by Moore and Buchanan)

Temperature 25°		Temperature 0°	
CO_2 pressure Atmos.	pH	CO_2 pressure Atmos.	pH
1.0	3.7	1.0	3.5
1.7	3.5	1.4	3.4
2.5	3.4	2.6	3.3
2.9	3.4	3.6	3.3
3.7	3.4	8.3	3.3
3.8	3.4	15.3	3.2
5.4	3.3	23.4	3.2
5.8	3.3		
7.2	3.3		
7.8	3.3		
9.5	3.3		
10.5	3.3		
12.7	3.3		
18.7	3.3		
33.3	3.3		

Action of Carbonic Acid on Calcium Compounds. Since the time of Cavendish (1766) it has been known that carbon dioxide precipitates calcium carbonate from a solution of calcium hydroxide and that continued addition of the gas redissolves this precipitate. Furthermore Irvine[27] found that heat was given off during the first stage of this reaction and another heat evolution was obtained when the precipitate started to dissolve. The usually accepted explanation of this reaction is that the calcium carbonate, $CaCO_3$, formed during the precipitation process combines with the excess carbonic acid to produce the soluble calcium bicarbonate $CaH_2(CO_3)_2$. This simple explanation, of course, does not take into consideration ionic reactions taking place between CO_3^{--}, HCO_3^-, H^+, OH^- and the molecules of H_2O, $CaCO_3$ and H_2CO_3 which produce them. The net result of all reactions is that the degree of solubility of calcium carbonate is a function of the carbon dioxide concentration and of course this concentration depends upon the partial pressure of carbon dioxide above the solution. Thus it can be shown that even a slight change in the partial pressure of carbon dioxide in normal air may bring about the solution or deposition of large quantities of calcium carbonate in natural surface waters.

Cameron and Robinson[28] questioned this explanation of the solubility of calcium carbonate in solutions of carbon dioxide and stated that it could be regarded just as logically and more conveniently as due to the specific solvent action of the carbon dioxide water mixtures. This idea has received practically no support from recent investigators and the belief in the bicarbonate formation is now stronger than ever. As a matter of

[27] Irvine, R., *Chem. News*, **63**, 192 (1891).
[28] Cameron, F. K., and Robinson, W. O., *J. Phys. Chem.*, **12**, 561-73 (1908).

fact it is believed that the isolation of calcium bicarbonate in the solid condition is entirely feasible as in the case of magnesium bicarbonate which was found by Haehnel[29] to be sufficiently stable to be detected in the solid state at $-5°$ C.

From a practical point of view the solubility reactions involved in the system $CaCO_3-H_2O-CO_2$ have many applications. Some of the most important of these are, scale formation in steam boilers and in water pipes, bone calcification and blood equilibria in physiological processes as well as rock formation and solution under geological conditions.

The Solubility of Calcium Carbonate in Water Solutions of Carbon Dioxide. The reactions involved in the process of solution of calcium carbonate in water solutions of carbon dioxide are not simple as was indicated in this introductory statement. Johnston and Williamson[30] give a very clear and detailed explanation of the various ionic reactions taking place when metallic hydroxides of certain types are treated with solutions of carbon dioxide and the solubility curve of calcite in aqueous solutions of carbon dioxide which they used in this discussion is reproduced here as Figure 27.

When carbon dioxide gas is passed into a solution of $Ca(OH)_2$ the predominating hydration reaction is $CO_2+OH^-=HCO_3^-$. The $[OH^-]$ being thus decreased causes the formation of more Ca^{++} in order to keep the solubility product $[Ca^{++}]\ [OH^-]^2$ constant. The reactions taking place are:

$$Ca(OH)_2=Ca^{++}+2OH^-$$
$$CO_2+OH^-=HCO_3^-$$

or combined
$$Ca(OH)_2+CO_2=Ca^{++}+OH^-+HCO_3^-.$$

Now if one measures the solubility of $Ca(OH)_2$ under increasing partial pressures of carbon dioxide by a determination of its calcium ion the solubility of the base apparently increases, whereas if the hydroxyl ion is determined the solubility of the base seems to decrease. The solution, however, now contains in addition molecules of $Ca(HCO_3)_2$ produced by the equilibrium set up between the calcium and the bicarbonate ions. Furthermore the bicarbonate ion also dissociates slightly to produce H^+ and CO_3^{--} and when the product of $[Ca^{++}]\ [CO_3^{--}]$ reaches the proper value then $CaCO_3$ is precipitated. This final reaction results in a decrease of the Ca^{++} which starts at point P_1 (Fig. 27) and continues with the addition of carbon dioxide until the minimum value is reached at P_0. Meanwhile the OH^- has decreased until a point is reached (P_0) where the predominating hydration reaction is $CO_2+H_2O=H_2CO_3=H^++HCO_3^-$ (according to Faurholt this reaction predominates below pH 8) and the formation of bicarbonate ion becomes the important reaction. The $[CO_3^{--}]$ then decreases and the $[Ca^{++}]$ increases until at the concentration represented by point P_2 the precipitation value of the product $[Ca^{++}]\ [HCO_3^-]^2$ is reached, which is a transition pressure at which both carbonate and bicarbonate are present as

[29] Haehnel, O., *J. prakt. Chem.* (2), **108**, 61-74 (1924).

[30] Johnston, J., and Williamson, E. D., *J. Am. Chem. Soc.*, **38**, 975-83 (1916).

stable solid phases. Beyond P_2 the bicarbonate alone is stable, and its total solubility falls off very slowly with further increase in the partial pressure of carbon dioxide.

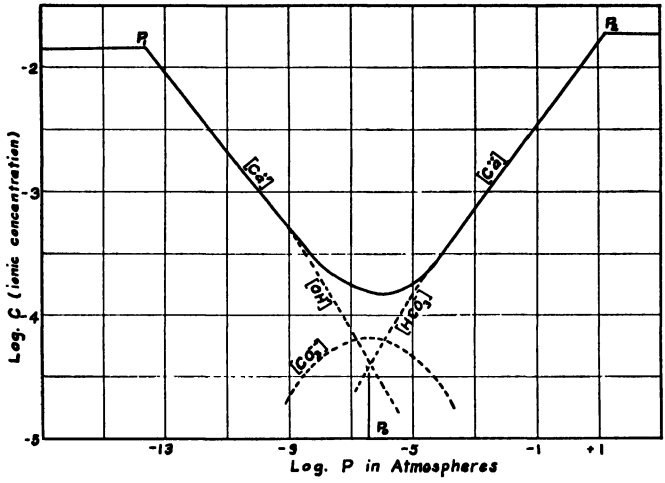


FIGURE 27. System $CaO—H_2O—CO_2$ at 16° C. The stable solid phase to the left of P_1 is hydroxide, between P_1 and P_2 is carbonate and to the right of P_2 bicarbonate. The curve represents the solubility as determined by estimation of calcium. The dotted lines by the determination of solubility from the various ions. (From Johnson and Williamson.)

The data on which Figure 27 was based were calculated by Johnston and Williamson and the results of these calculations are given in Table 57. For the methods of calculation and the values of the constants used one is referred to the original paper.

Recently determinations of the solubility of calcite in water solutions of carbon dioxide have been made by W. D. Kline[31] at partial pressures of

TABLE 57.—*Calculated Ion-Concentrations and Solubility of Calcite in Water at 16° C. in Contact with Air Containing the Partial Pressure P of CO_2.*
(By Johnston and Williamson)

P atmos.	$[HCO_3^-]\times10^4$	$[OH^-]\times10^4$	$[CO_3^{--}]\times10^4$	$[Ca^{++}]\times10^4$	Parts $CaCO_3$ per million
2.15×10^{-4}	10.0	0.0147	0.188	5.197	56
7.63×10^{-5}	7.0	0.034	0.260	3.777	40
7.62×10^{-6}	3.0	0.147	0.478	2.051	22
6.07×10^{-7}	1.0	0.614	0.666	1.473	16.0
3.85×10^{-7}	0.80	0.774	0.672	1.459	15.9
3.73×10^{-7}	0.787	0.787	0.672	1.459	15.9
2.19×10^{-7}	0.60	1.02	0.665	1.476	16.0
6.14×10^{-8}	0.30	1.82	0.593	1.654	18
9.78×10^{-9}	0.10	3.82	0.414	2.377	26
2.80×10^{-10}	0.01	13.3	0.144	6.81	74
3.16×10^{-14}	0.0000235	277.0	0.0071	138.5	2000

[31] See Frear, G. L., and Johnston, J., *J. Am. Chem. Soc.*, 51, 2086 (1929).

carbon dioxide from about 1 atmos. down to 0.00031 atmos. These data seem to be more reliable than any hitherto available and they are reproduced here as Table 58.

TABLE 58.—*Solubility of Calcite in Water Solutions of Carbon Dioxide at 25° C.*
(Data by W. D. Kline)

Partial pressure of CO_2 atmos.	Ca^{++} Millimoles per kilo H_2O	HCO_3^- Millimoles per kilo H_2O
0.00031	0.52	1.02
.00038	0.56	1.10
.00093	0.76	1.50
.00334	1.17	2.32
.00690	1.51	3.01
.0160	2.01	4.01
.0432	2.87	5.74
.1116	4.03	8.06
.9684	8.91	17.82

A plot of the most reliable solubility data including those of Kline was made by Frear and Johnston for the system $CaCO_3-H_2O-CO_2$ at a temperature of 25° C. Values read from this curve are as follows:

CO_2 partial pressure atmos.	0.00032	0.001	0.01	0.1	1.0	10
$CaCO_3$, millimoles per kilo H_2O....	0.53	0.78	1.7	3.9	9.0	22.5

The temperature coefficient of solubility of calcite in carbonic acid solutions has also been determined by these investigators. They find that within the accuracy of the measurements, this coefficient is independent of the partial pressure of carbon dioxide especially below one atmosphere. Therefore it is sufficient to give the ratio r of the solubility at $t°$ to that at 25° These ratios for various temperatures are:

t	0°	10°	20°	25°	30°	50°
r	1.8	1.4	1.1	1.0	0.9	0.6

Carbon Dioxide in Natural Waters. Carbon dioxide in natural waters such as well water, surface waters and the ocean plays an important rôle in determining the extent of temporary hardness. Johnston[32] gives an excellent discussion of the chemistry involved and discusses practical methods of making determinations. A detailed discussion of the subject here, perhaps, would lead too far afield. It might be mentioned, however, that one of the uses of carbon dioxide is the treatment of city water supplies for the control of hardness and this use seems to be growing in importance.[33]

The change in the pH of natural waters with change of carbon dioxide and calcium carbonate concentration has been calculated by Newell[34] with

[32] Johnston, J., *J. Am. Chem. Soc.*, 38, 947-75 (1916).
[33] Kelly, E. M., *J. Am. Water Works Assoc.*, 24, 1165-72 (1932).
[34] Newell, I. L., *J. Am. Water Works Assoc.*, 24, 560-1 (1932).

the aid of an equation proposed by Tillman. This equation may be put into the following form:

$$pH = \log \frac{\text{Alkalinity (as } CaCO_3) \times 0.203 \times 10^r}{\text{Free } CO_2} \quad \ldots\ldots\ldots \quad (44)$$

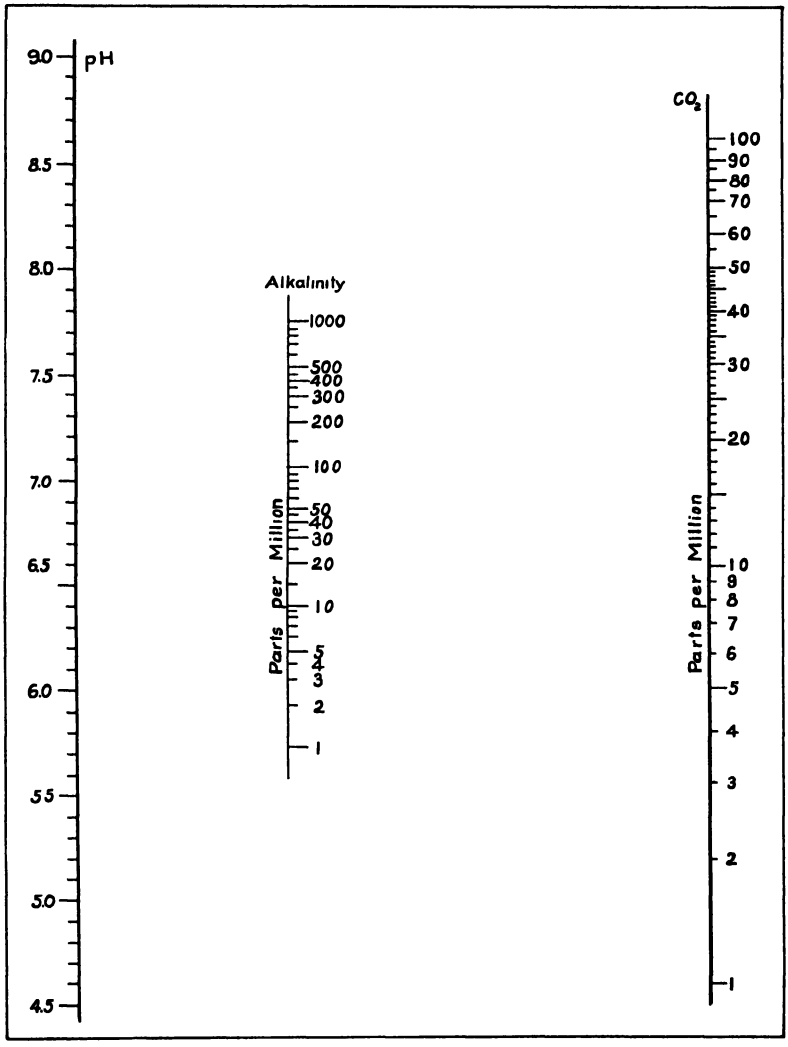


FIGURE 28. Alignment Chart for pH, Alkalinity and CO_2. Based upon Tillman's Formula

$$pH = \log \frac{\text{Alkalinity} \times 0.203 \times 10^r}{\text{Free } CO_2}$$

when Alkalinity (as $CaCO_3$) and CO_2 are in parts per Million.
(Chart Constructed by Newell)

where alkalinity and carbon dioxide are expressed in parts per million. Figure 28 shows a nomogram constructed by Newell giving the relation between these variables which has considerable value for quickly making such calculations.

Action of Carbon Dioxide on Calcium Cyanamide. Franck and Meppen[35] while attempting to find a method of removing the free carbon from commercial calcium cyanamide made a careful study of the system $CaCN_2-C-CO_2$. They found that between the temperatures 600° and 1000° C. two reactions were possible; first $2\ CaCN_2+CO_2=2CaO+3C+2N_2$ and second $CO_2+C=2CO$. Also above 1000° C. a third reaction takes place in which the CO from the second reaction combines with the calcium cyanamide producing CaO, N and C. The second reaction is the fastest, yet it was found to be impossible to separate the carbon from the cyanamide because the first reaction takes place to a considerable extent before the end of the reaction between carbon and carbon dioxide.

Action of Carbon Dioxide on Sulfides of Sodium and Calcium. A method has been developed in which carbon dioxide is used for treating alkali waste for the recovery of sulfur or sulfur compounds. This process was at one time of some commercial importance in connection with plants using the LeBlanc process for making soda ash. According to Berl and Rittener[36] the carbon dioxide is used for freeing the raw soda liquors from sulfides, silicates and aluminates as well as from what iron may be present. The reaction on the sodium sulfide in the solution is $Na_2S+CO_2+H_2O \rightleftarrows NaSH+NaHCO_3$ and $NaSH+CO_2+H_2O \rightleftarrows NaHCO_3+H_2S$. These authors show that all the hydrogen sulfide is not expelled from the solution until the Na_2CO_3 present has been completely converted into $NaHCO_3$. On treating the calcium sulfide with carbon dioxide the reaction follows somewhat the same course, the final reaction being $Ca(SH)_2+CO_2+H_2O=CaCO_3+H_2S$. The gas escaping from the reaction tank has an H_2S concentration from 44 per cent to 71 per cent. The carbon dioxide used in this reaction is usually obtained from kiln gas.

Action of Carbonic Acid on Calcium Phosphate. Carbonic acid reacts to a certain extent with secondary and tertiary calcium phosphates with the production of primary calcium phosphate. The equation for the reaction between carbonic acid and secondary calcium phosphate may be written $2CaHPO_4+H_2CO_3=Ca(H_2PO_4)_2+CaCO_3$. The calcium carbonate also reacts with carbonic acid to produce calcium bicarbonate. This reaction has recently been studied by Müller and Knöfel[37] who found that $Ca_3(PO_4)_2$ dissolves to the extent of 0.754 grams of P_2O_5 per liter of solution saturated with CO_2 at 60 atmospheres pressure. Under the same conditions bone ash dissolves to the extent of 0.589 grams P_2O_5 at 0° and 0.333 grams P_2O_5 at 20° C. Phosphorite is much less soluble giving only

[35] Franck, H. H., and Meppen, B., *Z. angew. Chem.*, **43**, 726-32 (1930).
[36] Berl, E., and Rittener, A., *Z. angew. Chem.*, **20**, 1637-42 (1907).
[37] Müller, E., and Knöfel, J., *Z. anorg. allgem. Chem.*, **194**, 258-60 (1930).

TABLE 59.—*Solubility of Secondary Calcium Phosphate in Solutions of Carbon Dioxide Saturated Under a Pressure of 60 Atmospheres.*

(Data by Müller and Knöfel)

Temp. ° C.	P_2O_5 gm. per liter	CaO gm. per liter	Temp. ° C.	P_2O_5 gm. per liter	CaO gm. per liter
0	1.386	1.117	100	0.458	0.266
20	1.037	0.840	120	0.490	0.242
40	0.937	0.800	140	0.488	0.214
60	0.743	0.632	160	0.484	0.240
80	0.444	0.374			

0.035 grams of P_2O_5 per liter at 0° C. The effect of temperature changes on the solubility of secondary calcium phosphate is shown in Table 59.

Action of Carbon Dioxide Solutions on Alkaline Earth Silicates. The action of carbonic acid on alkaline earth silicates may be illustrated by the calcium silicate reaction simply expressed as $CaSiO_3+2H_2CO_3=Ca(HCO_3)_2+H_2SiO_3$. It is at once apparent that this reaction has a considerable bearing on rock and soil disintegration. Several studies having to do with this phase of rock action have been made but perhaps the most interesting is the recent work published by Müller and Lubberger.[38] The change in solubility of the alkaline earth silicates with change in temperature as determined by these authors is indicated in Table 60 while the change in solubility with change in pressure of carbon dioxide is given in Table 61.

TABLE 60.—*Solubility of Alkaline Earth Silicates in Solutions of Carbon Dioxide Under 50 Atmospheres Pressure.*

(Data by Müller and Lubberger)

Reaction time 3 hours.

Temp. ° C.	$CaSiO_3$ gm. per liter	$SrSiO_3$ gm. per liter	$BaSiO_3$ gm. per liter
0	3.712	4.123	6.001
20	3.503	3.799	5.751
40	3.309	3.563	5.401
60	2.900	3.111	4.853
80	2.104	2,323	4.179
100	0.907	1.012	2.582
120	0.950	1.040	2.594
140	0.956	1.050	2.590

TABLE 61.—*Solubility of Alkaline Earth Bicarbonates and Silicates in Water Solutions of Carbon Dioxide Under Varying Pressures at 20° C.*

Concentrations expressed as grams of salt per liter of solution.

(Data by Müller and Lubberger)

Pressure of CO_2 Atmos.	$Ca(HCO_3)_2$	$CaSiO_3$	$Sr(HCO_3)_2$	$SrSiO_3$	$Ba(HCO_3)_2$	$BaSiO_3$
50	4.875	3.503	4.858	3.799	6.981	5.751
40	4.875	3.501	4.859	3.800	6.975	5.746
30	4.871	3.498	4.856	3.797	6.975	5.746
20	4.325	3.106	4.266	3.336	6.453	5.316
10	2.993	2.149	3.088	2.416	6.376	5.253
0	1.387	0.996	1.349	1.055	3.218	2.651

[38] Müller, E., and Lubberger, W., *Z. anorg. allgem. Chem.*, 194, 161-7 (1930).

Action of Carbonic Acid on Magnesium Compounds. The existing data on the action of carbon dioxide solutions on magnesium compounds is not as extensive as those on the action of carbon dioxide on calcium compounds. The reactions, however, are quite similar and the way compounds of calcium and magnesium are associated in nature makes a study of both systems of considerable importance. It will serve our purpose here to consider only a few of the most modern researches on the solubility of magnesium carbonate in aqueous solutions of carbon dioxide. The importance of the work done previously to this should not be depreciated, however, as most of the information we now have on the subject has been contributed by such men as Raikow,[39] Davis,[40] Cameron and Robinson[41] and especially Johnston[44] as well many other investigators.

Solubility of Magnesium Carbonate in Solutions of Carbon Dioxide. Haehnel[43] reports some interesting results from solubility measurements on magnesium carbonate. He found that at 18° C. the solubility of magnesium carbonate in water saturated with carbon dioxide increased with increasing carbon dioxide pressures up to 18 atmos. and that no further

TABLE 62.—*Molal Concentration (Expressed as Millimols per Kilo. of Water) of Ions in Equilibrium with a Series of CO_2 Pressures in the System*

$MgCO_3 \cdot 3H_2O—H_2O—CO_2$ at 25° C.

(Data by Kline)

Pressure Atmos.	$[Mg^{++}]$ $\times 10^3$	$[HCO_3^-]$ $\times 10^3$	$[CO_3^{--}]$ $\times 10^3$	Ionic strength	$[OH^-]$ $\times 10^5$	Solid phase
0.000107	4.33	4.88	1.89	0.0149	3.84	
.000113	4.45	5.01	1.95	.0153	3.73	
.000170	5.77	7.45	2.05	.0194	3.69	
.000179	5.93	7.63	2.12	.0199	3.59	
.000197	6.58	7.95	2.61	.0224	3.40	$Mg(OH)_2$
.000210	7.08	8.06	3.05	.0243	3.23	
.000233	7.80	8.37	3.61	.0270	3.03	
.000251	8.07	8.55	3.80	.0280	2.87	
.000310	10.13	11.84	4.21	.0346	3.22	
.000376	12.96	14.04	5.94	.0448	3.14	
.000380	13.55	14.32	6.39	.0470		
.000510	14.37	17.10	5.82	.0489		
.000680	15.12	18.72	5.76	.0511		
.000845	15.66	19.90	5.71	.0527		
.000887	15.93	20.46	5.70	.0535		
.000930	16.24	21.19	5.65	.0544		
.00160	18.59	26.98	5.10	.0609		$MgCO_3 \cdot 3H_2O$
.00334	22.10	35.48	4.36	.0707		
.00690	25.07	44.68	2.73	.0779		
.0150	31.27	60.22	1.16	.0950		
.0432	46.01	89.98	1.02	.1390		
.1116	62.66	123.6	0.85	.1889		
.9684	213.5	426.9	....	.6405		

[39] Raikow, P. N., Chem.-Ztg., **31**, 55 (1907).
[40] Davis, W. A., *J. Soc. Chem. Ind.*, **25**, 788, 973 (1905).
[41] Cameron, F. K., and Robinson, W. O., *J. Phys. Chem.*, **12**, 561 (1908).
[44] Johnston, J., *J. Am. Chem. Soc.*, **37**, 2001 (1915).
[43] Haehnel, O., *J. prakt. Chem.* (2), **108**, 61-74 (1924).

increase in solubility took place between this pressure and 56 atmos. At the point of maximum solubility the solution contained 7.49 grams of $MgCO_3$ or 13.00 grams of $Mg(HCO_3)_2$ in 100 grams of water. He also found that a solution of $Mg(HCO_3)_2$ prepared at high pressures of carbon dioxide is quite stable at ordinary temperatures but if heated to 65° C. a vigorous evolution of carbon dioxide takes place with a precipitation of crystals of $MgCO_3 . 3H_2O$. He also found that magnesium bicarbonate is sufficiently stable to be detected in the solid state at −5° C.

The solubility measurements made by Kline[44] on magnesium carbonate (nesquehonite) in carbon dioxide solutions are not only confidence inspiring but cover a range of carbon dioxide pressures of considerable importance. His results include determined and calculated concentrations of the ions concerned and are given in Table 62 while Table 63 lists the concentration

TABLE 63.—*Molality of Magnesium in Saturated Solutions of the Carbonate at Various Pressures of Carbon Dioxide.*

Temp.=25° C.
(Data by Kline)

Pressure Atmos.	[Mg]	Pressure Atmos.	[Mg]
0.001	0.0178	0.7	0.181
.01	.0270	1.0	.217
.05	.0489	2.0	.287
.1	.0660	5.0	.384
.3	.117	10.0	.471
.5	.152	15.0	.526

of magnesium in water solutions of carbon dioxide under pressures extending as high as 15 atmospheres. These latter data were interpolated from the curve of most probable solubility measurements.

Solubility measurements of magnesium carbonate in aqueous solutions charged with carbonic acid gas were also made by Terada.[45] His work, however, was concerned principally with the velocity of the reactions. Thus the solution of MgO or $Mg(OH)_2$ in water solutions of carbon dioxide was found to be very rapid while $MgCO_3.3H_2O$ dissolved very slowly. Studies of bicarbonate reactions of Ca and Mg have also been made recently by Stumper[46] but his measurements also dealt with reaction velocities especially where they were related to the industrial process of softening hard water.

Action of Carbon Dioxide on Aqueous Lead Acetate Solutions. When gaseous carbon dioxide is passed through a solution of lead acetate, either normal or basic lead carbonate is precipitated. The nature and yield of precipitate depends upon several factors, the concentration of the acetate solution being one of the most important. Thus Altmann[47] on passing

[44] Kline, Walter, *J. Am. Chem. Soc.*, **51**, 2093-7 (1929).
[45] Terada, Kiyomatsu, *Bull. Inst. Phys. Chem. Research (Tokyo)*, **7**, 452-65 (1928).
[46] Stumper, R., *Z. anorg. allgem. Chem.*, **202**, 227-60 (1931).
[47] Altmann, A., *Z. anorg. allgem. Chem.*, **52**, 219-28 (1907).

carbon dioxide through a $N/2$ lead acetate solution at 20° C. obtained 32.8 per cent of the lead precipitated and when the temperature was raised to 100° C. only 6.32 per cent of the lead was precipitated. In a $N/50$ solution of lead acetate at 20° C., 80.21 per cent of the lead was precipitated and at 100° C., 48.25 per cent of the lead was precipitated. Solutions of higher concentrations gave precipitates of normal carbonate while hot dilute solutions gave basic lead carbonate ($2PbCO_3.Pb(OH)_2$). Hot concentrated solutions of lead acetate gave various mixtures of the normal and basic carbonates.

These conclusions were confirmed in general by Yamasaki[48] who found that diluting the lead acetate solution down to 0.1 N increased the precipitate of lead carbonate but that in less concentrated solutions the amount of precipitate was independent of the concentration. Concentrations of 0.1 N or below give a ratio of acetic acid to lead acetate as 4.3 is to 1. When

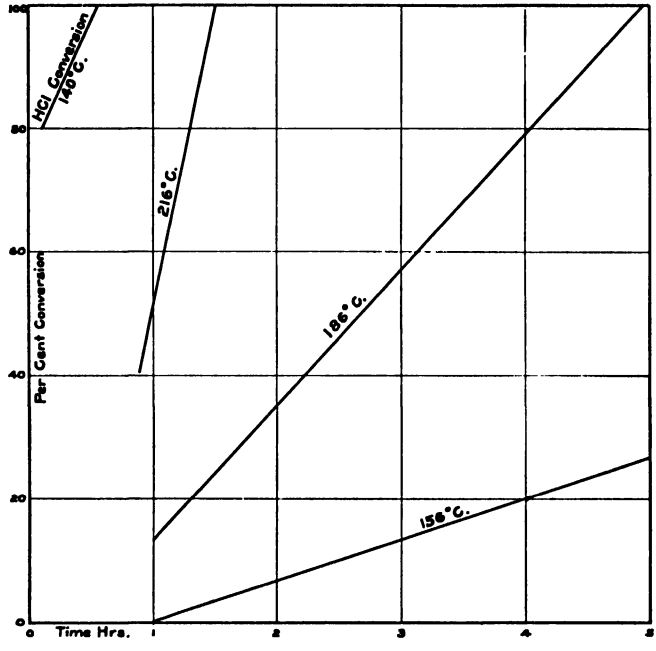


FIGURE 29. Conversion of Starch to Dextrose by Carbon Dioxide Solution at 1000 lbs. per square inch.

acetic acid was added to the lead acetate solution and carbon dioxide passed through, the proportion of acid to lead acetate was the same as in the case where no acid was added, if the total concentration of the acetate radical was lower than 0.1 N. In dilute solutions of lead acetate, the lead was almost completely precipitated by carbon dioxide when sodium acetate was added in quantity more than equivalent to the lead salt.

[48] Yamasaki, K., *Mem. Coll. Sci. Eng., Kyoto Imp. Univ.*, 1, 177-83, 275-76 (1907).

The Hydration Action of Carbonic Acid on Starch. Under high pressures (up to 2500 pounds per square inch) carbon dioxide solutions displace acetic acid from aqueous solutions of calcium acetate until the resulting acidity corresponds to a solution containing about 10 per cent by weight of acetic acid.[49] While it is true that this acid concentration is only moderate, it is conceivable that certain commercial reactions might be carried out in carbon dioxide solutions to an advantage. Dewey and Krase[50] studied the effect of aqueous solutions of carbon dioxide, saturated at about 1000 pounds per square inch, on starch and found that the hydrolysis of the starch to dextrose is a linear function of the time. It was also found that at 216° C. complete hydrolysis of the starch required 1.5 hours, while at 180° C. 5 hours were necessary to complete the reaction. The results obtained by these investigators at three different temperatures are shown in Figure 29.

Reactions with Gaseous Carbon Dioxide

The carbon dioxide molecule is relatively stable and under ordinary conditions does not break up readily into simpler compounds. It is possible, however, to decompose it to a certain extent at high temperatures. It has already been shown (see page 64) that the degree of dissociation is a function of the temperature. The dissociating reaction under these conditions is $2CO_2 \rightleftarrows 2CO + O_2$. Various other conditions will also bring about this decomposition reaction, as for instance, ultra-violet light which decomposes it to the extent of 3 per cent at atmospheric pressure and up to 46 per cent at 36 mm. pressure.[51] That the presence of moisture in the gas tends to greatly decrease the degree of dissociation has been shown by several investigators. Sulfur dioxide and potassium cyanide likewise retard the decomposition reaction. Radium radiations tend to decompose carbon dioxide but the reaction is slow and proceeds only slightly towards the carbon monoxide and oxygen side of the equation. Electric sparks passed through carbon dioxide gas also decomposes it slightly. When the carbon monoxide and oxygen concentration reaches a certain value a recombination takes place which apparently stops the decomposition. A silent discharge also decomposes carbon dioxide and the resulting oxygen is partially converted to ozone. The action of the ozone on the carbon monoxide reverses the reaction thus preventing any considerable dissociation.

Reduction of Carbon Dioxide by Hydrogen. Perhaps the most usual reduction reaction produced by hydrogen on carbon dioxide is $CO_2 + H_2 \rightleftarrows CO + H_2O$. However this is by no means the only reaction possible as various carbon compounds such as formaldehyde, methane, ethane and various other reduction products may be formed under certain conditions and especially under the influence of certain catalytic agents.

[49] Goodman, J. B., and Krase, N. W., *Chem. Met. Eng.*, **36**, 162 (1929).
[50] Dewey, M. A., and Krase, N. W., *Ind. Eng. Chem.*, **23**, 1436-7 (1931).
[51] Chadwick, S., Ramsbottom, J. E., and Chapman, D. L., *J. Chem. Soc.*, **91**, 942 (1906).

A few of the most modern researches dealing with this subject will be considered. Randall and Shiffler[52] suggest that the deposition of carbon from reacting mixtures of CO_2 and H_2 may take place according to the equation $CO_2+2H_2 \rightleftarrows C+2H_2O$ with all of the reactants in the gaseous form except carbon which is graphitic. Srikantan[53] studied the reaction under the influence of the catalytic action of platinum and platinum iridium alloy. His results were concerned more especially with reaction velocities at various temperatures and conditions of catalysts. Peters and Kuester[54] found that a mixture of CO_2 and H_2 under the influence of an electric discharge at reduced pressure reacted according to the equation $CO_2+H_2 \rightarrow H_2O+CO-10.4$ Cal. Bahr[55] studied the reaction at moderate temperatures using various catalysts to promote the reaction. He found that with metallic Cu the reaction was noticeable at 200° C. With the employment of $Cu.Cr_2O_3$, Fe.Cu, Fe.Co and Co.CuZn as contact materials with temperatures between 200° and 450° C. the CO quantities obtained were as high as 16 per cent of the gas mixture. With a slow current of the gas mixture of CO_2 and H_2 over the catalysts the reduction of the CO_2 went to methane.

Reduction of Carbon Dioxide with Carbon. The reduction of carbon dioxide with carbon at elevated temperatures is of considerable commercial importance. Its most important application is in the combustion of ordinary carbonaceous fuels during which carbon monoxide is practically always produced, to some extent, by the reduction of carbon dioxide. This topic will be treated under the subject of combustion (see page 148) and at this point perhaps a very brief reference to it will suffice.

It so happens that a large number of reported data on the equilibrium relations of the gaseous components of the system $CO_2+C \rightarrow 2CO$ have been made at 800° C. This rather arbitrary temperature selection was made because of the fact that at this temperature the speed of the reaction is sufficiently great to permit of laboratory treatment and that the carbon dioxide concentration at this point is sufficiently high to make its determination easy. Data at this temperature can be selected from a number of sources although it must be admitted that the agreement between them is not especially good. Dent and Cobb[56] however, point out that this lack of agreement is without doubt due to the various forms of carbon used by the different investigators. Thus one would hardly expect reactions of carbon dioxide with coke, charcoal and graphite to follow exactly the same course because of their different energy contents. Some of the results of various investigators in this field have been selected and the composition of the gaseous phase under equilibrium conditions at 800° C. are as follows:

[52] Randall, Merle and Shiffler, W. H., *Ind. Eng. Chem.*, **21**, 941 (1929).
[53] Srikantan, B. S., *J. Indian Chem. Soc.*, **6**, 931-47, 949-58, 959-67 (1929).
[54] Peters, K. and Kuester, H., *Z. physik. Chem.*, Abt. A, **148**, 284-303 (1930).
[55] Bahr, Herbert, *Ges. Abhandl. Kenntnis Kohle*, **8**, 219-24; *Chem. Zentr.*, **1930**, I, 185-6.
[56] Dent, F. J., and Cobb, J. W., *J. Chem. Soc.*, **1929**, 1903-12.

CO_2 %	CO %	Observer	Reference
7.0	93.0	Boudouard,	*Ann. chim. phys.*, 24, 1 (1901).
13.1	86.9	Mayer and Jacoby,	*J. Gasbeleucht.*, 52, 282 (1909).
11.4	88.6	Arnt and Schraube,	Dissertation Techn. Hochschule, Berlin (1911).
13.85	86.15	Rhead and Wheeler,	*J. Chem. Soc.*, 97, 2178 (1910).
9.95	90.05	Bodmer,	Dissertation Techn. Hochschule, Zurich (1926).
13.85	86.15	Dent and Cobb (with graphite)	*Loc. cit.*
9.1	90.9	Dent and Cobb (with coke)	*Loc. cit.*

In the reaction between carbon and carbon dioxide the presence of water vapor affects the rate at which equilibrium is established as is often the case in many other reactions. A study of the effect of moisture on this reaction has been made by Topley[57] who shows that there is an approximate proportionality between the concentration of water vapor and the rate of the reaction.

For the production of carbon monoxide either in the pure condition or in low concentrations the reduction of carbon dioxide offers the cheapest and most convenient method of obtaining it. For producing pure carbon monoxide on a large scale it is usual to pass carbon dioxide and oxygen into a thick bed of coke heated to a high temperature. The reaction between the coke and carbon dioxide being endothermic and that between coke and oxygen being exothermic it is possible to control the temperature of the coke mass very accurately by the simple process of varying the quantity of carbon dioxide and oxygen admitted to the reaction.

Action of Carbon Dioxide on Metals. The reduction of carbon dioxide with metals is a very common procedure and is often carried out in elementary laboratory work by chemical students. Producing the element carbon from solid carbon dioxide by burning aluminum or magnesium in a cavity made in a block of the solid is also a common and spectacular lecture demonstration experiment. It is possible, however, to control the experimental conditions so the reduction may go only part way and this is well illustrated by the reaction between metallic tin and carbon dioxide. The reaction is somewhat analogous to the carbon reduction and may be expressed as $Sn+2CO_2=SnO_2+2CO$. For theoretical reasons the reduction of carbon dioxide by means of tin has received considerable study.[58]

The following equilibrium constants were found by Fraenkel and Snipischski:

Temp. °C.	K	Temp. °C.	K
600	0.28	950	0.18
650	0.27	1000	0.13
700	0.27	1050	0.09
750	0.26	1100	0.07
800	0.25	1150	0.06
850	0.23	1200	0.05
900	0.22		

[57] Topley, B., *Nature*, 125, 560-1 (1930).

[58] Fraenkel, W., and Snipischski, K., *Z. anorg. allgem. Chem.*, 125, 235-51 (1922). Maeda, Tsutomu, *Bull. Inst. Phys. Chem. Res. (Japan)*, 2, 350-61 (1923). Eastman, E. D., and Robinson, P., *J. Am. Chem. Soc.*, 50, 1106-14 (1928). Meyer, G., and Scheffer, F. E. C., *Rec. trav. chim.*, 51, 569-73 (1932).

These values were obtained by analyzing the gas mixture in equilibrium with tin at various temperatures and calculated from the expression $K = C_{CO_2}/C_{CO}$ where the concentrations were expressed in volume per cent.

The best values of the equilibrium constant obtained by Eastman and Robinson were:

Temp. °C.	650	700	750	800	850	900
$K = C_{CO_2}/C_{CO}$	0.321	0.296	0.277	0.260	0.245	0.232

In a very recent work published by Meyer and Scheffer the values of Fraenkel and Snipischki at lower temperatures were confirmed but values above 800° C. were found to be too low. A good agreement was found, however, with the work of Eastman and Robinson.

By treating carbon dioxide with metallic sodium or potassium it is possible to take the reduction down to salts of oxalic acid according to the general equation $2CO_2 + M_2 = C_2O_4M_2$. Lemarchands and Roman[59] have investigated this type of reduction and found that potassium produced a greater yield of the oxalate than was obtained with sodium. Thus at 230° C. the potassium reacted with the carbon dioxide to an extent that yielded 17 per cent of oxalic acid. Sodium on the other hand, produced only 1.5 per cent oxalic acid when heated to 350° C. In this latter reaction the reduction goes principally to carbon.

The Manufacture of Urea. The synthesis of urea is a question of sufficient commercial importance to justify its inclusion in the discussion of industrial uses of carbon dioxide, yet its chemistry is quite interesting and a brief mention of it here perhaps will not be out of place. Urea has recently become of considerable importance as a concentrated fertilizer and as a reagent in the rapidly growing field of organic plastics. It now seems not at all unreasonable to expect it to be one of the important concentrated nitrogen carriers of the future.

Carbon dioxide and ammonia under the proper conditions may react together to form ammonium carbamate and this compound on dehydration produces urea. The chemical reactions involved may be represented as follows:

$$CO_2 + 2NH_3 = (NH_3)_2CO_2$$

Ammonium carbamate

and

$$(NH_3)_2CO_2 = (NH_2)_2CO + H_2O$$

Urea

The water liberated in the above reaction may also combine with some of the carbamate present to produce ammonium carbonate or ammonium bicarbonate thus:

$$(NH_3)_2CO_2 + H_2O = (NH_4)_2CO_3$$

and

$$(NH_4)_2CO_3 = NH_4HCO_3 + NH_3$$

The reactions involved in this system have received extensive study by many investigators who have treated them mostly from a phase point of view. Some of these investigations were made by Terres and Behrens,[60]

[59] Lemarchands, M., and Roman, H. L., *Compt. rend.*, 192, 1381-3 (1931).

[60] Terres, E., and Behrens, H., *Z. physik. Chem.*, Abt. A 139, 695-716 (1928).

Jänecke,[61] Jänecke and Rahlfs,[62] and Davis and Black.[63] A very careful and complete thermodynamic analysis was made by Klemenc[64] and the system studied from a practical point of view by Krase and his associates.[65]

When anhydrous ammonia and anhydrous carbon dioxide are mixed in the proportion of 2 moles of NH_3 to 1 mole of CO_2 and the mixture is then heated to 150° C. the resulting reaction will come to equilibrium when about 44 per cent of the carbamate first produced has been converted to urea. The conversion can be increased to 70 per cent at the same temperature if the molal ratio of ammonia to carbon dioxide is increased to 4 to 1. The yield of urea, while important, is perhaps of less importance than a complete recovery of the uncombined ammonia and carbon dioxide in the reaction mixture. This recovery can be made successfully and a unit for carrying it out becomes a part of any commercial plant.

A very interesting description of an experimental plant, having a ten-ton ammonia input per day, is given by Krase, Gaddy and Clark. Their process uses liquid ammonia and liquid carbon dioxide in a reaction autoclave and a conversion of 35 to 37 per cent can be obtained. The uncombined ammonia and carbon dioxide are recovered from the discharge solution and used over again. For the details of this interesting experimental work one is referred to the original paper of these investigators.

[61] Jänecke, E., *Z. Elektrochem.*, **35**, 716-28 (1929).

[62] Jänecke, E., and Rahlfs, E., *Z. Elektrochem.*, **36**, 645-54 (1930).

[63] Davis, R. O. E., and Black, C. A., *Ind. Eng. Chem.*, **23**, 1280-82 (1931).

[64] Klemenc, A., *Z. anorg. allgem. Chem.*, **191**, 246-82 (1930).

[65] Krase, H. J., and Gaddy, V. L., *J. Ind. Eng. Chem.*, **14**, 611 (1922); *J. Am. Chem. Soc.*, **52**, 3085 (1930). Krase, H. J., Gaddy, V. L., and Clark, K. G., *Ind. Eng. Chem.*, **22**, 289-93 (1930).

Chapter V

Carbon Dioxide and Vital Processes

The fact that carbon dioxide is a product of the metabolic activity of animals and a food substance vital to the life of plants, makes it very closely related to all kinds of life. It is not surprising that many attempts have been made to determine the effect of increasing the normal carbon dioxide content of the atmosphere around growing plants or that numerous experiments have been conducted to determine the effect of this gas on animal life. These experiments have added considerably to our knowledge of vital processes and many of them have given results of some practical importance.

Stimulating Plant Growth with Carbon Dioxide. Plant growth may be stimulated by increasing the concentration of carbon dioxide in the atmosphere around the leaves. This increase in growth rate is the result of the increased rate of diffusion of carbon dioxide through the stomata of the leaves caused by the increased concentration of the carbon dioxide surrounding them. Growth may also be stimulated indirectly by the action of carbon dioxide solution in ground water acting on soil materials with the liberation or formation of fertilizing materials necessary to plant life. It is evident that the former action gives promise of the most important results and it is in this field that most of the experimental work has been done.

As one might expect, carbon dioxide is only one of the factors essential to plant growth and therefore a simple gassing of the plant with carbon dioxide may or may not increase its growth. The failure to recognize the importance of all other factors, except carbon dioxide concentration, lead some of the investigators in the beginning of this study to obtain negative results and for some time there was considerable debate as to whether increasing the carbon dioxide concentration of the atmosphere would actually increase the rate of plant growth or not. However, modern investigators have demonstrated without the least doubt that with properly controlled conditions, plants will grow faster and larger and produce a greater crop yield when the carbon dioxide concentration is increased in the atmosphere around the leaves.

Many of these investigations have been conducted in closed boxes or in green houses where it was possible to control accurately the concentration of the carbon dioxide in the atmosphere. Field experiments have also been conducted on small plots as well as on very large tracts. Cummings and Jones[1] conducted experiments in inclosed boxes in which they were able to increase the carbon dioxide content of the gas. It was found by these

[1] Cummings, M. B., and Jones, C. H., *Vermont Agr. Expt. Sta. Bull.*, 211, (1919).

investigators that legumes showed an increase in production of pods and beans and that the chemical composition of the plant was slightly changed with the carbon dioxide treatment. Potatoes also showed an increase in yield of tubers and foilage. In these experiments, gassing the plants increased the hydrocarbon content and decreased the protein content. A little later, Fischer[2] published the results of experiments carried out on a large scale in the Ruhr coal region. The gas was furnished to large plots of land from the waste gases from blast furnaces. These gases were purified and distributed to the field in concrete pipes. A very large increase in production of potatoes was reported. Ranc[3] conducted his experiments in hothouses with potatoes, radishes, and tomatoes; also some outside experiments with spinach, beets, potatoes, lupine and barley. In all cases, a greatly increased yield was obtained. Indications that interest in this subject is very much alive at present are shown by the many recent publications dealing with it.[4] Jaccard[5] found that the consumption of carbon dioxide by a plant at constant illumination was a direct function of the temperature. Small and White[6] obtained increased yields of tomatoes in greenhouse experiments with increased carbon dioxide concentration.

The economic aspect of fertilizing growing plants with gaseous carbon dioxide is indeed an interesting one. Now that the fact is well established, that increasing the carbon dioxide concentration in the atmosphere around plants will actually increase growth and yield of product, the question naturally arises as to whether this can be done at a profit. Riedel has emphasized this phase of the question considerably and has devised methods of applying carbon dioxide to large tracts of land and to smaller inclosed spaces. Others have also treated the problem from a commercial point of view, but up to the present time there seems to be no possibility of successfully gassing large tracts of growing plants. The question of economically treating plants with carbon dioxide in greenhouses may be an entirely different one, however. Here, of course, the cost of carbon dioxide and the ease of application are important factors. Commercial liquid carbon dioxide does not enter into this phase of the subject at all. Low grade carbon dioxide-air mixtures serve the purpose, and the methods of producing these usually depend upon the combustion of carbon containing materials such as alcohol, oil, coke, or upon the utilization of waste flue gases from certain industrial operations.

[2] Fischer, H., *Z. angew. Chem.*, **33**, 197-8 (1920).

[3] Ranc, A., *Industrie Chimique*, **7**, 349-51 (1920).

[4] Bolas, I. B. D., and Henderson, F. Y., *Ann. Botany*, **42**, 509-24 (1928). Bornemann, *Mitt. deut. Landwges.*, **1920**, Ehrenberg, P., *Z. Pflanzenernärh. Düngung*, **B5**, 85-6 (1926). Fischer, H., *Gartenflora*, **61**, 298-307; *Zentr. Biochem. Biophys.*, **14**, 487; *Ber. deut. botan. Ges.*, **45**, 331-9, (1927); *Naturwissenschaften*, **8**, 413-17 (1920); *Angew. Botan.*, **1**, 138-46 (1919). Gering, A., *Fühling's Landw. Ztg.*, **70**, 137-53, 181-97 (1921). Hawkins, *Florida Grower*, **25**, (1922). Heydemann, F., *Gartenbauwissenschaft*, **1**, 100-40 (1928); *Expt. Sta. Record*, **60**, 339-40. Janert, Heinz, *Botan. archiv.*, **1**, 155-76 (1922). Jess, *J. agr. prat.*, **35**. 229 (1921). Lundergardh, H., *Annew Botan.*, **4**, 120-51 (1922). Reinan, E., *Angew. Botan.*, **2**, 290-302 (1920); *Chem.-Ztg.*, **44**, 808 (1920). Riedel, F., *Gartenwelt*, **25**, No. 31, 302-4; No. 34. 336-8 (1921); *Expt. Sta. Record*, **45**, 834; *Chem.-Ztg.*, **45**. 829-30 (1921); *Gesundh-Ing.*, **53**, 257-61 (1930). Schmidt, W., *Fortsch. Landw.*, **4**, 360 (1929). Schulte-Overbeck, *Brennstoff-Chem.*, **11**, 28-30 (1930). Wagner, H., *Umschau*, **27**, 785-6 (1923).

[5] Jaccard, Paul, *Bull. soc. chim. biol.*, **12**, 156-70 (1930).

[6] Small, T., and White, H. L., *Ann. Applied Biol.*, **17**, 81-9 (1930).

The Indirect Fertilization of Plants with Carbon Dioxide. Under this topic one might consider the action of various carbon dioxide-producing reactions which take place in the soil, thus increasing the carbon dioxide in the soil air, and also in the air above the soil. Or one might consider the importance of the action of carbon dioxide-water solutions on the rock materials of the soil which liberate fertilizing materials necessary to plant growth. A short discussion of both of these phases will be given here.

It is generally recognized that organic manures have a more favorable action as fertilizers than those not containing organic materials. It is thought that this added advantage may be due to the carbon dioxide liberated to the soil by the oxidation of the organic matter present. Whether this is entirely true or not, is somewhat doubtful. Bornemann[7] believes that part of this favorable action of dunged soil on plants may be due to the increased carbon dioxide produced. However, Gerlach's[8] experiments failed to confirm the idea and led this investigator to state that the only favorable action of organic manures is due to the addition of nitrogen, potash and phosphoric acid to the soil. Yet Reinau[9] holds that the soil air must have considerable effect on the rate of plant growth. While one finds in the literature many conflicting ideas on this subject, the fact yet remains that gassing plants with moderate amounts of carbon dioxide will increase the rate of growth and that organic manures do increase the carbon dioxide concentration of soil air. It therefore seems perfectly reasonable to expect at least some favorable action on plant growth due to this factor.

In an attempt to increase the fertility of the soil, various so-called carbon dioxide fertilizers have been proposed and some attempts have been made to commercialize some of them. One such fertilizer, composed of peat, and charcoal, with small amounts of nitrogenous material, potash and phosphates, was investigated by Gerlach and Seidel[10] and was found ineffective in increasing the yield of plant crops. Niklas, Scharrer and Strobel[11] experimented with a mixture containing 50 per cent peat, 45 per cent charcoal and 5 per cent pyrolucite with negligible amounts of nutrient substances. In 45 cylinder experiments, 23 showed definite increase in yield due to the fertilizer, while 18 showed no effect and 4 showed a decrease in yield. In 12 field experiments, 7 gave increased yields and 5 showed no effect. Riede[12] also investigated "CO_2-fertilizers" with practically no positive results.

The effect of carbonic acid solutions on rock material to liberate soluble potassium and phosphorous salts has already been discussed under the action of carbon dioxide on rocks. The importance of soil carbon dioxide in increasing the available nutrients in sufficient quantities to be of immediate use to plants is somewhat doubtful. Vandecaveye[13] studied this phase

[7] Bornemann, *Mit. deut. Landwges.*, 1920. *Biedermann's Zentr.*, **50**, 296-9 (1921).
[8] Gerlach, *Mitt. deut Landwges.*, **36**, 147-50 (1921); *Expt. Sta. Record*, **46**, 424.
[9] Reinau, E. H., *Festschr. Stoklasa*, **1928**, 305-18.
[10] Gerlach and Seidel, *Z. Pflanzenernähr. Düngung*, **B4**, 241-7 (1925)).
[11] Niklas, H., Scharrer, K., and Strobel, A., *Z. angew. Chem.*, **38**, 251-8 (1925).
[12] Riede, W., *Z. Pflanzenernähr. Düngung*, **5**, 383-5 (1926).
[13] Vandecaveye, S. C., *Soil Science*, **16**, 389-406 (1923).

of fertilization but discovered no relation between soil change and carbon dioxide production or the liberation of potassium salts. There was some indication, however, that a H-ion concentration less than pH 6 decreased the potassium adsorbing power of soil colloids.

The Physiological Action of Carbon Dioxide on Animals. Probably no one subject connected with physiology has been treated in such an exhaustive manner as the physiological action of carbon dioxide. The literature is filled with references to this important waste gas and the many ways that it affects body functioning. Here it will suffice to treat only a few phases of this subject and these only from the point of view of carbon dioxide utility and hazards connected with its presence in the air.

Respiratory Stimulant. The carbon dioxide excreted through the lungs of animals acts as a definite regulator of breathing and insures a sufficient supply of oxygen to the system. This fact is of tremendous importance from a physiological point of view. The adjustment between expired carbon dioxide and depth and frequency of respiration are so delicately balanced that the slightest decrease or increase in the carbon dioxide production in the body, induces immediately an almost proportional increase or decrease of the volume of breathing. It seems reasonable, therefore, for one to be able, by artificially changing the carbon dioxide in the lungs, to control breathing to a certain extent. This control can actually be accomplished and to a much larger extent than might at first be expected. By voluntarily ventilating the lungs, thus decreasing the alveolar carbon dioxide, breathing can be suspended for a considerable time. On the other hand, the administration of carbon dioxide causes a considerable increase in the depth and frequency of respiration. Higher concentrations of carbon dioxide than 25 to 30 per cent have a narcotic effect and tend to stop respiration even with a sufficient oxygen supply, but with a decreased oxygen supply, a very much lower concentration of carbon dioxide will depress breathing and even cause death. The response of normal individuals to the breathing of carbon dioxide-air mixtures is variable from person to person, and is not constant even with the same person at different times. The maximum increase in breathing is obtained with a 7 per cent carbon dioxide-air mixture.[14] From this point on, breathing is slowed down by increasing the carbon dioxide concentration. It has been found further that persons could work without decreased efficiency in a submarine if the carbon dioxide did not exceed 5 per cent.[15] The efficiency curve falls off rapidly, however, between 5.5 and 6 per cent. Six per cent is considered a critical point for men working and it is believed that the majority would be completely incapacitated in a short time in an atmosphere containing more than 6 per cent carbon dioxide.

Lethal mixtures of carbon dioxide and air are hard to define exactly. Deaths have been reported as caused by widely varying concentrations.

[14] Heller, E., Killiches, W., and Drinker, C. K., *J. Ind. Hyg.*, 11, 293-300 (1929).
[15] Brown, E. W., *U. S. Naval Med. Bull.*, 28, 721-733 (1930).

Thus an atmosphere showing 88 per cent nitrogen, 10.6 per cent carbon dioxide, and 1.4 per cent oxygen was responsible for the death of three men in a deep manhole.[16] In another case, four men were killed by jumping into a silo filled during the previous day with cut, immature corn. In five minutes each was dead or in a cyanotic condition from which he could not be revived. The air in the silo showed carbon dioxide 38 per cent, oxygen 13.5 per cent, and nitrogen 48.5 per cent.[17] Many examples of this type could be given but about the only conclusion one could draw from them is that the oxygen concentration perhaps plays a bigger part in the toxic properties of a gas mixture than does the presence of carbon dioxide. This can be shown by the results obtained by Schultzig.[18] He found no apparent evidence of carbon dioxide poisoning in a man exposed to an atmosphere containing 60 to 80 per cent carbon dioxide but with an adequate supply of oxygen; evidence of poisoning appeared, however, on exposure for fifty minutes to an atmosphere containing 9 to 9.5 per cent carbon dioxide with a deficient oxygen supply.

Therapeutic Uses of Carbon Dioxide Gas. The application of carbon dioxide in therapeutics depends largely upon its property of acting as a respiratory stimulant. A gas mixture containing 5 per cent carbon dioxide and 95 per cent oxygen is sold under the trade name "carbogen" and this gas mixture is a standard remedy for carbon monoxide poisoning, drowning, shock, and as an aid in anesthesia and in the treatment in alkalosis.

Drinker and Shaughnessy[19] suggest as a treatment for acute carbon monoxide poisoning a 7 per cent carbon dioxide-93 per cent oxygen mixture for the first 5 to 20 minutes followed by a 5 per cent carbon dioxide-95 per cent oxygen mixture. The use of pulmotors or any other positive pressure apparatus for the administration of this gas mixture is not favored at present. The usual method of administration is to furnish the gas to the patient by means of a device, such as an inhalator, and to promote respiration artificially, if necessary, by the prone pressure method.

The use of carbon dioxide-oxygen mixtures for the induction and termination of other anesthetics has now become widespread. Most modern mechanical devices designed to administer anesthetics, such as nitrous oxide, ethylene or ether, are fitted with carbon dioxide and oxygen cylinders and arranged so that various mixtures of these gases can be used if desired. It seems to be especially successful for terminating the anesthesia, and cases of post-operative pneumonia are rare where it has been used.

Experiments conducted on dogs suffering with pneumonia indicate that carbon dioxide mixtures with oxygen may become valuable for relieving a partial lung collapse. This collapse which seems to be a stage in pneumonia was quickly stopped and the lung redistended when carbon dioxide was administered.[20]

[16] Tankard, A. R., and Bagnal, D. J. T., *Analyst*, **55**, 673-6 (1930).
[17] Havhurst, E. R., and Scott, E., *J. Am. Med. Assoc.*, **63**, 1570-2 (1914).
[18] Schultzig, R., *Arch. Hyg.* **102**, 366-90 (1929).
[19] Drinker, C. K., and Shaughnessy, J., *J. Ind. Hyg.*, **11**, 301-14 (1929).
[20] Henderson, Y., Haggard, H. W., Coryllos, P. N., Birnbaum, L., and Radloff, M., *Arch. Internal Med.*, **45**, 72-91 (1930).

That carbon dioxide administration to insane patients has some temporary beneficial effect has been demonstrated at the University of California Medical School. Experiments conducted with patients suffering with *dementia praecox catatonia,* showed that a fleeting return of intelligence was obtained when carbon dioxide was inhaled. These periods of sanity were brief, lasting from ten to fifteen minutes, but the patient was able to answer questions rationally, or to exhibit recognition of his surroundings. Whether any practical application of this information is possible, remains to be determined by further experimentation.

The behavior of carbon dioxide as an anesthetic has been studied by Leake and Waters.[21] Dogs were successfully anesthetized in one minute with a mixture of 30 to 40 per cent carbon dioxide in oxygen. The anesthesia seemed to become smoother and deeper the longer the animal remained under it. Dogs have been kept under the anesthetic for periods of time up to two hours.

The treatment of hiccough with pure carbon dioxide is quite common. While it cannot be relied upon to effect a cure in all cases, numerous reports show that in certain types of hiccough it is a safe and reliable remedy.[22]

Whooping cough can also be treated with carbon dioxide and it is said that in many cases its administration was successful in decreasing the intensity and duration of the coughing spasms.

Certain forms of infantile tetany have been treated with atmospheres containing excess carbon dioxide and in practically all cases a definite improvement was noticed. When a case failed to respond to all other methods of treatment, it was exposed to a concentration of 40 per cent oxygen and the expired carbon dioxide was allowed to accumulate until it reached a concentration of 2 to 3 per cent. In 21 cases so treated, only one failed to improve with this treatment.[23]

The Use of Solid Carbon Dioxide as an Escharotic. The treatment of certain dermatologic affections with solidified carbon dioxide was first suggested by Dr. Pusey in Chicago in 1905. The efficiency of this therapeutic agent was soon demonstrated and its use became quite widespread. Mechanical devices for the preparation of the solid from liquid carbon dioxide which could easily be obtained from commercial cylinders of the substance, were soon developed so the snow could be formed into pencils of the proper shape. However, the trouble necessary in preparing the snow just before use, placed a serious handicap on this method of treatment and carbon dioxide gradually lost in competition with other therapeutic agents until today it is used but little for this purpose. Modern developments in the commercialization of solid carbon dioxide should, however, materially decrease this handicap and it seems that the availability of solid carbon dioxide today should make it again a valuable escharotic.

[21] Leake, C. D., and Waters, R. M., *J. Pharmacol.*, **33**, 280-1 (1928).
[22] Sheldon, R. F., *Anesthesia and Analgesia*, **6**, 31-34 (1927).
[23] McCrea, E. F., and Raper, H. S., *Univ. Manchester Quart. J. Med.*, **22**, 269-79 (1929).

When solid carbon dioxide is pressed onto the skin, immediate freezing of the tissues in contact with the snow takes place, while the conduction of heat from below, gradually extends this freezing, deeper and deeper. The rate and depth of freezing depends entirely upon the pressure of the application and its time. The skin at the point of contact with the solid is considerably depressed, becomes very hard and white in color. After thawing, the skin regains its former level and in the course of a few minutes there results a well developed wheal. In mild freezings the damaged tissues are usually absorbed in a few days to a week without a crust or scar formation. More prolonged freezings usually result in a crust formation which disappears in about 10 days. In very serious freezings there may be a serum-like discharge, occasionally co-associated with pustular discharge where the lesion has been of the infective type, or has been secondarily infected, which continues for several days to a week with the formation of a decided scab. The scab often becomes black in color and remains from two to even six weeks after which it separates, leaving a very slight scar. The pain associated with solid carbon dioxide treatment is usually very slight, depending of course upon the place of application and the nature of previous treatments. Bernstein[24] gives a detailed account of many cases treated with solid carbon dioxide. A summary of his experience has been arranged in Table 64.

Carbonated Baths. Carbonated baths, both natural and artificial, have enjoyed various degrees of popularity for many years. The idea originated in the naturally carbonated waters of Europe and much faith was at one time placed in these waters as therapeutic agents. That waters saturated with carbon dioxide have a decided physiological action on the skin can hardly be doubted,[25] yet the actual beneficial action is more or less vague.

One of the most evident effects of carbon dioxide action is a reddening of the skin, a stimulation of circulation because of the dilation of the capillaries, a lowering of the blood pressure and a generally stimulated feeling. Experiments with dry baths of carbon dioxide conducted by Kimetowicz[26] gives one a good idea of its physiological action. The effects of dry carbon dioxide baths for 10 to 20 minutes at ordinary temperatures were: (1) The capillaries were dilated and the respiration was slowed. (2) The pressure in the brachial artery fell an average of 30 mm. from the maximum. (3) The diastolic pulse, which by the ascillometer normally registered 3.5 to 4, fell to 2.0 to 2.5. (5) The pulse rate was between 68 and 74 per minute. (6) The quantity of carbon dioxide in the atmosphere of the bath chamber increased during the bath from 0.1 to 0.5 per cent. (7) The quantity of carbon dioxide in the expired air of the subject was increased after a bath of 10 minutes from 3.7 to 5.0 per cent. (8) The respiratory volume

[24] Bernstein, R., "Solidified Carbon Dioxide," A. S. Aloe and Co., St. Louis, Mo.

[25] Waledinsky, J. A., *Z. physik. diätet. Therapie*, 17, 18-26; *Zentr. Biochem. Biophys.*, 14, 575. Hirschefeld, A., *Veröffentlich. Zentralstelle Balneol.*, (1912), No. 6; *Zentr. Biochem. Biophys.*, 13, 447. Schott, A., *Lancet*, (1928), I, 546-8.

[26] Kimetowicz, E., *Compt. rend. soc. biol.*, 96, 565-6 (1927).

TABLE 64.—*Treatment of Skin Diseases by Freezing with Solid Carbon Dioxide.*
(According to Bernstein)

Disease	Time of treatment, sec.	Pressure applied	No. of cases	Result of treatment
Acne Pustulosa	5–10	light	numerous	very successful
Acne Indurata	10–15	medium	–	very successful
Acne Keloid	15–20	heavy	2	very successful
Adenoma Sebaceum	10–15	light	1	very successful
Angioma Naevus Vasculosus	10–30	light	–	several freezings successful
Telangiectasis	20–30	medium	–	numerous freezings successful
Cavernous Angioma	30–50	heavy	–	successful
Angiokeratoma	30	heavy	1	two treatments, successful
Callositas	60	heavy	–	several freezings, successful
Carbuncle	30–60	medium	several	very successful
Chaloasma (liver spot)	10–20	light	numerous	very successful
Clavus (corns)	60	heavy	–	very successful
Colloid degeneration of the skin	30	medium	1	very successful
Cornu Cutaneum	30	medium	2	very successful
Dermatitis Repens	20	medium	1	very successful
Eczema	5–20	medium	2	very successful
Epithelioma	30–60	heavy	numerous	very successful
Erythema Pernio (frost bite)	5–10	light	1	very successful
Folliculitis Decalvans	10	medium	1	successful
Hydrocystoma	15	medium	1	successful
Keloid	60	heavy	3	successful
Keratosis Follicularis	20	medium	1	successful
Lentigo (freckles)	10	light	–	successful
Leprosy	30–60	heavy	–	helpful
Leukoplakia	10	medium	1	doubtful
Lichen Planus	15	medium	2	helpful
Lupus Erythematosus	20–40	medium	many	very successful
Lymphangioma	45	heavy	1	many treatments were successful
Milium	10	medium	2	successful
Molluscum Contagiosum	40–60	heavy	4	successful
Morphea	15	light	1	successful
Naevus Pigmentosus	10	light	–	successful
Naevus Pilosus	20	medium	–	successful
Naevus Lipomatodes	45	heavy	–	successful
Paget's Disease	60	heavy	2	many treatments were successful
Psoriasis	10–15	medium	2	helpful
Rosacea	15–20	medium	1	fair success
Seborrhoea	30–45	heavy	–	successful
Steatoma	30–60	heavy	2	successful
Lupus Vulgaris	60	heavy	2	successful
Tuberculosis Verrucosa	60	heavy	1	doubtful
Scrofuloderma	60	heavy	1	successful
Ulcer (Chronic leg ulcer)	15	light	–	successful
Verruca Vulgaris (warts)	45–60	heavy	–	successful
Verruca Plana	30–45	heavy	–	successful
Verruca Filiformis	20–30	light	–	successful
Xanthoma Tuberosum	45–60	heavy	2	successful
Xeroderma Pigmentosum	20–30	medium	1	successful
X-Ray Keratoses	45–60	heavy	–	successful

measured by the spirometer was raised from 80 liters during 10 minutes before the bath to 103 liters during 10 minutes of the bath.

Carbon Dioxide as an Insecticide. The action of carbon dioxide as an insecticide may be utilized in several different ways. First it may be used as a source of power for projecting liquid sprays onto trees or shrubs; second, it serves as a respiratory stimulant to make poisonous gases more effective; and third, it may be used as a fumigating gas.

Armet[27] advocated the use of carbon dioxide in place of compressed air in spraying devices. It was claimed that the use of carbon dioxide tended to promote thorough mixing and better subdivision of the spray because of the evolution of the dissolved gas. It was also thought that at the same time it exerted a solvent action upon the basic copper sulfate of Bordeaux mixtures and a beneficial effect on the foliage.

Regardless of the specific advantage of carbon dioxide as such, it certainly has an advantage as a detached power source. This is especially true where small units of spraying equipment are used and where the use of a more expensive air compressor would be uneconomical.

The mixing of carbon dioxide with gaseous insecticides has been found especially advantageous as it permits a reduction in both dosage and exposure time.[28] The action on the insect is well illustrated by means of the American cockroach (*Periplaneta americana*). When at rest, at room temperature, this insect displays no respiratory movements and its tracheal valves are nearly closed. If it is brought into an atmosphere containing 2 or 3 per cent carbon dioxide, the valves open immediately, allowing a more rapid diffusion of respiratory gases. When the carbon dioxide concentration is brought to 7 or 10 per cent, respiratory movements of the abdomen appear. The width of the spiracle opening is therefore regulated by the concentration of carbon dioxide in the vicinity of the spiracle.[29]

In the fumigation of food materials carbon dioxide holds an important place. One of the most important grain fumigants is ethylene oxide and carbon dioxide. This gas mixture is practically 100 per cent efficient, when properly applied, against the grain weevil, even at winter temperatures. The compounds are mixed in the proportion of 10 pounds of carbon dioxide (preferably in the form of solid carbon dioxide) to 1 pound of ethylene oxide. Thirty-three pounds of this mixture is added to 1000 bushels of grain. The process of applying this gas, consists of mixing the ethylene oxide and solid carbon dioxide together in large pails and introducing the mixture into the grain as it is being run into the bin, the mixture being carried down with the grain and well distributed through it. No odor of chemicals is left in the grain by these compounds.[30]

Second only in importance to the stimulation of respiration in insects, is the property of carbon dioxide to reduce the fire hazard when mixed with

[27] Armet, H., *Prog. agr. vit.*, **81**, 592-7 (1924); *ibid.*, **82**, 88-96 (1924).

[28] Cotton, R. T., and Young, H. D., *Proc. Entomol. Soc. Washington*, **31**, 97-102 (1929).

[29] Hazelhoff, E. H., *J. Econ. Entomol.*, **21**, 790 (1928).

[30] Back, E. A., Cotton, R. T., Young, H. D., and Cox, J. H., *U. S. Dept. Agr. Bur. Entomol.*, (1930). Russ, J. M., *Ind. Eng. Chem.*, **22**, 328-332 (1930). Fleck, W., *Anal. soc. rur. Argentina*, 673 (1931). Osburn, M. R., *J. N. Y. Entomol. Soc.*, **39**, 567 (1931).

inflammable fumigants. This is especially true when ethylene oxide is used for this purpose. When mixed in the proportion indicated above, the fire hazard is reduced practically to zero. The inflammability of carbon dioxide and ethylene oxide mixtures has been studied by Jones and Kennedy,[31] who found mixtures consisting of 1 pound of ethylene oxide to 7.5 pounds of carbon dioxide were uninflammable under normal conditions of temperature and pressure. The same investigators[32] also found that when ethylene dichloride was used as a fumigant, 1.25 pound of carbon dioxide per pound of ethylene dichloride made the mixture non-inflammable.

The use of carbon dioxide directly as a fumigant is perhaps of little importance. A method for fur preservation suggested by Tiepolt is interesting and practical. The furs are placed in a gas-tight container and a block of dry ice placed near them. The cold produced drives the moths away and the cold gaseous carbon dioxide falls to the bottom and gradually fills the container with an atmosphere in which no moth or other living organism can survive.

[31] Jones, G. W., and Kennedy, R. E., *Ind. Eng. Chem*, **22**, 146-7 (1930).
[32] Jones, G. W., and Kennedy, R. E., *Ind. Eng. Chem.*, **22**, 963-4 (1930).

Chapter VI

Commercial Manufacture of Liquid Carbon Dioxide

The Coke or Absorption Process

In the coke or absorption process for manufacturing liquid or solid carbon dioxide the raw gas on which the process operates is ordinarily made by the combustion of coke. The process, however, is fundamentally a method of purification or carbon dioxide separation from other gases by means of absorption and it is by no means confined to a gas produced in the above manner. As a matter of fact any gas reasonably free from dust, sulfur dioxide and gaseous hydrocarbons but containing carbon dioxide in sufficient concentrations can be treated by the absorption process for the removal of a fraction of its carbon dioxide content. Because of the limitations of the absorbing apparatus ordinarily used, such gas mixtures should contain carbon dioxide in concentrations at least from 10 to 15 per cent. The flue gases obtained from ordinary coal-fired furnaces do not meet the above requirements sufficiently to make them of much commercial value although in some cases coal is being used in small amounts for combustion in carbon dioxide plants.

The absorption process in general consists of the following steps: (1) The production of a gas containing carbon dioxide. (2) The purification of this gas by scrubbing with water, dilute sodium carbonate solution or both. (3) The absorption of a part of the carbon dioxide in an alkaline solution of sodium carbonate, potassium carbonate or monoethanolamine. (4) The liberation of the pure carbon dioxide from the absorbing agent by boiling. (5) The condensation and separation of water from the gas. (6) The drying and compression of the purified carbon dioxide. (7) The condensation of the gas to a liquid and then charging it into steel cylinders for shipment or converting it into the solid state. The following description of these operations must of necessity be a composite picture of the present industrial plants. No uniformity in equipment is found except in cases where several plants are under one management.

The Furnace. Boiler and furnace equipment in carbon dioxide plants does not differ to any considerable extent from that found in other industrial power installations. A surprising number of plants uses hand-fired furnaces but the advantage gained by the close supervision of the fuel bed offsets to a considerable extent the loss occasioned by admitting air over the fuel from time to time.

Methods of calculating boiler capacities and grate sizes do not differ much from those used for coal-fired furnaces. For hand-fired furnaces, a grate area of 1 square foot for 7 pounds of coke consumed per hour is not far from the average.[1] Where conditions allow, increasing the grate surface over this figure permits lower operating temperatures and economy in furnace repairs. Assuming a plant to be designed for a capacity of 1000 pounds of liquid carbon dioxide per hour and with a recovery ratio of one pound of coke to each pound of carbon dioxide recovered (most plants do considerably better than this) then for 1000 pounds of coke consumed each hour a total grate area of about 143 square feet would be required. As a fair grade of coke will evaporate about 10 pounds of water from and at 212° F. per pound of coke burned the resulting boiler horse-power would be about 290. Such a heating plant could be conveniently divided into three furnaces with 100 horse-power boilers over each.

Where automatic stokers are used somewhat smaller grate areas are permitted. Also an auxiliary blower may be used for recharging some of the flue gas back into the furnace to effect a more complete mixing of the combustion gases. Higher possible carbon dioxide concentrations are claimed for this arrangement.

✓ Heat exchangers or "economizers" attached to the flues of coke furnaces may be used for heating boiler feed water or heating the strong lye on its way to the lye boiler. The latter arrangement is to be preferred, however, as most of the feed water comes directly from the heating coils in the lye boiler and at a temperature not far below its boiling point (in one plant at 90° C. or 194° F.). The flue gases leaving the economizer can be brought to a temperature near 170° C. or 338° F.

✓Draft for the furnaces is usually obtained by a blower located between the scrubbers and the coke towers. This fan can be operated by means of a steam engine, the throttle of which is automatically controlled by the steam pressure in the steam boiler.

✓ **Fuel.** The fuel used in a carbon dioxide plant is an important factor. A good grade of foundry coke gives the best results but this is not always obtainable at a reasonable price. Such coke may be 48-hour or 72-hour, the latter being preferred. By-product coke from an artificial gas plant is sometimes used but it is not entirely satisfactory. Coal is being used in some plants to a small extent but the authors know of no plant where it is used exclusively. The use of natural gas would seem to offer a solution to the fuel problem but the carbon dioxide concentration in such a flue gas is low and its use results in a decrease of plant capacity. The sulfur content of any fuel used must be very low otherwise the sulfur dioxide formed during its combustion contaminates the flue gas seriously and unless this is all removed it is taken up by the alkaline solution in the absorbing tower thus decreasing its absorbing capacity.

[1] See Nicol, E. W. L., "Coke and Its Uses," Ernest Benn, Ltd., London (1923).

Chemistry of Combustion. The chemical reactions involved in the combustion of coke are quite simple and perhaps some of the theoretical and practical aspects of this operation may be given here to an advantage.

As the primary air for the combustion of coke enters the bottom layer of the highly heated fuel, its oxygen combines with the carbon of the coke according to the following equation: $C+O_2=CO_2+97{,}000$ calories. This carbon dioxide, passing up through the mass of heated carbon, may then be partly reduced to carbon monoxide, according to the equation: $CO_2+C=2CO-39{,}000$ calories. Other secondary reactions may also take place, such as the direct combination of carbon with oxygen, to produce carbon monoxide and the reduction of water vapor which enters the furnace as moisture in the air or in the coke. It is evident at once that it should be the aim of the operator to promote the first reaction and to prevent as far as possible all secondary reactions which produce compounds other than carbon dioxide. Air is usually admitted over the top of the coke mass to complete, by secondary combustion, the burning of the carbon monoxide. This reaction is usually not complete so one may expect a small amount of carbon monoxide in the gaseous products of any coke fire. It stands to reason, however, while the quantity of carbon monoxide should be kept just as low as possible, excess air should not be added in sufficient quantities to decrease the per cent of carbon dioxide in the flue gas. If all of the oxygen in the air could be made to combine with coke to produce carbon dioxide, a flue gas of 20.9 per cent carbon dioxide would result. Practically, this is not possible, and a flue gas of about 17 to 18 per cent is the best that can be expected. However, to keep the flue gas up to this concentration requires much care and considerable experience in firing a coke furnace.

The factors which affect the per cent of carbon dioxide in a flue gas from a coke furnace are: first the depth of the fuel bed, second the flow of air to the furnace, together with the admission of secondary air over the fire, and third the temperature of the fire. The first factor can be readily controlled by proper firing. The second, however, depends upon the speed of the draft fan and in many plants this is automatically controlled by the steam consumption. The temperature of the fire is also somewhat of a fixed character as it is more or less determined by the design of the furnace.

Figure 30 shows in graphical form the results obtained by analyzing the gases in a coke mass at various points above the grate.[2] These curves show at a glance the conditions necessary for producing the maximum percentage of carbon dioxide. First, the fuel bed should not be above the height indicated at the inflexion point. The evaluation of this height in centimeters or inches is not possible from the diagram but can be determined, in most cases, with sufficient accuracy by experience with the furnace in question. It should be noted that a depth slightly below that indicated by the inflexion point would give a lower carbon monoxide concentration while affecting the carbon dioxide concentration but slightly. An increase

[2] From Walker, Lewis and McAdams, "Principles of Chemical Engineering," McGraw-Hill Book Co., New York. Based on data of Kreisinger, Ovitz and Augustine, *U. S. Bureau Mines, Tech. Paper,* 137 (1917).

in gas velocity increases the carbon dioxide and decreases the carbon monoxide but this factor, as has already been mentioned, is not subject to direct control. Perhaps next to the fuel depth, the temperature of the coke is the next important factor. High temperatures increase the carbon monoxide concentration and decrease the carbon dioxide content, therefore the grate area should be sufficiently large to maintain a moderate temperature and yet produce sufficient heat for the plant requirements. The combination of oxygen with carbon, to produce carbon dioxide, starts at a temperature between 600° and 800° C. (1112° and 1472° F.). Increasing the temperature above this point, raises the carbon monoxide content of the flue gas needlessly.[3]

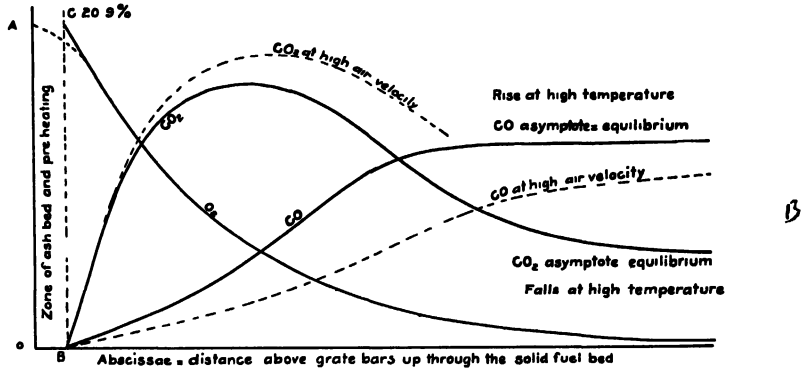


FIGURE 30. The Change in Gas Composition at Various Points Above the Grate in a Coke Fire.

The widespread use of natural gas as an industrial fuel naturally leads to the question of its application to the carbon dioxide industry. At first glance, it would appear to be an ideal fuel, furnishing a flue gas of exceptional purity without the presence of dust or sulfur dioxide. Much of the natural gas of Texas, Oklahoma and Wyoming is practically pure methane which would burn to carbon dioxide and water according to the equation:

$$CH_4+2O_2=CO_2+2H_2O.$$

The oxygen necessary therefore for burning one volume of this gas would be furnished by 9.5 volumes of air and the carbon dioxide in the resulting combustion gas would be about 11.8 per cent if all of the water produced, was condensed. This theoretical maximum carbon dioxide concentration for the combustion products of natural gas, compares quite unfavorably with the value of 21 per cent from burning coke. In spite of its unfavorable characteristics, however, natural gas is being used more and more for this purpose. At the present time the authors know of two carbon dioxide plants in Los Angeles, California, that are making use of it and Goosmann[4]

[3] Some of the newer types of furnaces operate at a temperature of 1400° C. (2552° F.) and above, and the carbon monoxide concentration is decreased by recirculation of part of the flue gas through the combustion zone.

[4] Goosmann, J. C., *Ice and Refrigeration*, 79, 397-401 (1930).

refers to a plant in Texas that operates with natural gas with very satisfactory results. The flue gas in this plant, however, hardly ever exceeds 10.5 per cent.

In all carbon dioxide plants the flue gases are moved through the system by means of fans or blowers. These blowers are often located in the line directly after the scrubbing system and are, in many cases, connected with an engine the speed of which can be adjusted to produce just the right draft on the furnaces. Automatic devices can be and are sometimes used to regulate the speed of the blower engine and thus hold the steam pressure at a constant value.

Scrubbers. The simplest type of scrubber is a tower or tank made of steel, concrete or wood, and packed with small pieces of limestone. Water from the condensing system is flowed over the packing by means of a specially arranged spreader at the top of the tower. The sulfurous acid produced

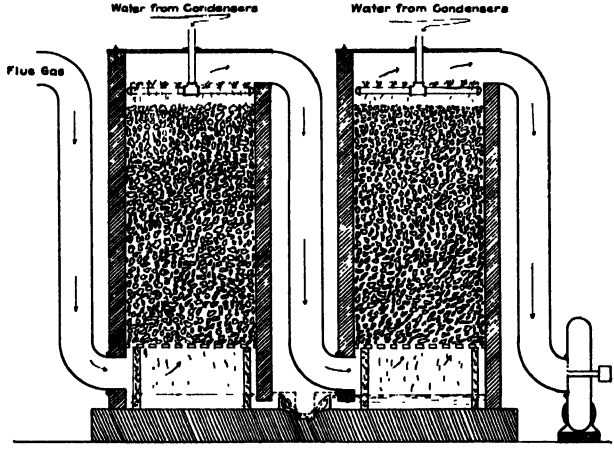


FIGURE 31. Limestone Scrubbers for Removing Sulfur Dioxide from the Flue Gas.

by water and sulfur dioxide in the flue gas as it rises through this rock packing, reacts with the calcium carbonate, producing carbon dioxide and calcium acid sulfite. The soluble calcium acid sulfite thus produced, is washed out of the tower with the waste water, while the carbon dioxide goes into the gas stream. This reaction decreases the volume of the limestone packing very slowly and as it settles it is only necessary to add more to the top to keep the scrubbers in perfect operating condition. A diagram of such a scrubbing system is shown in Figure 31.

A scrubbing system consisting of two scrubbers 5 ft. internal diameter by 8 ft. high, with a flue gas flow of 200 cu. ft. per min. and a water flow of 20 gals. per min. to each scrubber, when tested showed that 88.7 per cent of the total sulfur dioxide was removed from the flue gas. The first scrubber removed 85.2 per cent of this amount and the second removed the rest. The 11.3 per cent of the sulfur dioxide remaining in the flue gas

passed into the absorber where it reacted with the alkaline solution thus decreasing its efficiency.

The use of a dilute solution of sodium carbonate as a scrubbing liquid was suggested by Luhmann[5] in 1917. A number of important carbon dioxide plants now use scrubbing systems consisting of a coke-packed tower with water as the washing agent and in series with this a similar tower with a solution of sodium carbonate and bicarbonate as the scrubbing medium. The wash water from the first tower is run to waste but the solution of soda lye from the second is recirculated by means of a pump and is only discarded when the sulfate concentration becomes high enough to make further use unprofitable.

Absorption. This operation is, of course, considered of great importance in the production of carbon dioxide. At the point where absorption takes place that carbon dioxide which is eventually compressed into cylinders, and that which goes out into the atmosphere as waste gas, are separated. Naturally anything which prevents this unit from operating at maximum efficiency is reflected at once on the capacity of the plant and for this reason this operation and the equally important process, the lye boiling, is closely watched.

The absorption of carbon dioxide in potassium carbonate, sodium carbonate or monoethanolamine is a continuous process conducted in a countercurrent absorbing tower or a series of such towers. In nearly all cases these towers are packed with coke over which the absorbing liquid is pumped while the flue gas passes from the bottom upwards. Experience has shown that this arrangement gives good results and while its efficiency is not high, its simplicity, lack of back pressure and cheapness of construction, as well as operation, makes it the almost universally used absorber for this purpose. In the past most absorbing units have been designed with but little real engineering data to work on. Capacities have been estimated from the observed behavior of other units already in operation and in general it has been, more or less, a hit or miss proposition. Recently, thanks to the investigators working in this field, much information has been gained and many data collected which put the whole question on a more rational basis, but even yet it cannot be said that exact computations of coke tower design and operation can be made.

Absorption in Water. The absorption of moderately soluble gases in liquids in which no new chemical substance is formed is a case of simple solution and the relations between the solute and the solvent are expressed rather closely, in most cases, by Henry's law. The usual mathematical equation expressing this law is, $W = Kp$ where W is the weight of gas dissolved under the partial pressure p and K is the proportionality constant. Where the above relationship holds, the rate at which this absorption tends to come to equilibrium, under isothermal conditions, depends upon a number of factors such as surface area of liquid, the difference in concentration of

[5] Luhmann, *Z. ges. Kohlensäureind.*, 23, 471-2, 483-6 (1917).

the gas in the vapor and the liquid phases and the specific characteristics of the solute and solvent. The specific characteristics of the solute and solvent change with the temperature in such a way that the value of K decreases with an increase in temperature. The nature of this decrease, however, cannot always be predicted and the values of K are best determined experimentally. In the case of carbon dioxide and water Henry's law is valid[6] at low pressures i. e. from 1 atmosphere down to 1/20,000 atmosphere, therefore the validity of the law may be assumed for all conditions affecting ordinary absorption processes.

Commercially the use of a pure liquid, such as water, is not as important as the use of an alkaline carbonate as an absorbing agent. In some plants carbon monoxide obtained from carbide furnaces is partially oxidized with steam to carbon dioxide and the resulting mixture of carbon dioxide, carbon monoxide and hydrogen is treated in an absorber of the pressure type for the removal of the carbon dioxide. The water solution of carbon dioxide thus obtained readily gives up its carbon dioxide when the pressure is decreased. The separated carbon monoxide and hydrogen, after some purification, are then passed into a catalyst chamber where they are converted into methanol.

Water absorption of carbon dioxide from air mixtures or from flue gases[7] cannot be so successfully accomplished, however. In the case of the carbon monoxide, hydrogen and carbon dioxide mixture, where the separated carbon dioxide is apt to be contaminated with hydrogen and carbon monoxide, the purification is easily accomplished by the simple oxidation of the impurities to carbon dioxide and water. On the other hand, when nitrogen is one of the impurities its removal becomes a very difficult matter and this purification process is one that cannot be readily adapted to commercial conditions unless the ordinary lye absorption process is employed.

✓**Absorption in Triethanolamine Solution.** A few years ago there appeared a new process for absorbing carbon dioxide which gave indications that a very radical change in carbon dioxide absorption was about to take place. This process made use of an organic absorbing agent having the chemical name of triethanolamine. As one might expect trade names have already been applied with the object of making it somewhat easier to say. The process of absorbing carbon dioxide in triethanolamine was of course patented and the compound itself put on the market.[8] During the process of commercial development it was discovered, as is often the case, that the economics of the reaction is of more importance than its chemistry and triethanolamine has not made the startling changes in the art of carbon dioxide manufacture that was at first predicted. As a matter of fact this absorbing agent is of practically no commercial importance at the present time but its chemistry is so interesting it may deserve a little space here.

[6] Buch, *Nord. Kemistmötet* (Finland), 184-92 (1928).
[7] Heirich, C., *Z. kompr. flüss Gase*, 22, 3-7, 21-2, 43-4 (1922).
[8] Carbide and Carbon Chemicals Corporation, "Triethanolamine" July 1, 1930.

Monoethanolamine is also a good absorbing agent for carbon dioxide and at least one commercial plant is using it for this purpose. This is a moderately sized plant of about 500 pounds of carbon dioxide per hour which originally operated with triethanolamine. It is reported that excellent results are obtained with this absorbent. The chemistry of absorption is essentially the same for both these compounds and the reactions for the triethanolamine absorption will be discussed.

This absorption process makes use of a concentrated water solution (about 50 per cent) of triethanolamine carbonate (triethanolammonium carbonate) which is formed as the first product in the reaction of carbon dioxide in a triethanolamine solution.

$$2N(C_2H_4OH)_3 + H_2O + CO_2 \longrightarrow ((N(C_2H_4OH)_3H))_2CO_3$$

Triethanolamine Water Carbon dioxide Triethanolamine carbonate

The absorber consists of a scrubbing tower containing the carbonate solution through which the gas is passed counter-current to the liquid flow. A temperature is maintained around 20° to 30° C. and the carbon dioxide reacts with triethanolamine carbonate to form the acid salt as follows:

$$[(N(C_2H_4OH)_3H)]_2CO_3 + H_2O + CO_2 \leftrightarrows 2[(N(C_2H_4OH)_3H)]HCO_3$$

Triethanolamine carbonate Water Carbon dioxide Triethanolamine bicarbonate

The solution of this triethanolamine bicarbonate is passed into a regenerator and heated to the boiling point, 100° to 110° C., whereupon carbon dioxide is quantitatively released and the neutral carbonate regenerated.

An inspection of this reversible reaction shows that, in the form of the neutral carbonate, 6.77 pounds of triethanolamine can absorb and release 1 pound of carbon dioxide, or 1 volume of triethanolamine can absorb and release 90 volumes of carbon dioxide at 20° C. and 1 atmosphere pressure. The factor which determines the actual volume of carbon dioxide gas absorbed per unit volume of carbonate solution is the partial pressure of gas over the bicarbonate solution. Absorption will continue until the carbon dioxide pressure above this solution equals that of the incoming gas, so that the process is increasingly efficient with higher carbon dioxide concentrations in the gas to be purified and with lower scrubbing temperatures. In practice the concentration of carbon dioxide can be reduced efficiently by counter-current scrubbing to less than 1 per cent.

In the regeneration stage, carbon dioxide begins to be evolved around 60° C. and the speed of evolution increases with rising temperature up to the boiling point of the solution. Since little water is distilled, the heat consumption in this stage is comparatively low.

✓ **Absorption in Solutions of Alkali Carbonates.** A satisfactory separation of carbon dioxide from gas mixtures can be made with an absorbing liquid containing certain inorganic compounds with which the carbon dioxide combines loosely and from which it can be again separated when placed under a new set of conditions. In practical operations either sodium

carbonate or potassium carbonate is used for this purpose and while the efficiency of the operation is not high it has certain advantages over other absorbing solutions. The use of a solvent containing both of these alkali carbonates has been advocated[9] because of the greater concentration possible and the consequent increase in absorbing capacity. No information is available, however, concerning the commercial application of this idea. The potassium compound produces a bicarbonate which is more soluble than the corresponding sodium compound thus making it a more efficient absorbing agent than the sodium salt.

The temperature of the lye solution used for absorbing carbon dioxide is important. In general the lye stream is held between 30° and 40° C. and in order to keep it at this temperature special water coolers are required.

Equilibrium Relations in Absorption Systems. The success of the absorption and desorption of carbon dioxide in a solution of alkali carbonate depends upon the reversibility of the following equation:

$$Na_2CO_3+H_2O+CO_2 \leftrightarrows 2NaHCO_3.$$

In general it may be considered that this reaction tends to go towards the right at low temperatures and towards the left at elevated temperatures. Certain other factors influence the equilibrium, however, in such a way that the degree of shift in equilibrium cannot be easily predicted.

The equilibrium relations in the above equation were studied some years ago by McCoy[10] in sodium carbonate solutions of concentrations from 0.1 to 1.0 N and from the resulting data he derived the following equation:

$$\frac{2f^2N}{(1-f)s\,p_{CO_2}}=k \quad \ldots\ldots\ldots\ldots \quad (45)$$

In this equation f is the fraction of sodium present as bicarbonate, $(1-f)$ the fraction of sodium present as carbonate, N the normality of solution with respect to the base, K the mass action constant which varies with the concentration and the temperature, s the solubility coefficient of carbon dioxide in water expressed as moles per liter and p_{CO_2} the partial pressure of carbon dioxide in the gas phase. This equation seems to hold with considerable accuracy under the conditions used for obtaining the data. It is unfortunate, however, that the experiments were not carried out in more concentrated solutions and with a wider range of temperatures and carbon dioxide pressures in order that the results could be more easily applied to practical operating conditions. The general applicability of this equation, nevertheless, is now pretty well accepted even at higher concentrations of alkali and carbon dioxide.

Walker, Bray and Johnston[11] have also made a very careful study of the equilibrium conditions in a system containing sodium carbonate, sodium bicarbonate and carbon dioxide as well as the corresponding system in

[9] Tomlinson, G. H., *Can. Chem. J.*, **4**, 189-90 (1920).
[10] McCoy, H. N., *Am. Chem. J.*, **29**, 437 (1903).
[11] Walker, A. C., Bray, U. B., and Johnston, J. *J. Am. Chem. Soc.*, **49**, 1235 (1927).

which potassium was the alkali metal. The partial pressure of carbon dioxide used by these investigators, however, was practically the same as that found in the air and this fact makes their results difficult to apply to the conditions found in a commercial carbon dioxide absorber.

The work best fitted to show the conditions in a coke tower, where equilibrium is reached, was published by Sieverts and Fritzsche[12] in 1924. These investigators used potash solutions of about 2 *N* with respect to the potassium, the carbon dioxide concentration was varied over a wide range and their temperatures covered pretty well the whole field as it is used in practice. The expression representing the equilibrium relations as given by these investigators is,

$$\frac{\alpha^2\,[KHCO_3]^2\;760}{\beta\,[K_2CO_3]\;z\gamma p_{CO_2}}=k. \qquad (46)$$

where α is the per cent dissociation of $KHCO_3$, β the per cent dissociation of K_2CO_3. γ is the degree of hydration of the CO_2, $[KHCO_3]$ is the molar concentration of the bicarbonate and $[K_2CO_3]$ is the molar concentration of the carbonate.

This expression can be simplified somewhat because it has been demonstrated that the ratio of α^2/β is independent of the concentration of the alkali, also the solubility of carbon dioxide z and therefore γ the degree of hydration will remain constant at any one temperature. The above equation then becomes:

$$\frac{[KHCO_3]^2}{[K_2CO_3]\;p_{CO_2}}=k \qquad (47)$$

or it may be written in a more convenient form as:

$$\frac{2f^2N}{(1-f)p_{CO_2}}=k \qquad (48)$$

which is, of course, the same as McCoy's equation. Sieverts and Fritzsche have determined the values for k at a number of different temperatures and have found a remarkable agreement between them under isothermal conditions, even when the partial pressure of carbon dioxide was varied over a very wide range. These values when plotted on large scale cross section paper, yielded a curve from which the values of k indicated in Table 65 were read.

In most cases the plant operator is interested in only two phases of this problem, the first is to keep the concentration of the bicarbonate as high as possible in the strong lye coming from the coke tower, and the second is to keep it as low as possible in the lye coming from the lye boiler. In order to bring about these conditions he knows that a high temperature is needed in the lye boiler and a much lower temperature in the coke tower. The relation between these variables is clearly indicated in Table 65

[12] Sieverts, A., and Fritzsche, A., *Z. anorg. allgem. Chem.*, 133, 1-16 (1924).

TABLE 65.—*Showing the Relation Between the Temperature, Bicarbonate and Carbonate Concentrations Under Equilibrium Conditions in the Presence of a Flue Gas Containing 15 Per Cent Carbon Dioxide.*

Temp. ° C.	*k*	% K as K_2CO_3	% K as $KHCO_3$
10	0.369*	8.5	91.5
20	.300*	9.5	90.5
30	.239	11.6	88.4
40	.182	14.2	85.8
50	.132	18.0	82.0
60	.096	22.2	77.8
70	.068	27.3	72.7
80	.045	34.0	66.0
90	.031	40.3	59.7
100	.020*	47.9	52.1
110	.011*	57.6	42.4

* Mechanically extrapolated.

which was calculated by means of equation 48. The calculations were based on a 2 *N* lye solution (about 12% K_2CO_3) in equilibrium with a flue gas with a partial pressure of carbon dioxide corresponding to a 15 per cent carbon dioxide mixture.

Some rather interesting points are brought out by this table. First it is evident that the lower the temperature the greater will be the bicarbonate concentration and that with 15 per cent carbon dioxide in the gas phase the bicarbonate in the liquid cannot be reduced below 40 per cent even at temperatures near the boiling point. This condition must not be confused with the process of boiling a bicarbonate solution, as in this case the partial pressure of carbon dioxide is decreased to a low value by the admixture of a very large volume of steam. It would seem from this table that the most efficient temperature for operating a coke tower would be about

TABLE 66.—*Showing the Relation Between the Volume Per Cent of Carbon Dioxide and the Concentrations of Carbonate and Bicarbonate of Potassium at 30° C. in a solution 2 Normal With Respect to the Potassium.*

CO_2 vol. % in the gas phase	% K as K_2CO_3	% K as $KHCO_3$
20	9.5	90.5
18	10.0	90.0
16	10.9	89.1
14	12.0	88.0
12	13.7	86.3
10	15.7	84.3
8	18.4	81.6
6	22.3	77.7
4	28.3	71.7
2	39.9	60.1
1	51.6	48.4
0.50	62.5	37.5
0.05	86.1	13.9

10° C. or less. While this would increase slightly the per cent of bicarbonate in the lye over that usually obtained at the operating temperature of about 30° to 40° C. the question of heat economy and rate of absorption makes a higher temperature more desirable.

In order to show the influence of carbon dioxide concentration in the gas above a lye solution, on the concentrations of carbonate and bicarbonate, Table 66 has been constructed from values calculated from the experimental results of Sieverts and Fritzsche.

Rate of Absorption. To a plant manager, the problem connected with the daily operation of the absorbing unit is simply one of keeping the available equipment continuously at the peak of its capacity. The foregoing discussion may help one to understand why certain conditions are necessary to get the maximum yield from an absorbing apparatus, but much more information is needed to aid one in designing and constructing a device for carrying it out. Plant capacities are usually rated on the pounds of carbon dioxide compressed into cylinders per hour. This is, of course, entirely dependent upon the absorption process because it is only that carbon dioxide removed from the flue gas that ever gets into the cylinders. The many factors which influence this rate of absorption seem worthy of as complete discussion as we may give them with our present knowledge of the subject.

Absorption Mechanism. Consider first, a solution of potassium carbonate and potassium bicarbonate, and over this liquid, a gas composed of carbon dioxide, carbon monoxide, oxygen and nitrogen. While the carbon monoxide, oxygen and nitrogen are soluble to some extent in this solution, this solubility is so small compared to carbon dioxide that they will be considered as inert gases as far as this discussion is concerned. If both the liquid and the gas remain undisturbed, the carbon dioxide in the gas phase for a short distance from the liquid-gas interface will dissolve, leaving a layer of inert gas molecules through which all of the carbon dioxide from the main body of gas must pass before going into the alkali solution. While in the gas phase the carbon dioxide molecules may move from point to point by either convection or diffusion, through this film of inert molecules they can move only by the relatively slow process of diffusion. On reaching the surface of the liquid the carbon dioxide molecules must again pass through a film of inert material which in this case is composed of the ions and molecules of water, carbonic acid, etc. after which they can move into the body of the liquid by either diffusion or convection. This layer of gas molecules at the interface, composed chiefly of the slightly soluble gases, will be spoken of as the gas film while the layer of unreactive molecules at the surface of the liquid will be called the liquid film.[13] Due to the slowness of the process of diffusion the amount of gas absorbed in an unagitated system in a unit of time must be comparatively small because of the thick-

[13] Whitman, W. G., *Chem. Met. Eng.*, **29**, 147 (1923).

ness of the gas and liquid films under these conditions, but in an agitated system the surface of the liquid is greatly increased and the thickness of the films is decreased therefore the rate of material transfer is greatly accelerated. In a well-agitated system where the transfer of material can take place by convection in the body of the gas and in the body of the liquid the concentration of carbon dioxide in either is essentially the same at all points. On the other hand, the gas and liquid films being free from convection currents can transfer the carbon dioxide only by the relatively slow process of diffusion. These films therefore, act as a resistance to the transfer of carbon dioxide from the gas mixture to the lye solution and a study of the behavior of these films may throw some light on the question of rate of absorption.

The driving force which causes the diffusion through the gas film is the difference in concentration of the gas P_G on the outside of the film and its concentration on the inside P_i or at the interface. The rate of diffusion is therefore proportional to $(P_G - P_i)$. Diffusion of carbon dioxide through the liquid film is, in like manner brought about by the difference in concentration of carbon dioxide at the interface C_i and in the main body of the liquid C_L and the rate of diffusion will likewise be proportional to $(C_i - C_L)$. It follows, therefore, that as long as all of the solute passing through the gas film must also pass through the liquid film the rates must be equal and that $k_G(P_G - P_i) = k_L(C_i - C_L)$ where k_G and k_L are diffusion coefficients for the gas and liquid films respectively.

The amount of carbon dioxide W transferred per unit time θ by diffusion through the two films is $dW/d\theta$ and if S is the surface of the interface through which the diffusion is taking place then $dW/d\theta S$ represents the diffusional current density.[14]

and
$$dW/d\theta S = k_G(P_G - P_i) = k_L(C_i - C_L) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (49)$$

It is possible to simplify this equation somewhat in cases where Henry's law holds by combining the two film coefficients into one *overall* coefficient K_G or K_L. Then the equation may be written

$$dW/d\theta S = K_G(P_G - P_L) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (50)$$

or
$$dW/d\theta S = K_L(C_G - C_L) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (51)$$

In calculations involving this *overall* coefficient, of course comparable units must be used in both the liquid and gas phases although the choice of units is purely arbitrary. In liquid-gas solutions, in cases where Henry's law holds, the concentration of the gas in the liquid is determined by the partial pressure of the gas above the liquid. When the solvent contains some other compound with which the solute combines, the situation is somewhat different. Then the equilibrium conditions depend upon the dissociation

[14] Walker, Lewis and McAdams, "Principles of Chemical Engineering," page 653. McGraw-Hill Book Co., New York (1917).

pressure of the compound in question, the amount of gas dissolved as such in the liquid and the partial pressure of the gas above the liquid. A solution of alkali carbonate in equilibrium with carbon dioxide gas is a system of this general type. These equilibrium conditions are very clearly shown in Figure 32. These curves were made by plotting the per cent of potassium existing as bicarbonate in a 2 *N* solution of potassium carbonate against the partial pressure of carbon dioxide in equilibrium with the solution, the partial pressures expressed in atmospheres. The data on which these curves are based were taken from Table 67 and are for a working temperature of 30° C.

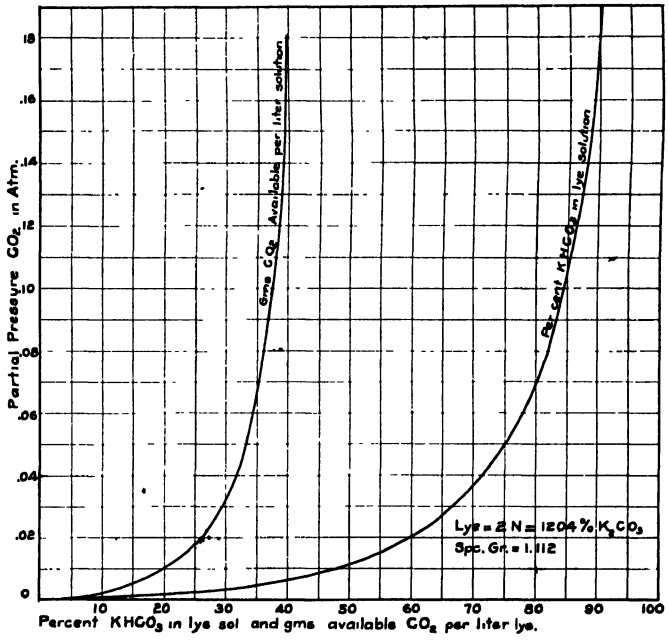


FIGURE 32.—Equilibrium Conditions in the System CO_2—K_2CO_3—$KHCO_3$—H_2O.

The driving potentials which cause the carbon dioxide to diffuse through the gas and liquid films can be determined very quickly from these plots. Thus with a 60% $KHCO_3$ lye solution the driving force, from a flue gas containing 18% CO_2 would be 16, but if the concentration of the lye becomes 90% then the driving force becomes zero. The speed with which the carbon dioxide diffuses into the solution of potassium carbonate is proportional to this driving force and later, use of it will be made for such calculations.

Experimental Verification. A study of the rates of absorption of carbon dioxide in potash or soda lye solutions has been made by Sieverts

and Fritzsche,[15] Riou,[16] Williamson and Mathews,[17] and by Whitman and Davis,[18] and in general their results confirm this theoretical treatment.

Figure 33 shows a number of curves representing the results obtained by Sieverts and Fritzsche on the rate of absorption of carbon dioxide from a gas mixture by means of a potash lye solution. Except for one curve, which is indicated, all of the data were obtained with solutions agitated at a constant rate. It is interesting to note that curve 1 *a* (without stirring) shows that the rate of absorption is a linear function of the time, as far as it is indicated, and that all other curves are nearly so up to the point

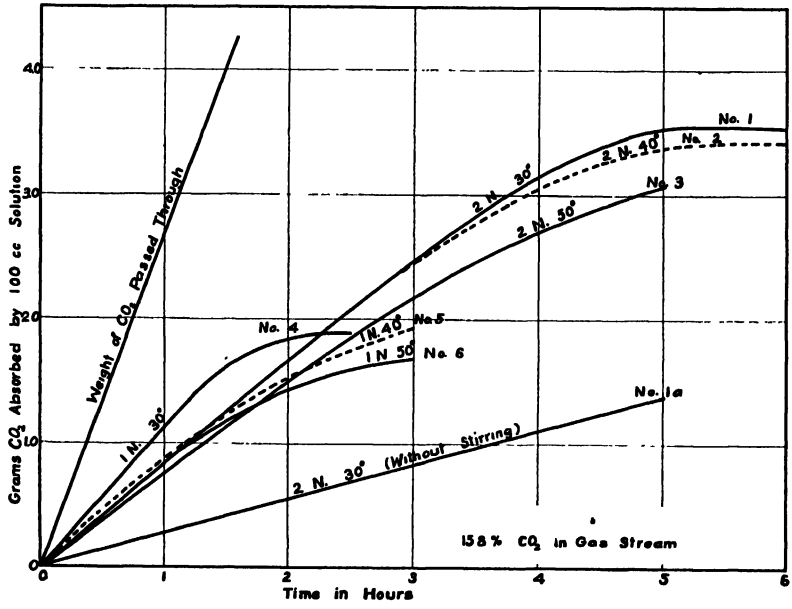


FIGURE 33. The Rate of Absorption of Carbon Dioxide in Solutions of Potassium Carbonate. Experimental work of Sieverts and Fritzsche.

where the rate falls off rapidly due to the high concentration of bicarbonate in the solution. The effect of agitation on the rate of solution is very pronounced, as one would expect. It will be noted that this rate is somewhat higher for the more dilute solutions, curves 4, 5 and 6, than for those of a higher alkali concentration curves 1, 2 and 3. This effect has also been observed by other investigators. Perhaps the most noteworthy thing, however, is the apparent decrease in rate of absorption at higher temperatures as is indicated by both sets of curves. This change of rate with temperature does not agree with the results obtained by Williamson and Mathews who found that the rate increased up to 70° to 75° C. and then decreased; and

[15] Sieverts, A., and Fritzsche, A., *Z. anorg. allgem. Chem.*, 133, 17-25 (1924).
[16] Riou, P., *Compt. rend.*, 174, 1017-9 (1922).
[17] Williamson, R. V., and Mathews, J. H., *Ind. Eng. Chem.*, 16, 1157-61 (1924).
[18] Whitman, W. G., and Davis, G. H. B., *Ind. Eng. Chem.*, 18, 264-6 (1926).

Whitman and Davis who found that the absorption rate coefficient in a bubble-plate tower doubled for every 24° C. increase in temperature. The conditions under which these various investigations were made, however, were quite different and this fact may account for the discrepancy.

Other Factors Affecting the Rate or Degree of Absorption. In the process of absorbing carbon dioxide in an alkaline solution the concentration and purity of the lye solution used is of considerable importance. It is not uncommon for a plant executive to find it necessary to discard the lye solution and start over with a fresh one because of the building up of impurities within it. The expense involved in such a step is great, of course, especially so when potash lye is being used. It would seem therefore, that it is quite desirable to investigate as fully as possible what effect the admixture of various substances has on the degree and the rate of absorption.

Riou and Cartier[19] studied the effect of various concentrations of glycerol, dextrose and sucrose on the rate of absorption of carbon dioxide in solutions of sodium carbonate. This was done primarily to test the effect of viscosity, of the absorbing liquid, on the rate of solution. It was found, however, that all three compounds in low concentrations, increased the rate of absorption. It also appeared from the first set of experiments that the viscosity of the absorbing liquid had but little to do with the rate of absorption. On the addition of 0.029 to 0.044 mole of sucrose per liter of solution the rate of absorption was more than doubled. The addition of 0.056 mole of dextrose also more than doubled the rate of absorption while the addition of glycerol up to concentrations of 0.43 mole affected the absorption but slightly.

In a later work Riou and Cartier[20] extended their investigation to include ethylene glycol, levulose, methyl alcohol, ethyl alcohol, formaldehyde and lactose. From the results of these investigations as well as of the previous ones they arrived at the following conclusions: (1) While the viscosity of the absorbing solution has some effect on the rate of absorption of a gas by a liquid, it is in no case the principal factor involved. (2) The chemical function of the added organic crystalloid plays a very important, if not the preponderant rôle in influencing the rate of absorption. (3) Organic crystalloids, not producing combinations with sodium carbonate, increase the rate of absorption even though they increase the viscosity. These investigators suggest that these rather surprising results might be produced by catalytic action and that they might lead to industrial applications.

In 1929 Riou and Lortie[21] experimented on solutions of sodium carbonate containing colloids. Peptone, pepsin, gelatin and starch were used for the colloidal substances and they found that the velocity of absorption was decreased on the addition of these colloids up to $\frac{1}{8}$ per cent concentra-

[19] Riou, P., and Cartier, P., *Compt. rend.*, **184**, 325-6 (1927).
[20] Riou, P., and Cartier, P., *Compt. rend.*, **186**, 1727-9 (1928).
[21] Riou, P., and Lortie, L., *Compt. rend.*, **186**, 1543-6 (1929).

tion after which they no longer affected the rate of solution. The new velocity was about two-thirds that of the initial one.

The effect that sulfating of a lye solution has on the rate of absorption of carbon dioxide has, unfortunately, never received the attention of research workers that it deserves. From a practical point of view this is a very important problem. Even with the most efficient scrubbing system known for the removal of sulfur dioxide from a flue gas, there is a slight but continuous addition of this compound to the lye solution. The resulting sulfite ions in the presence of the free oxygen in the flue gas, soon become oxidized to sulfate ions. The net result is the loss of carbonate ions with a corresponding decrease in absorbing power.

There are several disadvantages connected with the sulfating of a lye solution, the most important of which is the loss of active carbonate which will, of course, decrease the absorption rate. In addition the slight solubility of potassium or sodium sulfate at low temperatures often cause crystals to separate on cold nights thus endangering the pump impellers and stopping liquid lines. Whether there is any negative effect on absorption rates due to the sulfate ion, has in the past never been definitely known although some operators believe that such an effect is present. The theory of absorption just discussed, however, points to the probability that sulfate ions would actually decrease the rate of solution. It is well known that the presence of sodium sulfate in water decreases very greatly its absorption capacity for carbon dioxide. Thus the absorption coefficient for carbon dioxide in pure water at 15° C. is 1.019 but in a 2 molar solution of sodium sulfate at the same temperature it is only 0.234 while a 2 normal solution of potassium sulfate has an absorption coefficient of 0.676 at 15.5° C. This being the case, reference to the equilibrium equation shows at once that the carbon dioxide concentration at equilibrium would be decreased and therefore the rate of absorption would be decreased also. Then again, any foreign material in the solution would tend to increase the liquid film thickness thus setting up a greater resistance to the passage of carbon dioxide through it with a resulting decrease in the rate of absorption. The experiments of Riou and Lortie with colloids confirm this view of the situation but the behavior of crystalloids such as sugar, etc. do not substantiate it. A recent unpublished research conducted by Clark and Austin[22] seems to indicate that the addition of potassium sulfate or sodium sulfate to the corresponding alkaline carbonate solution does not decrease the rate of absorption even when such substances are added to the saturation point. The work of these investigators is, perhaps, of sufficient importance to justify a more detailed description here.

The experiments of Clark and Austin were carried out on a miniature carbon dioxide plant which is represented diagrammatically in Figure 34. An artificial flue gas, made from air and pure carbon dioxide, was sent through an absorption tower counter-current to the absorbing liquid. Absorption experiments were made on solutions of sodium carbonate and

[22] Clark, W., and Austin, R., Dissertation, University of Utah (1932).

potassium carbonate and various mixtures of these with other compounds. It was possible to control the purity and concentration of these absorbents very accurately. The capacity of this carbon dioxide plant varied with the operating conditions up to 6 or 8 cu. ft. of carbon dioxide per hour. Pure carbon dioxide liberated from the lye boiler was collected in a standard gasometer and its volume carefully determined. The ingoing carbon dioxide used for making the artificial flue gas was measured with a calibrated recording meter and the volume thus obtained was used with the readings of the standard gasometer for calculating the absorption efficiency for each run. The absorption efficiency was the ratio of carbon dioxide recovered to that entering the system. The absorption tower was packed with steel

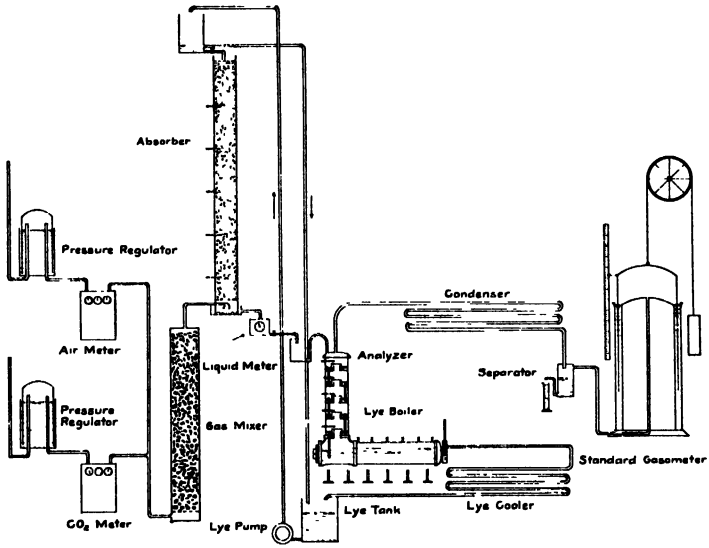


FIGURE 34. Experimental Carbon Dioxide Plant of Clark and Austin.

borings and had an absorbing capacity so great that in some cases the concentration of the lye solution had to be decreased considerably in order to bring the absorption down into a region where comparisons between runs could be made.

A series of experiments with a 1.44 *N* potassium carbonate solution gave an average absorption efficiency of 75.7 per cent. When potassium sulfate was added sufficient to make a 5 per cent solution, the absorption efficiency was 77.9 per cent, whereas a saturated solution of the sulfate gave 78.7 per cent efficiency. The probable error of these measurements is somewhat difficult to estimate but without doubt it is not greater than two or three per cent.

Clark and Austin also attempted to determine the action of dextrose on the absorption efficiency of potassium carbonate solutions. It will be recalled that a commercial application of a dextrose-alkali carbonate solu-

tion had already been suggested. A series of runs gave the average absorption efficiency of a 2 *N* solution of potassium carbonate as 70.8 per cent, 5 per cent dextrose raised this to 94.2 per cent and 10 per cent dextrose increased it again to 104.9 per cent. Only two runs were made on this more concentrated dextrose solution but both of them showed a yield better than 100 per cent. The gas had a very disagreeable odor and showed only 99.3 per cent carbon dioxide. It is very probable that only one definite conclusion can be drawn from these results, and that is, while the dextrose does increase the absorption as has been reported there is absolutely no commercial possibility of its use because of the odor it imparts to the gas.

The experiments these authors conducted with sodium and potassium carbonate solutions, to which had been added triethanolamine, are exceptionally interesting. A 0.5 *N* potassium carbonate solution showed an absorption efficiency of 54.9 per cent, 1 per cent triethanolamine increased it to 73.6 per cent and 2 per cent triethanolamine raised it again to 76.0 per cent. When a 0.5 *N* solution of Na_2CO_3 was used it showed an absorption efficiency of 43.8 per cent, 1 per cent triethanolamine raised it to 54.9 per cent and 2 per cent triethanolamine gave 55.0 per cent. The gas produced by this absorbing agent seemed to be free from objectionable odors and as far as one could tell from a superficial examination no appreciable decomposition of the triethanolamine took place.

The Coke Tower. The coke tower is a vertical tube of sheet steel with connections for gas intake and liquid exit at the bottom and gas exit and liquid intake at the top. Figure 35 shows in section the conventional design of such absorption towers together with the lye tanks and pipe connections. It is necessary to have several supporting platforms spaced from 10 to 15 feet apart within the tower to support the load of coke or other packing in it, thus relieving the packing at the bottom of the tower from the weight of that above. Another important structural detail is the method of spreading the lye over the top of the coke. Unless this is well done there is apt to be a large amount of coke unwet with the resulting loss in absorbing capacity. A simple and effective spreader can be made by running a main feed pipe across the top of the tower in a plane at right angles to the tower, a number of lateral pipes are connected with this feed line and extend to the edge of the tower. These lateral pipes are capped at the ends, as is also the open end of the main feed line. A calculated number of holes are drilled in the top side of all these pipes so the lye is forced up through them in the form of small fountains. With this arrangement the spreading of the lye is uniform over the top of the coke regardless of the variations in the rate of flow.

Two coke towers are often connected in series and arranged so that the exit gas from the first passes to the bottom of the second and the exit liquid from the second passes to the top of the first. In some cases a coke tower is used for washing the flue gas with the stronger lye solution after which the gas stream is divided and sent to two finishing towers for the

final treatment with a weak lye solution. Two towers 10 feet in diameter by 100 feet high, connected in series will absorb about 1000 pounds of carbon dioxide per hour from a high grade flue gas if the rest of the plant is properly designed.

Other Types of Absorbers. Iron borings and turnings are being used in some plants for absorber packing. The surface exposed by this type of filling material is very much greater than that exposed by coke and therefore a much greater absorption efficiency is obtained. The initial cost of filling such towers is much greater than in the case of coke packing.

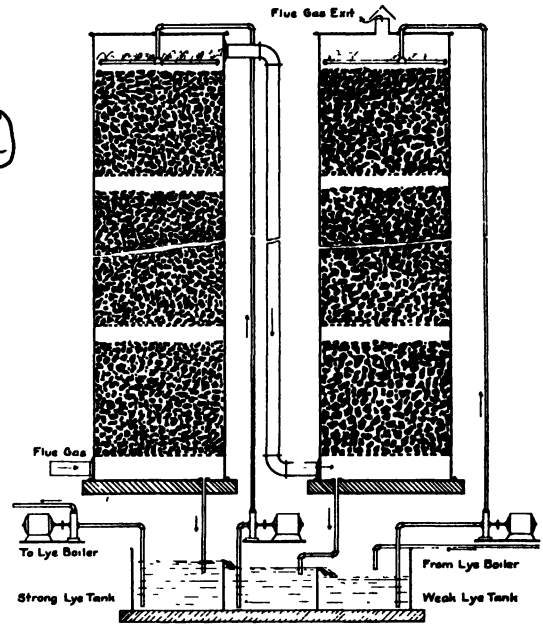


FIGURE 35.

Arrangement of Lye Tanks and Coke Absorption Towers.

The difficulty of cleaning oil from the iron before packing the tower is very great and an item of no small expense. This is accomplished by boiling the iron in sodium carbonate solution and then washing with water but even then traces of oil get into the system causing considerable trouble. How this type of packing will stand up with continual use is not known at present. Certain recent developments seem to indicate that this tower packing is not as successful as was hoped for at first. Reports are current that certain plants have removed this packing from the absorbers and refilled them with coke. The exact reason for this change is, however, not generally known.

Experiments with bubble-plate towers indicate a very high absorption efficiency. This is to be expected because of the rapidly changing liquid film as the bubbles of gas pass through the absorbing liquid. Such an absorber is expensive and requires a flue gas under several pounds pres-

sure. Table 67 from Goosmann[23] shows the relative efficiencies of the coke-packed tower and the bubble-plate tower.

TABLE 67.—*Comparison of Absorption Efficiencies of Coke-packed Towers and Bubble-plate Towers*

CO_2 in flue gas %	*Sodium carbonate solution*							
	Exit gas %		Conversion %		Gals. per min.		Coke per hr.	
	Coke Tower	Bubble Tower	Coke Tower	Bubble Tower	Coke Tower	Bubble Tower	Coke Tower	Bubble Tower
16	9.0	6.5	60–30	70–30	786	590	3,540	2,640
14	8.5	6.3	58–30	68–30	848	615	3,950	2,820
12	8.0	6.1	54–30	66–30	986	654	4,650	3,150
10	7.6	5.9	50–30	64–30	1,180	700	6,460	3,790
	Potassium carbonate solution							
16	No coke tower used	4.5	No coke tower used	70–30	No coke tower used	243	No coke tower used	2,160
14		4.3		68–30		256		2,240
12		4.2		66–30		270		2,385
10		4.1		64–30		283		2,630

The soda solution contained 6.14 lbs. of Na_2CO_3 per cu. ft. and the potash solution contained 19.5 lbs. K_2CO_3 per cu. ft.

The Operation of a Coke Tower. Drane[24] summarizes the factors affecting the operation of a gas scrubbing tower as follows:

(a) Solubility relationships of gas and scrubbing liquid.
(b) Special considerations: (1) Temperature changes, (2) formation of compounds, (3) viscosity.
(c) Rates of liquid and gas flow.
(d) Scrubbing surface, nature and extent.

The solubility relationships of gas and scrubbing liquid have already been considered, as well as such special considerations as temperature, formation of compounds, viscosity, etc. Attention will now be directed to the effect of rates of liquid and gas flow.

When a change is made in the rate at which an absorbing liquid is pumped over the packing in a coke tower there are several variables which may affect the rate of absorption. First, the area of wet surface may be increased or decreased resulting in an increased or retarded rate of absorption. These changes in rate of absorption will, of course, be proportional to the change in the active surface. Increasing the rate of liquid flow beyond the point where all of the coke is wetted will, by its turbulence, increase the surface of lye and therefore the rate of absorption. The extent

[23] Goosman, J. C., *Ice and Refrigeration*, **79**, 399 (1930).
[24] Drane, H. D. II., *J. Soc. Chem. Ind.*, **43**, 329-34 T (1924).

of this increase depends largely upon the nature of the tower packing and the quantity of liquid passing over it. Williamson and Mathews[25] investigated this effect for three different types of absorbers: (1) a baffled tower; (2) the same tower packed with approximately round pebbles 2.5 cm. in diameter; (3) a specially constructed absorption box in which the surface of the liquid was nearly level and without movement in any particular direction, although the liquid beneath the surface was flowing at the rate of 10 cm. per second.

By increasing the rate of liquid flow by 100 per cent after the surface over which the solution flowed was completely wet, the following increases in rate of absorption were observed:

Pebble-packed tower	66 per cent
Baffled tower	50 per cent
Special absorption box.....	25 per cent

These values seem to indicate that the increase in rates were due largely to the surface increase as it was more pronounced in cases where the greater turbulence resulted.

In most plants the rate of flow of flue gas is not subject to control. It depends on the rate of combustion, and the rate of combustion is determined by the steam consumption or in some cases by the quantity of lye boiled. An increase in the rate of gas flow will increase the rate of absorption because of the higher average carbon dioxide content of the gas within the tower and the decrease of the gas film due to the turbulence of gas flow. Yet the carbon dioxide lost to the atmosphere will become greater because of the larger quantity of it that escapes in the exit gases. Williamson and Mathews found that an increase of 100 per cent in the rate of gas flow, when a slight excess of carbon dioxide was passing through the tower, caused an increase of 40 per cent in the rate of absorption and a loss of slightly over 60 per cent of the increased flow of carbon dioxide. This means that the percentage loss was multiplied many times by doubling the rate of gas flow over that which produced a slight excess in the tower. The application of this data to coke tower design is quite clear. For the maximum efficiency, that is ratio of gas recovered to that produced, a flow rate for gas should be as low as is consistent with the cost of the tower. This low rate may be obtained by increasing the diameter of the absorber.

Lye Boiling. The liberation of carbon dioxide, taken up by the lye stream during its passage through the absorber, is accomplished by boiling. This operation is essentially the reverse of the absorption process. While it has been stated that the absorber is a very important part of the carbon dioxide plant it must also be emphasized that the lye boiler is no less important. The equipment used for removing carbon dioxide from the strong lye may vary from a very simple fire-tube steam boiler to an elaborate and carefully engineered lye boiler designed for the most economical heat utilization.

[25] Williamson, R. V., and Mathews, J. H., *Ind. Eng. Chem.*, **16**, 1157-61 (1924).

Most plants are designed so that not more than 20 to 25 per cent of the lye flowing through the coke tower is diverted through the lye boiler. Thus the absorbing lye passes through the absorber about 4 to 5 times for each passage through the desorber. As the amount of carbon dioxide transferred in each case is exactly the same the two units must be designed so they will have the same working capacity.

Figure 36 shows a sectional drawing of an old-type vertical, steam-heated lye boiler. The rated capacity of this boiler with dimensions as

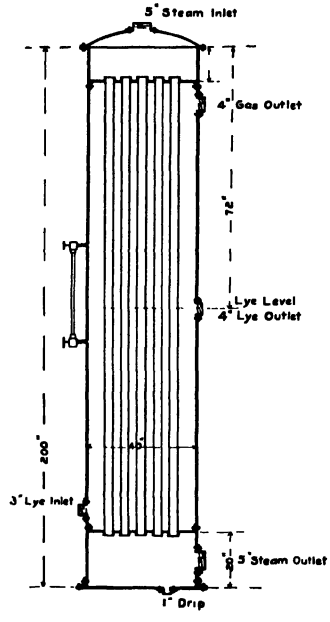


FIGURE 36.
Vertical Lye Boiler.

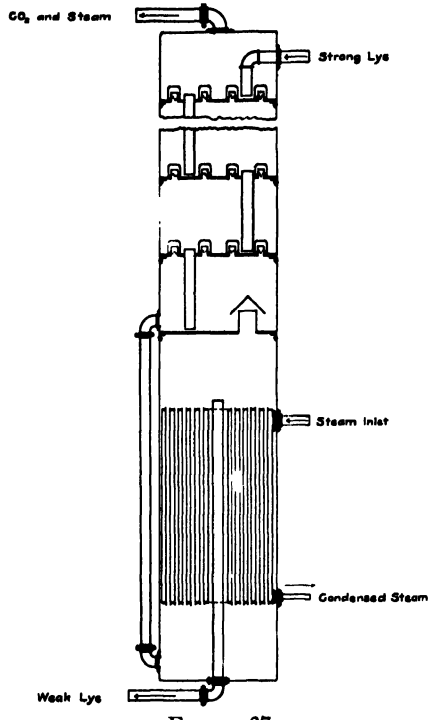


FIGURE 37.
Modern Vertical Lye Boiler.
6 feet in diameter.
50 feet high.
15 bubble plates.
Capacity 2000 lbs. Carbon Dioxide per Hour.

indicated, is about 250 pounds of carbon dioxide per hour provided the lye flow is about 50 gallons per minute and the heating surface is not less than 300 square feet. Figure 37 shows a diagram of a modern, steam-heated vertical lye boiler. This boiler, 6 feet in diameter, 50 feet high and with a tubular heating area of about 1300 square feet is capable of producing approximately 2000 pounds of carbon dioxide per hour. The rectification is accomplished by means of fifteen bubble plates arranged above

the boiler. Rectification in a case of this kind is very simple as the bubble plates act more like heat exchangers or steam condensers. The hot strong lye is fed to the top plate direct from the lye heat exchanger and at a temperature not far below the boiling point. The heat picked up in the lye heat exchanger comes from the hot lye discharged from the bottom of the lye boiler. The carbon dioxide is discharged from the top plate chamber of this lye boiler under a pressure of about 20 pounds per square inch.

The horizontal lye boiler requires more floor space but it has certain advantages which make up for this to a certain extent. Figure 38 shows in section the details of a "Carbondale" lye boiler and its rectifier. This boiler is heated by exhaust steam obtained from the pumps and engines in the plant; a small amount of live steam may also be necessary. As in the case of all steam-heated lye boilers the condensed steam is returned as feed water to the steam boiler. The rectifier on this lye boiler is essentially a

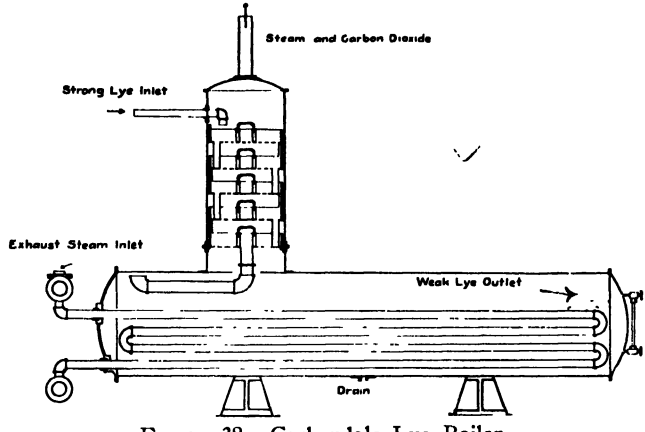


FIGURE 38. Carbondale Lye Boiler.

bubble-plate column but it lacks the efficiency obtainable with the more carefully designed bubble-caps in the vertical boiler just described. While boiling, the lye moves slowly from one end of the boiler to the other and is finally discharged through the weak lye outlet. The boiler is capable of very exact control of lye flow and boiling rate.

Many lye boilers are fitted with a constant level float valve so arranged that when the level of the lye falls a little, more steam is admitted to the strong lye pump which, in turn, speeds up and increases the flow of lye into the boiler. In this way the level is kept constant and smooth boiling results which relieves the operator of much care and trouble. The temperature of the solution and therefore its rate of boiling, can be kept practically constant regardless of changes in the rate of lye flow, by one of the many excellent temperature regulators now on the market. The thermometer of this regulator is usually placed in the weak lye exit pipe and the control mechanism connected with the live steam inlet to the heating

coils. When the temperature of the lye falls this device opens the valve slightly on the live steam line and permits more steam to enter the boiler which quickly brings the temperature up to the desired value.

Theory of Desorption or Lye Boiling. Perhaps it will not be out of place at this point to add a short discussion of the theory involved in the separation of carbon dioxide from lye solutions. For this purpose data obtained on potassium carbonate solutions are more modern and complete and this discussion can be based on this data to an advantage. The question of how closely commercial systems approach equilibrium conditions is always difficult to estimate and therefore a theoretical discussion is apt to deviate considerably in some cases from industrial experience.

By means of the equation

$$\frac{2f^2N}{(1-f)k}=p_{CO_2}$$

and a value of 0.02 for k obtained by extrapolating the data of Sieverts and Fritzsche to 100° C. one can calculate the partial pressure of carbon dioxide in equilibrium with solutions containing various percentages of bicarbonate of potassium at the boiling temperature of the solution. The other component of the gas phase being steam makes it a simple matter to calculate the weight of carbon dioxide per pound of steam coming from the lye boiler at different percentages of bicarbonate in the solution. Table 68

TABLE 68.—*Composition of Gas and Liquid Phases Obtained in Lye Boiling $t=100°$, $k=0.02$.*

Per cent bicarbonate	Lbs. CO_2 per lb. of lye	p CO_2 mm. of Hg	Per cent CO_2 in gas mixture	Per cent H_2O in gas mixture	Lbs. CO_2 per lb. H_2O
80	0.0316	640	84.2	15.8	13.02
75	.0295	450	59.2	40.8	3.55
70	.0277	326	41.5	58.5	1.73
60	.0237	180	23.6	76.4	.755
50	.0198	100	13.1	86.9	.368
40	.0158	53	6.9	93 1	.181
30	.0118	26	3.4	96.6	.086
20	.0079	10	1.3	98.7	.032
10	.0039	2	.3	99.7	.007

shows the results of such calculations and Figure 39 shows the equilibrium curve obtained by plotting the weights of carbon dioxide per pound of steam in the gas phase against the per cent bicarbonate in the liquid phase. The most striking thing about this curve is the very rapid increase in the partial pressure of carbon dioxide in the gas phase at concentrations of bicarbonate above 70 per cent and the very slight increase at concentrations below 50 per cent bicarbonate. If one could produce, by absorption in a coke tower, a lye containing 80 to 85 per cent bicarbonate the process of lye boiling would indeed be a very simple one. The solution would hardly require boiling as the carbon dioxide would be evolved copiously at temperatures near the boiling point. On the other hand solutions con-

taining less than 40 or 50 per cent bicarbonate would require a great deal of boiling to obtain an appreciable yield of carbon dioxide. As the attainment of high bicarbonate concentrations seems to be impossible with the present method of absorption the working range is limited to the section between about 50 and 75 per cent bicarbonate.

The curve in Figure 39 shows at a glance why the concentration of bicarbonate in a lye solution is not decreased in a commercial plant to a lower value. The cost of separating the carbon dioxide from the alkaline

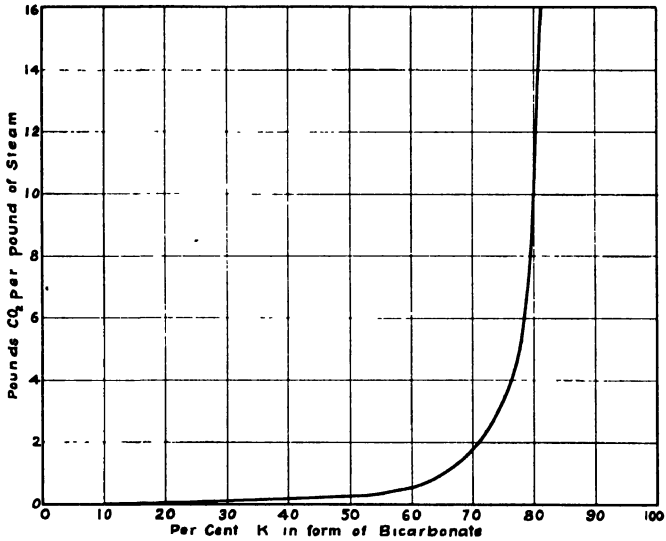
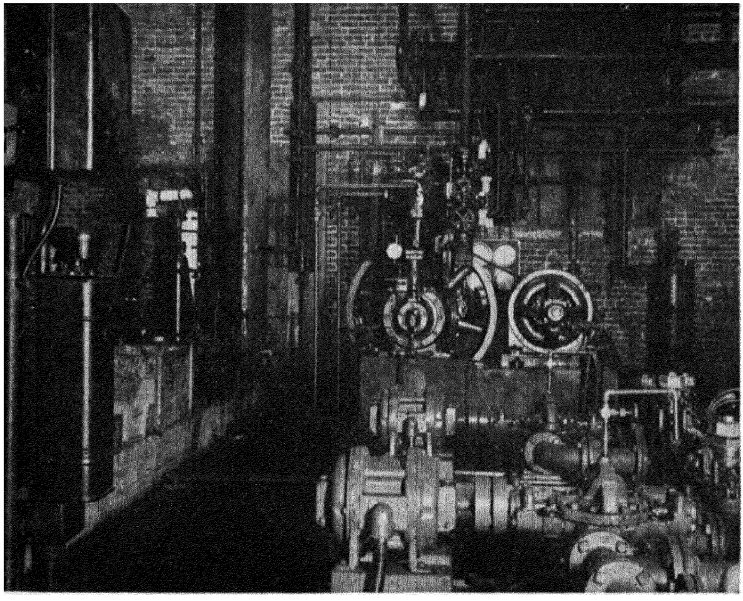


FIGURE 39. Curve Shows Carbon Dioxide in Equilibrium with Potassium Bicarbonate Solution at its Boiling Temperature.

solution increases very rapidly as bicarbonate concentration decreases and a point is soon reached where continued boiling of the solution is no longer economical.

Condensers. The particular type of condenser used for condensing the steam from the gaseous carbon dioxide is of no great importance as long as the condensation equipment is sufficient to meet the plant needs. Surface condensers consisting of a simple coil of pipe over which the cooling water is flowed have some advantage because of the ease of cleaning. Inclosed tubular condensers, however, are more economical in water consumption. A surge tank or a condenser sufficiently large to serve this purpose is desirable to take care of the hot lye which at times is apt to froth over from the boiler. This tank is, of course, connected to the lye tank through a trap so any lye collected in it will be returned to the absorption system. A trap is also connected to the condensing system to separate the condensed water from the carbon dioxide and returning the former to the lye solution.

Gasometer. In some plants a small gasometer is placed in the carbon dioxide line to smooth out the inequalities in the rates of production and compression. This can be used to an advantage only where the lye boiler operates under a pressure near atmospheric. Many plants, however, operate the lye boiler so as to furnish gas to the suction port of the compressor at a pressure of about 20 pounds per square inch. In such cases the operation of the lye boiler and compressor is so conducted that a gasometer is unnecessary.



Courtesy, Safety Mining Company.

FIGURE 40. Showing End View of Carbon Dioxide Compressor, Solution Pumps in the Foreground, Silica Gel Dryer and Potassium Permanganate Scrubber in the Left Background.

Purification. The carbon dioxide at this point besides being saturated with water vapor often contains a faint but undesirable foreign odor. The cause of this odor is unknown but it is generally supposed to be due to oxidizable organic bodies carried from the raw flue gas by the carbon dioxide. Chemical treatment for the removal of these odors is often resorted to in which case the gas is scrubbed with a solution of potassium permanganate. Such a chemical purifier is shown in Figure 40.

The first step in the process of dehydration of the carbon dioxide is to lower its temperature, by means of a simple cooler, to that of the water supply. Assuming a gas saturated with water at 25° C. and a cooling water of 12° C. the cooling operation will then change the water content from 0.01304 pounds per pound of carbon dioxide to 0.00569 pounds of water per pound of carbon dioxide. The difference between these two

values represents the water separated by condensation. Such a cooler soon pays for itself by removing much of the load from other dehydrating units.

The final dehydration operation may be conducted with a calcium chloride tower, by means of refrigeration, by adsorption of water on silica or alumina gel, or by a combination of these methods.

The calcium chloride tower is the most important chemical dehydrator. Such an apparatus will dry a carbon dioxide gas stream very effectually when it is kept in the proper working condition. These dryers require considerable attention, however, and the authors have seen some in such a state of neglect that they served no purpose whatever. As a matter of fact some plants make no effort to dry the gas beyond the point reached with a good gas cooler.

Dehydration by means of refrigeration is not a new process nor is it confined to carbon dioxide gas alone. The cooling may be produced by means of a separate refrigeration unit or by simply expanding some of the liquid carbon dioxide back into the suction gas stream. One type of dehydrator found by the authors in a liquid plant is quite interesting and a

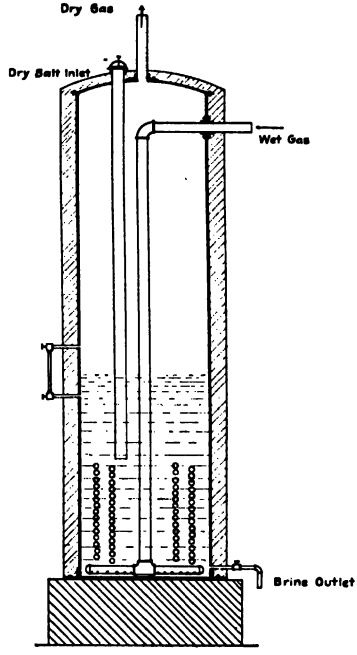
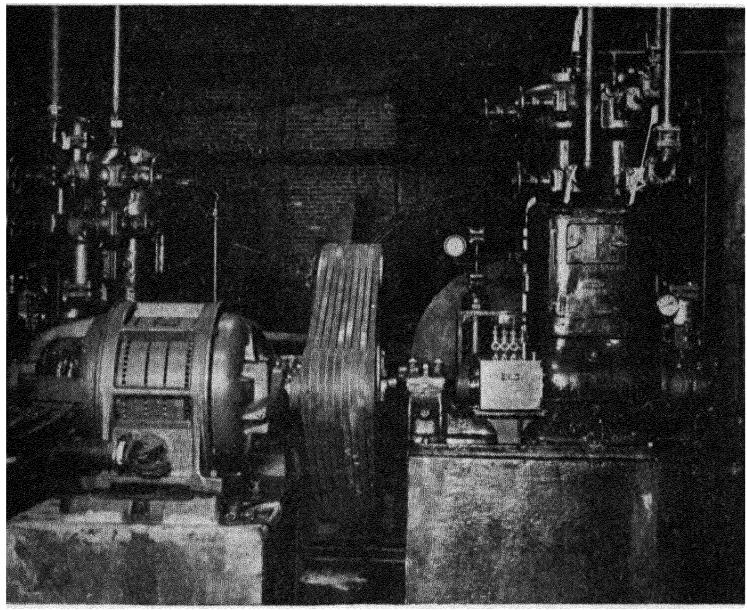


FIGURE 41.
Carbon Dioxide Dehydrator.

drawing of it is given in Figure 41. The cooling of the salt brine in this dehydrator is effected by an auxiliary refrigeration machine. The carbon dioxide gas is passed through this brine and as the water content of the solution increases by the resulting condensation more solid salt is added and the excess brine is drawn off. This refrigerating unit or any other capable of reducing the temperature of the gas stream to $-5°$ C. (23° F.)

will decrease the water content to 0.0017 pound per pound of carbon dioxide. A recent development in the art of drying gases, with the aid of silica gel, is especially fitted to the carbon dioxide industry. This dehydrating substance, which has a remarkable adsorptive capacity for water and other gaseous impurities, is being used more and more in the process of



Courtesy, Safety Mining Company.

FIGURE 42. Carbon Dioxide Compressor with a Capacity of 600 pounds of Carbon Dioxide per Hour. Built by the York Ice Machine Company.

carbon dioxide purification. The adsorption process on which its drying properties depends is entirely a physical reaction and can be reversed by simply changing the temperature of the charge.

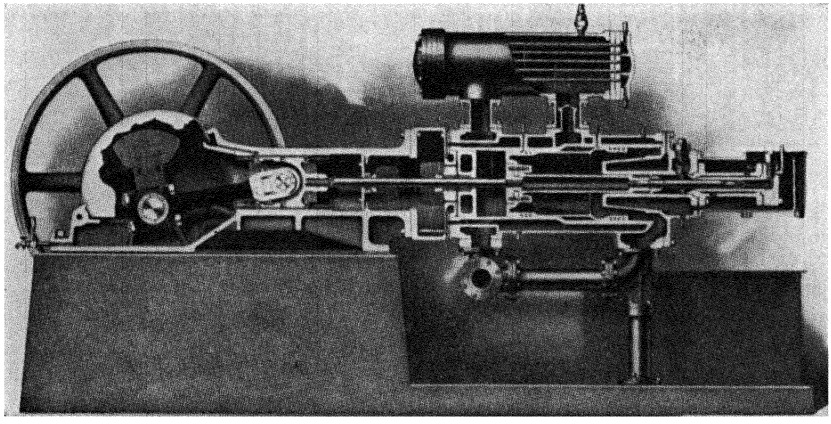
The adsorbers, in which carbon dioxide is brought in contact with the enormous surface exposed by the silica gel, are simple tanks designed to withstand the working pressure of the gas. These tanks are usually arranged in duplicate so that while adsorption is taking place in one the other is undergoing reactivation. After the silica gel becomes saturated with water, the adsorber is cut out of the system and air at a temperature of 300° to 500° F. is passed through until all of the water is vaporized and removed from the adsorber. The unit is then ready to be cut into the system again at 100 per cent of its original effectiveness. The two adsorbers are usually placed close together with an air pump and air heater mounted on the same frame. Changing the flow of gas from one to the other is accomplished by simply operating a valve. The adsorption cycle will vary from

2 to 10 hours depending upon the rate of flow and the size of the adsorber. It is stated that the operating cost varies from 5 to 15 cents per ton of carbon dioxide treated. The purified carbon dioxide can be dried to a water content of 0.006 per cent by weight or even less.

Silica gel adsorbers are designed for low pressures so they can be used on the suction line of the compressor. They are also designed for high pressures so they can be used between stages while the gas is being compressed. A favorite position is between the second and third stages on a three-stage compressor.

Liquefaction of Carbon Dioxide. The final major operation in preparing carbon dioxide for the market is the process of compressing and condensing. (See Figure 42). Increasing the gas pressure to a point where it is liquefied by the cooling effect of the condensers may be accomplished by several types of machines. Compressors have been constructed with one, two, three and four stages but the latter two are the only ones important at the present time. One also finds both the vertical and the horizontal types of machines. Figure 43 shows a sectional view of a standard horizontal three-stage compressor.

The problems connected with carbon dioxide liquefaction differ but slightly from those encountered in liquefying other gases. In this case,



Courtesy, Norwalk Company, Inc.

FIGURE 43. Sectional View of a Standard Carbon Dioxide Compressor.

however, the liquefaction takes place at temperatures only a little below the critical point while most other liquefied gases used for commercial purposes have relatively high critical points.

The proper lubrication of a carbon dioxide compressor has always been somewhat of a problem. Lubricating oils unless very highly refined impart to the carbon dioxide an undesirable odor which lowers the grade of the product. For this reason glycerol was largely used as a lubricant. Glycerol, however, is not an ideal lubricant. The fact that it is miscible with water

in all proportions makes it liable to dilution in the cylinders of a compressor to a point where it has no lubricating properties. Furthermore high temperatures tend to decompose glycerol with the formation of acrolein a substance having a very penetrating and disagreeable odor which would be needed in only a trace to make the carbon dioxide unmarketable. The general practice now, is to use a very highly refined mineral oil for compressor lubrication. Several types of oil, suitable for compressor lubrication, are available and in general they are odorless, tasteless and colorless.

Oil Removal. The tendency for oil droplets to leave the compressor with the highly compressed carbon dioxide is sufficient to make an oil separator necessary. It is not possible to state definite upper limits below which

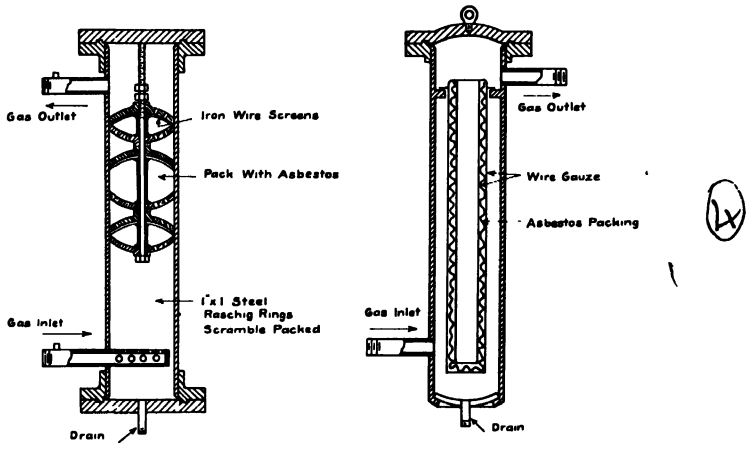


FIGURE 44. Typical Oil Filters.

oil must be reduced, because of the variety of conditions under which commercial liquid and solid carbon dioxide is used. Amounts in no way objectionable for industrial application of either liquid or solid, will meet instant rejection of the solid when applied to paper carry-home ice cream packages. The oil content of commercial products ranges from none at all when glycerol is used as a lubricant, to 0.02 per cent, although percentages as high as 0.03 are not objectionable in the shipping of most food products, packed with the solid, when colorless compressor oils are employed.

Two types of oil traps are illustrated in Figure 44, and it is obvious that any construction suitable for high pressure gases, and embodying features of low gas velocity and change of direction, will serve the purpose.

It is important, regardless of the mechanical detail of oil separation equipment, that oil separators should be operated above the critical temperature of carbon dioxide, since otherwise the liquid carbon dioxide will dissolve and flood out of the separator a portion of the oil. Also while lubricating oil will readily separate as a bottom layer with liquid carbon dioxide at temperatures above about 10° C. at lower temperatures the two

layers change places thus making it possible for the oil to flow from the top of the trap into the liquid carbon dioxide system.[26] On the other hand, separation is more effective at low temperatures than at high; hence, certain plants have made a practice of removing a portion of the superheat prior to oil separation, maintaining oil separators at temperatures from 100° to 120° F. and this practice has much to commend it.

Liquid Carbon Dioxide Condensers. The only characteristic of importance in the condensers used for the liquefaction of the highly compressed carbon dioxide is that they be constructed to withstand the very high pressures to which they are subjected. Coils exposed to the atmosphere, over which water is flowed, coils submerged in cooling water and the double-pipe condenser are perhaps the most popular types. Accessibility for repairs is often necessary because of the serious corrosion to which these condensers are sometimes subjected. In some cases, this corrosion is serious enough to make a renewal of the condenser necessary every few months. The cause of this was shown by Hackspill and Couder[27] to be due to the formation of nitrites from the combined nitrogen of the coke which is absorbed by the alkali carbonate solution to form potassium nitrite. On boiling the lye solution, containing small amounts of the nitrite, a small amount of HNO_2 is liberated ($KNO_2+H_2CO_3=KHCO_3+HNO_2$) which decomposes as follows: $3HNO_2=H_2O+HNO_3+2NO$. It is supposed that the corrosion is due to this nitric acid.

The Sürth System for Manufacturing Carbon Dioxide

Some years ago, the Sürth Machine Works in Sürth, Germany, introduced a radical departure in the coke process for manufacturing carbon doxide.[28] The principal difference between this and the common coke process was in the method of burning the coke and the process of absorbing the carbon dioxide from the combustion gases. The coke or coal was burned in a generator for the production of a high-grade producer gas. After purification the producer gas was burned in an internal combustion engine for the production of power and an exhaust gas rich in carbon dioxide. The exhaust gas from such a motor may contain from 18 to 18.8 per cent carbon dioxide.[29]

The absorption of carbon dioxide from the motor exhaust gas was conducted under a pressure of from 4 to 5 atmospheres. Furthermore, the absorption took place at a temperature near the boiling point of the lye solution, thus making unnecessary the cooling of the lye stream after the expulsion of the carbon dioxide in the lye boiler. This made heat exchangers of little value and the heat saved in this way was expected to be a factor towards a high thermal efficiency in the process. However, the need of

[26] Quinn, E. L., *Ind. Eng. Chem.*, 20, 735-40 (1928).

[27] Hackspill, I., and Couder, A., *Compt. rend.*, 176, 1811-13 (1923); *Chimie et industrie*, Special No., 404-5 (May, 1924).

[28] D. R. P. 162,655 and 173,130 to E. A. Behrens and J. Behrens.

[29] Espenmüller, *Z. kompr. flüss. Gase*, 25, 10 (1926).

compressors to raise the pressure of the exhaust gas to the required value added a power expense which offset this heat saving to a considerable extent. Then the expense of constructing an absorber sufficiently strong to withstand this high absorption pressure, together with the difficulties encountered in operation took away practically all advantage gained by the thermal efficiency. This process, to a certain extent, was an isothermal reaction in which the carbon dioxide formed bicarbonate of potassium because of its increased partial pressure in the flue gas stream and was again separated in the boiler by the reduction of this pressure. The yield of carbon dioxide per pound of coke in this process, was said to be from 1.3 to 2 pounds.

The original Sürth process has been modified considerably in recent years. The generator gas plant as a source of cheap fuel has been retained but the pressure absorption system has been discarded. This modified process spoken of as the Linde-Sürth process has certain advantages over the common coke process, especially in places where a high-grade coke is expensive or difficult to obtain.

Figure 45 shows in diagrammatic form the most important features of the Linde-Sürth process. The gas producer (1) consists of a universal closed shaft furnace on the grate of which a thick layer of fuel rests. Air drawn through this mass of heated fuel, by suction, produces a combustible gas consisting of carbon monoxide with perhaps a little hydrogen, formed by the water gas reaction from the moisture in the air used. Automatic charging devices may be used in the larger plants to keep the fuel level in the generator at the proper height. The gas stream from the producer is first purified in the wet scrubber (2) and then in the dry purifier (3). The part of the gas needed for operation of the lye boiler is removed from the dry purifier with a special blower (4) while that used for power is drawn out by the suction of the gas engine (5). The exhaust gas from the engine is passed through the water scrubber (7) and then combined with the combustion gas from the lye boiler (6) after which the combined gases are washed in the water purifier (8) and the soda lye scrubber (9). The blower (10) then forces the purified flue gas up through the coke tower (11) counter-current to the stream of potassium carbonate which is sprayed over the coke packing. The bicarbonate solution thus formed is then forced, by means of the lye pump (12) through the heat exchanger (13) and (14) to the dome of the lye boiler (6). In the dome of the lye boiler the incoming solution is preheated as it passes down over the Rauschig rings, used as packing for the dome, which are in turn heated by the mixture of steam and carbon dioxide coming from the lye boiler. The spent lye coming from the lye boiler is returned to the absorption system, through the heat exchanger (14) (15) where it gives up heat to the incoming strong lye. The exchanger (15) is water-cooled and gives to the lye the right temperature for maximum absorption rate. The lye pump (16) returns the weak lye to the top of the absorbing tower

where it goes through the cycle again. The carbon dioxide with some water vapor coming from the top of the lye boiler is first cooled in the exchanger (13), the water thus condensed is separated and sent back to the lye stream, while the gas is sent to the gas holder (17). In the purifying and compression system the gas is first dried with calcium chloride in the drier (18) and then sent through the carbon purifier (19). After the

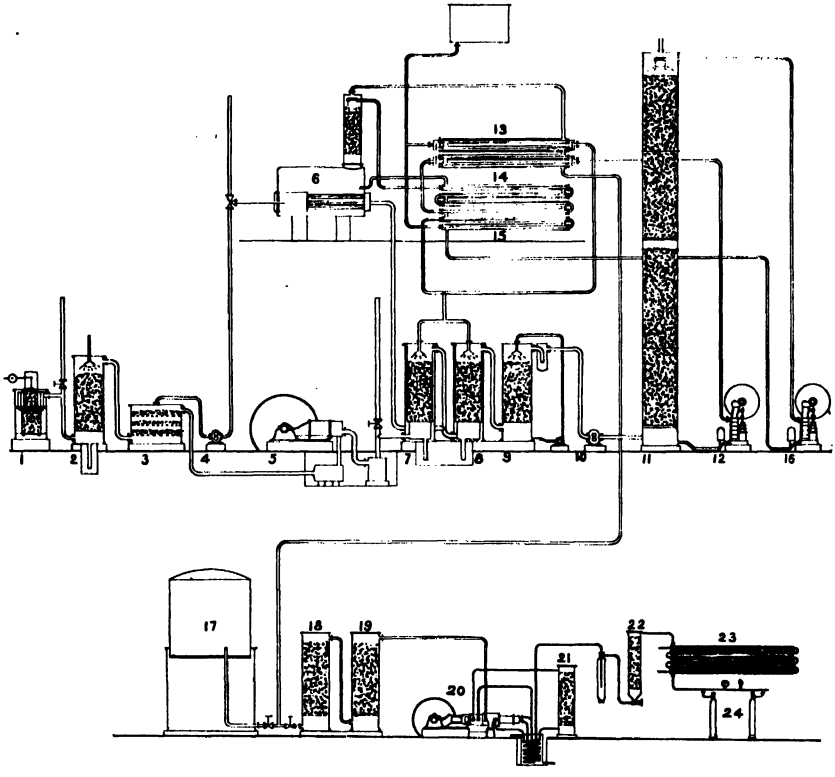


FIGURE 45. The Linde-Sürth Process for Manufacturing Carbon Dioxide.

first stage of compression in the compressor (20) the gas is further dried in the tower (21). From the third stage of the compressor it passes through the oil separator (22) and to the condenser (23) and finally filled into the steel cylinders (24).

CARBON DIOXIDE FROM CARBONATES

The liberation of carbon dioxide from calcium and magnesium carbonates by means of acids was one of the first industrial methods of preparing commercial carbon dioxide. This process is still of some importance at least to a certain extent from an industrial point of view. Natural carbonates found in tremendous quantities contain high percentages of carbon

dioxide, a large amount of which is readily recovered on a commercial scale. Thus limestone, marble, chalk, aragonite, calcite, etc., all more or less pure carbonates of calcium, may contain up to about 44 per cent carbon dioxide. Magnesite, a naturally occurring carbonate of magnesium, may run as high as 52 per cent carbon dioxide.

The thermal decomposition of calcium and magnesium carbonates, for the production of lime and magnesia, is carried out on a vast scale in nearly all parts of the world. Gases produced in the decomposition kilns, used in this industry, may contain as much as 40 per cent of carbon dioxide by volume. This is a source of industrial carbon dioxide of considerable importance and many lime plants are making use of it to increase the profits of their companies. It is not intended to imply, however, that every gas stream containing carbon dioxide in high percentages is a source of profit. Even gases containing nearly 100 per cent of carbon dioxide may be of little value unless the location is favorable to the existing or potential market. One finds a number of plants in this country making liquid or solid carbon dioxide from by-product gas obtained from lime or magnesia burning. What is said to be the largest solid carbon dioxide plant in the world, producing about 250 tons of the solid per day, is operated with carbon dioxide obtained from kilns.

It is sometimes difficult to make a distinction between plants making carbon dioxide as a main-product and those making the gas as a by-product. There are, however, some plants the operation of which is adjusted to produce as high carbon dioxide-containing gas as possible and some which are operated so as to produce as high-grade lime as possible. In the former case the grade of lime produced may at times be very inferior and the authors know of at least one plant where hand picking of the lime is necessary to produce a marketable product.

In connection with kiln gases it might also be stated that cement kilns often produce gases of high carbon dioxide content. This is a potential supply of carbon dioxide which may become of great industrial importance. The authors are not aware of any plant of importance at present operating on such kiln gases however.

The chemistry involved in the process of burning lime and magnesia will not be considered here as such a discussion belongs more properly to a book on that subject.[30] The removal of the carbon dioxide from the kiln gases produced in these operations, however, is usually accomplished by means of the absorption process. A schematic arrangement of such an absorption plant is shown in Figure 46.

Processes producing pure carbon dioxide by the burning of carbonates in retorts are used for special purposes all over the world. The process of the Gillette Research Corporation[31] is an interesting example. This process is a continuous operation in which limestone, oyster shell or marble crushed

[30] Knibbs, N. V. S., "Lime and Magnesia," Ernest Benn, Ltd., London (1924).
[31] Gillette, E. P., U. S. Patent 1,923,084, Aug. 22, 1933.

to sizes of about $\frac{1}{8}$ to $\frac{3}{4}$ inch, is passed into a vertical retort heated from the outside with oil or gas as a fuel. The preheating which takes place in three stages is a very important step because this eliminates all foreign matter such as organic material and moisture. The retorts are arranged so the carbon dioxide is taken from the calcining chamber as fast as it is produced and requires no further purification as a purity of 99.5 per cent is easily obtained.

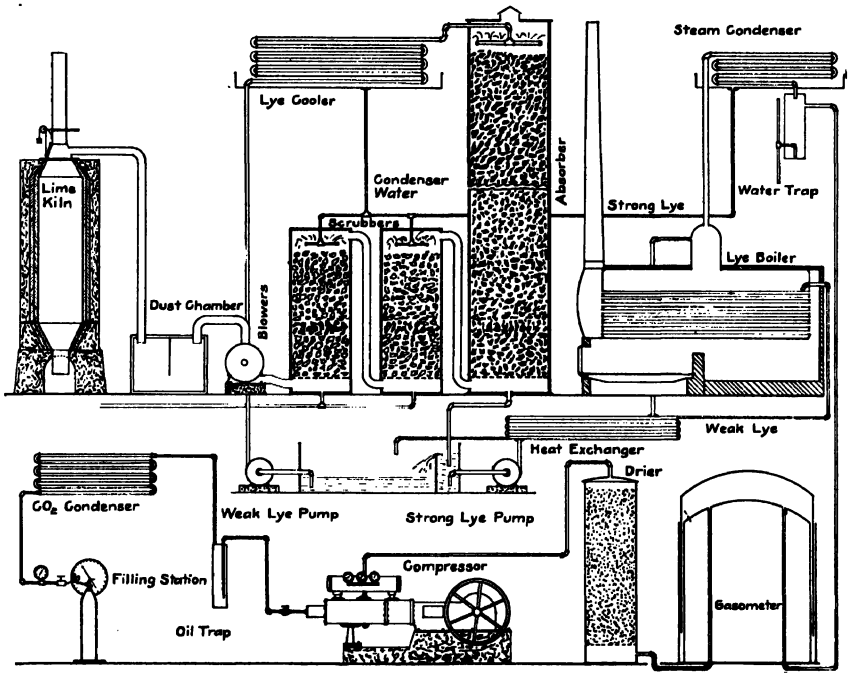


FIGURE 46. Schematic Arrangement of a Plant for Making Carbon Dioxide from Kiln Gas.

One's interest in carbon dioxide is usually dominated by the production of the liquid or the solid states, yet the large amounts of kiln gas, with varying amounts of carbon dioxide, used without concentration or even purification is also worthy of consideration. Some of the industries making use of such gases are: the ammonia-soda (Solvay) process for making soda ash and sodium bicarbonate, the refining of sugar and the manufacture of precipitated chalk and magnesium carbonate.

Carbon Dioxide from Dolomite. A most interesting and unusual method of manufacturing carbon dioxide is that used by the Crystal Carbonic Laboratory in Atlanta, Georgia. This process has been described by Heath,[82] as a wet process in which the dolomite is treated with sulfuric

[82] Heath, W. P., *Ind. Eng. Chem.*, 22, 437 (1930).

acid, the carbon dioxide separated, the residue in the retorts which consists of sulfates of calcium and magnesium principally are separated and the magnesium sulfate in the form of Epsom salts is purified for the market.

The dolomite used in this process is obtained from large limestone deposits located at Cartersville, Georgia. The average analysis is as follows:

Calcium carbonate	54.00%
Magnesium carbonate	45.00
Ferrous oxide	0.05
Alumina	0.05
Silica	0.50
Total	99.60

This stone after its arrival at the plant is first prepared for the generators by passing it through the Sturtevant Mill Company's equipment consisting of a jaw crusher, ringroll mill and an air separator. This treatment reduces it to pass a 60-mesh screen. It is then stored above the lead-lined generators into which it is weighed as each charge is prepared.

A charge for each generator consists of 1400 pounds of dolomite, 1000 pounds of water and 2000 pounds of 60° Bé. sulfuric acid. The acid is slowly added to the dolomite over a period of one hour and the carbon dioxide produced by the reaction is washed in a gas washer and sent directly to a large rubber gas bag having a capacity of 2500 cu. ft. which is located in the basement of the plant. From this gas holder it is taken to a compressor and reduced to a liquid in the usual manner, after which, it is filled into standard carbon dioxide cylinders for shipment. The gas produced by this process has an average purity of 99.5 per cent carbon dioxide the rest being air.

While this process is conducted primarily for the production of carbon dioxide it also produces a valuable by-product in the form of Epsom salts. It seems evident that such a process could not compete with the coke process without the aid of such a by-product.

By-Product Carbon Dioxide from Fermentation

In the fermentation industry, the principal chemical reaction is the conversion of sugar such as dextrose, into ethyl alcohol and carbon dioxide. This reaction is promoted by an enzyme secreted from yeast cells and its course may be represented by the simple equation

$$C_6H_{12}O_6=2C_2H_5OH+2CO_2.$$

Theoretically, 180 pounds of dextrose will produce about 92 pounds of alcohol and 88 pounds of carbon dioxide. Practically, these values are not quite reached, because of secondary reactions and incompleteness of the fermentation, nevertheless, the weights of carbon dioxide and alcohol are usually very nearly equal. The carbon dioxide produced in this reaction is largely if not completely discharged into the atmosphere in most industrial establishments. For years, attempts have been made to convert this

waste product to some practical use. Joseph Priestly was perhaps the first to attempt its utilization. He collected the carbon dioxide from the top of the fermentation vats in a brewery near his home and with it attempted to carbonate small quantities of water. This and many other attempts, however, attained indifferent success from a commercial point of view. Gaseous impurities, and even entrained liquids and solids were carried by the carbon dioxide from the fermenting material and these impurities made its use for carbonating beverages quite impossible. The gaseous impurities carried by the raw gas consists of aldehydes, higher alcohols and other compounds and these give a decidedly obnoxious odor to the gas which must be completely removed before the carbon dioxide can be used in food products. The early manufacturers, in attempting to put this by-product carbon dioxide on the market, failed to realize the importance of complete purification, with the inevitable consequence the fermentation carbon dioxide fell into disrepute.

Recently, by-product carbon dioxide has assumed a much more prominent place in the industry, a condition that has resulted from the rapid development of uses for the solid state. Solid carbon dioxide, which but a few years ago, found its principal use on the chemistry lecture table, and in a few cases as a refrigerant in the research laboratory, developed to a commercial commodity with such speed that practically all sources of cheap carbon dioxide were utilized. The principal use for solid carbon dioxide is for refrigerating food products and it must, therefore, be without foreign odor or discoloration. To make a gas which when converted to the solid will meet these specifications requires the use of an elaborate purification process under the constant supervision of well-trained technical men.

The Process of Fermentation. In this country the fermentation carbon dioxide industry is confined largely to the manufacture of industrial alcohol although one very large plant operates on carbon dioxide produced by the fermentation of starch to produce butanol and acetone. Immense quantities of carbon dioxide are produced annually in the fermentation industries. In 1929 something like 348,000 tons of carbon dioxide was produced from industrial alcohol manufacture alone in the United States. The present production from this and other fermentation industries must be many times this value.

The fermenters in which molasses is converted to alcohol and carbon dioxide are immense tanks having a working capacity sometimes as high as 125,000 gallons. Many of these fermenters are made of wood while others are made of steel copper alloy. Some means of controlling the temperature of the fermenting mass is necessary and this is usually accomplished by means of copper coils in the tanks through which cooling water is circulated or an arrangement for spraying the cooling water on the outside of the fermenters. In installations where it is desired to collect the carbon dioxide for purification, these fermenters are closed at the top

or in the case of certain types of wooden fermenters, a large copper hood is placed over them, the lower edge resting in a water seal around the top of the tank. These covers are provided with glass windows and an electric lamp inside permits the progress of the reaction to be observed. The carbon dioxide is discharged under a pressure of about five inches of water, first to the atmosphere until all of the air originally in the charge is washed out of the system and then to a gasometer from which it is delivered continuously to the purification system.

The charge in a 125,000 gallon fermenter consists of 25,000 gallons of molasses containing about 6 pounds of sugar per gallon. The molasses is then diluted with 100,000 gallons of water, to which is added the yeast and the salts necessary for their proper growth. The period of fermentation may be from 40 to 60 hours and during that time, about 75,000 pounds of carbon dioxide is produced. The evolution of gas starts gradually, works up to its maximum intensity, and gradually subsides. In many cases, only that gas which is liberated during the period of most active fermentation is collected and in order to produce a continuous supply of carbon dioxide for the purification plant, the fermenters are started at definite time intervals and the gas stored in a gasometer of sufficient capacity to equalize the fluctuations in flow.

In some cases, especially in Europe, the brewing industry also recovers its waste carbon dioxide for purification and compression.[33] The problems of purification of by-product carbon dioxide from fermenting beer mash are somewhat different from those encountered in the alcohol distillery. In general, however, it may be said that they are solved in much the same manner. According to Goosmann,[34] during the manufacture of 100 gallons of 4 per cent beer there will be generated about 15 pounds of carbon dioxide. It is quite evident from these values that it requires an immense brewing establishment to put carbon dioxide on the market in anything like commercial quantities.

The simple equation given above for the decomposition of sugar into ethyl alcohol and carbon dioxide does not account for all of the products of the reaction. Many secondary reactions also take place and, in addition to the two main products just named, there are formed acetaldehyde, acetic acid, succinic acid, glycerol, higher alcohols, furfural and glycols.[35] In the gases coming from fermenting beer mash hydrogen sulfide is also found. This is produced during the fermentation by the sulfur of the beer mash. Most of the sulfur comes from the sulfur containing proteins of barley and malt, although small amounts may be derived from gypsum or free sulfur.[36]

Purification of Fermentation Carbon Dioxide. The removal of the impurities from fermentation carbon dioxide is a problem of great impor-

[33] Pierre, L., *Brasserie et malterie*, 17, 20-6 (1927).
[34] Goosman, J. C., *Ice and Refrigeration*, 79, 295-98 (1930).
[35] Farine, A., *Tech. Ind. Schweiz. Chem. Ztg.*, 178-82 (1926).
[36] Wanderscheck, *Wochschr. Brau.*, 45, 441-6, 463-8 (1928).

tance and one that is not always completely solved. There are two general methods of treating this raw gas and either one or both of them may be used depending upon the nature of the gas and the experience and preference of the designer. The first process removes the impurities from the raw gas by adsorption on some adsorbing agent such as activated charcoal or silica gel. The second treats the gas chemically for the oxidation of the impurities and removes the oxidation products other than carbon dioxide by means of either an adsorption or an absorption process. There are in operation two patented processes, namely the Backus and the Reich, the operating details of which are well known. It therefore seems desirable to go into the discussion of these somewhat in detail although it must not be assumed that these two processes comprehend the entire art of purifying by-product carbon dioxide. The largest Backus purification system yet installed is now operating at Deepwater, New Jersey, and the largest system of the Reich type at Philadelphia, Pennsylvania, yet there are a number of plants using systems quite different from either but employing the same general reactions indicated above.

The Backus Process of Purification[37]

This process is essentially one of adsorption by which the impurities are separated on activated charcoal. One of the large distilleries using this process of purification is located at Curtis Bay, Maryland, and is owned by the U. S. Industrial Alcohol Company.[38] In this plant, fermentation is carried out in fifteen fermenters, each with a capacity of 125,000 gallons of mash. Five of these fermenters are filled each day, therefore the daily carbon dioxide production of this plant must be over 180 tons. However, only that gas which is liberated during the period of most active fermentation is collected, and therefore only a part of the total yield of carbon dioxide is utilized.

During the period of gas collection, the carbon dioxide is taken from the top of the fermenters, and forced with a Root blower through a Feld scrubber. Here the gas is washed with water for the purpose of removing a large part of the entrained material, alcohol, aldehydes, etc. The impurities still retained by the carbon dioxide are then adsorbed by passing the gas through purifiers filled with activated carbon.

The purifiers are steel tanks about 3.5 feet in diameter, by 13 feet high. Coils of pipe inside, serve as heaters when filled with steam, or as coolers when cold water is circulated through them. The activated carbon is packed around these pipes and the carbon dioxide passes up through the mass on which the foreign substances are adsorbed. This adsorption has a positive heat of reaction; therefore cooling becomes necessary, especially when the unit is first cut into the system, in order to keep the temperature of the carbon down to 43° to 49° C. (110° to 120° F.), at which temperature the

[37] U. S. Patents, 1,493,183 and 1,510,373, to Arthur A. Backus.
[38] Moore, W. C., *Ind. Eng. Chem.*, 18, 540-1 (1926).

adsorbers are most effective. Two of these purifiers are connected in series and when their efficiency falls, due to the accumulation of impurities, they are cut out of the system and subjected to a revivification treatment. This is accomplished by passing live steam through the mass of carbon and at the same time heating it by passing high pressure steam into the heating coils. After all of the adsorbed material has been steamed out of the purifiers, the carbon is dried with a stream of warm dry air. When the issuing air is perfectly dry, the high pressure steam in the steam coils is turned off and cold water circulated so as to bring the carbon quickly to the proper working temperature.

Carbon dioxide purified by this adsorption process is said to be free from foreign odors and to contain less than 0.1 per cent of moisture. The drying of the gas by the adsorbing material eliminates special drying apparatus and the gas can be sent directly to the compressors.

The Reich Process of Purification[39]

This method of treatment makes use of reactions which are more distinctly chemical than those used in the Backus adsorption process. In general, it is an oxidation process in which the impurities are converted by powerful oxidizing agents to carbon dioxide or to products which are easily separated by scrubbing with the proper liquids.

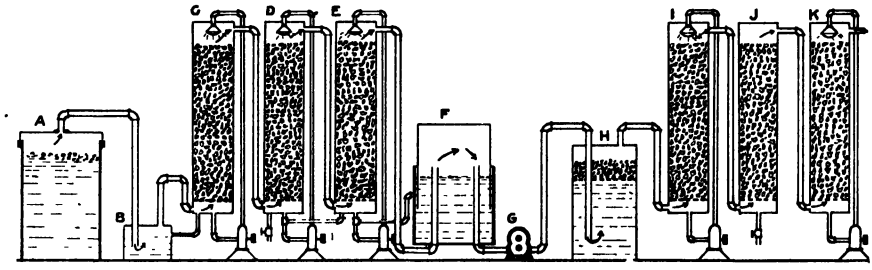


FIGURE 47. Reich Process.

A. Fermenter
B. Catchall
C. Alcohol Scrubber
D and E. Water Scrubbers
F. Gasometer
G. Blower
H. Dichromate Washer
I. H_2SO_4 Scrubber
J. Soda Ash Tower
K. Oil Washer

The carbon dioxide taken from the top of the closed fermenters is first bubbled through a dilute alcohol solution in a wash box called a *catch-all* (Figure 47). This serves to remove the entrained mash, some of the alcohols, esters, and aldehydes, and to maintain a proper pressure on the fermentation vat. It is then thoroughly washed in three wooden scrubbers operating in series. These washers, about 30 feet high by 3 feet in diameter, are packed with *spiral-ring* fillers. In the first tower, the gas is washed with a dilute alcohol solution, and in the second and third, with water to remove the alcohol. The wash water from the towers contains considerable

[39] U. S. Patent 1,519,932, to G. T. Reich.

alcohol and it is returned to the alcohol plant where it is either distilled or used in the fermenters. The wash water requirement is about one gallon per pound of carbon dioxide treated.

This preliminary washing removes a large part of the impurities but the gas still retains a trace of alcohol, ammonia, sulfur compounds and an odor of fermenting mash. It is then collected in a gasometer from which it is forced at a constant velocity by means of a blower to the rest of the purification train. The next step is the oxidation of the organic impurities by means of a solution of potassium dichromate, after which it passes into a sulfuric acid scrubber. The dichromate solution is contained in a tank through which the carbon dioxide is bubbled, but the sulfuric acid is circulated over the packing in a tower similar to that used in the first washing process. Any spray of sulfuric acid which may pass out of the tower with the gas stream is caught in another tower packed with dry sodium carbonate. This dry soda ash not only removes any sulfuric acid, but it also removes much of the moisture from the gas. The last washing is with compressor oil in a counter-current scrubber similar to the others. This treatment removes the oxidation products produced in the dichromate and sulfuric treatment. The gas is delivered to the compressors under a pressure of 2 to 3 pounds per square inch.

It is said that this process produces an excellent grade of gas, but the operation requires the constant supervision of specially trained men, and is by no means fool-proof.

Combination Adsorption and Chemical Treatment

One rather interesting installation, known to the authors, treats the gas under pressure by a combination of the adsorption and oxidation processes. One striking feature of the process is the way the treatments are given to the gas as it passes from one stage of the compressing operation to the next.

The carbon dioxide is taken from the fermentation vats through a five-inch water seal to a storage gasometer. From the gasometer, a boosting fan increases the pressure to 10 inches of water and forces it through a scrubber where the preliminary washing takes place. From this scrubber, the gas goes to the first stage of a three-stage compressor, where its pressure is raised to about 60 pounds per square inch. After passing through an intercooler, where the heat of compression is removed, it goes to a second scrubber, where it is thoroughly washed with an alkaline solution of potassium permanganate. The third washing tower scrubs the gas with a sodium bicarbonate solution, after which it goes to the second stage of the compressor and the pressure is raised to about 250 pounds. Again the heat of compression is removed with an intercooler and the gas sent through a purifying tank filled with activated carbon. This treatment is somewhat similar to the adsorption process of Backus, and the final impurities are there removed from the gas by adsorption. After the adsorbing agent becomes fouled by the impure carbon dioxide it is treated in a manner similar to that already described for the removal of the impurities. This

revivification process, however, is needed in this process only after a considerable quantity of carbon dioxide has been purified. The third stage of the compressor then increases the pressure of the gas to about 1000 pounds per square inch and sends it to a water cooled condenser.

When ordinary water is used in the scrubbers in which the carbon dioxide gas is washed, an appreciable quantity of dissolved air enters the system. This contamination may not be serious, as it only lowers the concentration of the carbon dioxide a few tenths of one per cent. For instance, in one plant the carbon dioxide was changed from 99.8 to 99.5 per cent by the air carried in with the scrubbing water. However, it is very desirable to eliminate even this slight contamination wherever it is possible. One manufacturer makes use of an ingenious and interesting method of preventing this dilution. The liquid carbon dioxide from the condenser is run into a specially designed cylinder about the size of a standard 50-pound container. A syphon tube extending nearly to the bottom of this cylinder, withdraws the liquid for the filling station, while any air, not soluble in the liquid carbon dioxide rises to the surface and mixes with the gas above the liquid. A bleeder pipe, connected to the top of the cylinder, continuously removes this gas mixture, consisting of nearly pure carbon dioxide and sends it back, where it is employed for deaerating the raw water before it is used for gas washing. The effectiveness of such a device, without doubt, lies largely in its deaerating action on the raw water. The solubility of air in liquid carbon dioxide is perhaps sufficient to prevent any very efficient separation in the liquid trap. Nevertheless such a device does improve the quality of the gas treated. This has been very definitely proved by analyses made on the gas when this apparatus was in operation and when it was not.

Carbon Dioxide from Butanol Fermentation Gases

A source of carbon dioxide of no small importance is furnished by the relatively new process of fermenting starch for the production of n-butanol, acetone and ethanol. This is the principal reaction used by the Commercial Solvents Corporation with plants located at Terre Haute, Indiana and Peoria, Illinois. In the Peoria plant the carbon dioxide is separated from the fermentation gases, part of it used for the production of methanol and the rest manufactured into the solid form and at present is being shipped in refrigerator cars to Dry Ice, Inc.

Briefly the process consists in mixing corn meal and water to make a mixture containing about 6 to 8 per cent of the meal. This mixture is then sterilized with steam at 30 pounds per square inch pressure for about 2 hours and after cooling is charged into closed fermenters of about 50,000 gallons capacity. The fermentation which requires from 48 to 72 hours is accomplished by means of a special ferment (*Clostridium acetobutylicum*), and the gaseous products of the reaction, which are produced at a maximum rate of about 8,000 to 10,000 cubic feet per hour, are

collected.[40] One hundred pounds of starch will, under favorable conditions, produce 33.3 pounds of mixed solvents, containing about 60 per cent n-butanol, 30 per cent acetone and 10 per cent ethanol, and 50 pounds of gas, consisting of hydrogen 45 per cent by volume and carbon dioxide 55 per cent by volume. Thus from 100 pounds of starch one may expect 20 pounds of butanol, 10 pounds of acetone, 3.3 pounds of ethanol, 1.767 pounds of hydrogen and 48.23 pounds of carbon dioxide.[41]

The gaseous product of this reaction is easily separated into its constituents. The crude gas is first passed through a charcoal adsorber in which the solvent vapor content, amounting to about 30 grams per 100 cubic feet, is removed by adsorption. The hydrogen is separated from the carbon dioxide by sending the gas at 250 pounds per square inch pressure through an absorption tower counter-current to a stream of water. The carbon dioxide is nearly all absorbed and the residual hydrogen, after passing through a caustic tower, is pure enough for making ammonia or methanol. On releasing the pressure over the water solution of carbon dioxide the gas separates carrying with it about 3 per cent hydrogen. A part of this impure carbon dioxide, which is not used for making synthetic methanol, is delivered to the dry ice plant where it is liquefied, passed through a series of rectifiers and the separated hydrogen returned to the methanol plant.

Storage and Transportation of Carbon Dioxide

The rate at which the carbon dioxide industry developed was controlled to a large extent by two factors; one the production of compressing apparatus for reducing the gaseous compound to a liquid and the other the development of tanks for holding the product. This latter phase of the industry is far more important than one might expect from a casual inspection. The problem is one of obtaining a steel tank or bottle sufficiently strong to withstand the high pressures under all conditions met with during transportation and use of this product. While there have been on the market at various times in the past cylinders of many sizes and shapes, these have now narrowed down to a few standard sizes, the most important of which are those of 50 and 20 pounds capacity. Others holding 5, 3 and 0.75 pounds of carbon dioxide are used mostly for medicinal purposes and as portable containers for use in automobiles etc. The manufacturer is interested mostly in the first two sizes as these are the containers into which most of his product is compressed. The method of making these steel cylinders is one of the most interesting metallurgical processes but a consideration of it here would, perhaps, be quite out of place.[42]

The condition and behavior of carbon dioxide while in a cylinder should concern everybody who has occasion to handle or use this substance. It is well known that the cylinder contains liquid and gaseous carbon dioxide but the relative proportions in which these exists, the influence of over-

[40] Killeffer, D. H., *Ind. Eng. Chem.*, **19**, 46-50 (1927). Woodruff, J. C., *Ind. Eng. Chem.*, **19**, 1147-50 (1927).

[41] Gabriel, C L., and Crawford, F. M., *Ind. Eng. Chem.*, **22**, 1163-5 (1930).

[42] Minor, J. C., *Ind. Eng. Chem.*, **4**, 88-96 (1912).

filling and the effect of impurities on the pressure are not so well known. Stewart,[43] some years ago, made a most exhaustive study of this question and developed methods and equations for designing these cylinders in order to obtain the maximum protection for those handling them while at the same time producing a cylinder of minimum weight.

The desirability of filling a cylinder to the limit of its capacity is unquestioned, on the other hand, over-filling is considered bad practice because of the decrease in the safety factor. The coefficient of expansion of liquid carbon dioxide is high and a cylinder completely filled with the liquid at temperatures considerably below the critical point has to withstand the hydrostatic pressure of the liquid when temperature increases occur. However, when part of the cylinder volume is occupied by liquid and the rest by the gas, then the pressure exerted on its walls is that of the vapor pressure of the liquid which changes in a moderate manner with a change in temperature. Increasing the temperature causes some of the liquid to evaporate thus decreasing its volume but this increase in temperature, because of the thermal expansion of the liquid, tends at the same time to increase the liquid volume. Thus we have two forces operating in opposite directions with the result that the volume of liquid increases if the thermal expansion predominates or decreases if the evaporation predominates. Which of these exerts the most influence depends upon the relative proportion of gas to liquid in the cylinder. Thus it is possible to have a cylinder only partly filled with liquid and by an increase in temperature cause it to be completely filled.

The effect of over-filling on the pressure of carbon dioxide in a cylinder is shown by the figures taken from table in Ullmann's work.[44] The pressure of carbon dioxide in atmospheres for normal and over-filled cylinders:

Temp. °C.	Normal filling 1 kg. in 1.34 l.	5% over filling 1.05 kg. in 1.34 l.	10% over filling 1.1 kg. in 1.34 l.
0	34.4 atm.	34.4 atm.	34.4 atm.
5	39.5	39.5	39.5
10	45 0	45.0	45.0
15	51.2	51.2	54.7
20	57.8	65.4	75.6
25	77.3	88.5	99.0
30	97.7	109.1	119.3
35	115.5	126.9	137.2
40	137.2	149.7	160.7
45	159.0	172.7	185.1

Above the brackets the pressure is the vapor pressure of the liquid, in the brackets the pressure is the hydrostatic pressure of the liquid and below the brackets it is the gas pressure of the substance above its critical temperature.

Figure 48 shows the behavior of liquid and gaseous carbon dioxide under different degrees of cylinder filling. This diagram plotted by Stewart

[43] Stewart, R. T., *Trans. Am. Soc. Mech. Eng.*, **30**, 1111 (1908).

[44] Ullman, F., "Enzyklopadie der technischen Chemie," **5**, page 693, Urban and Schwarzenberg, Berlin (1919).

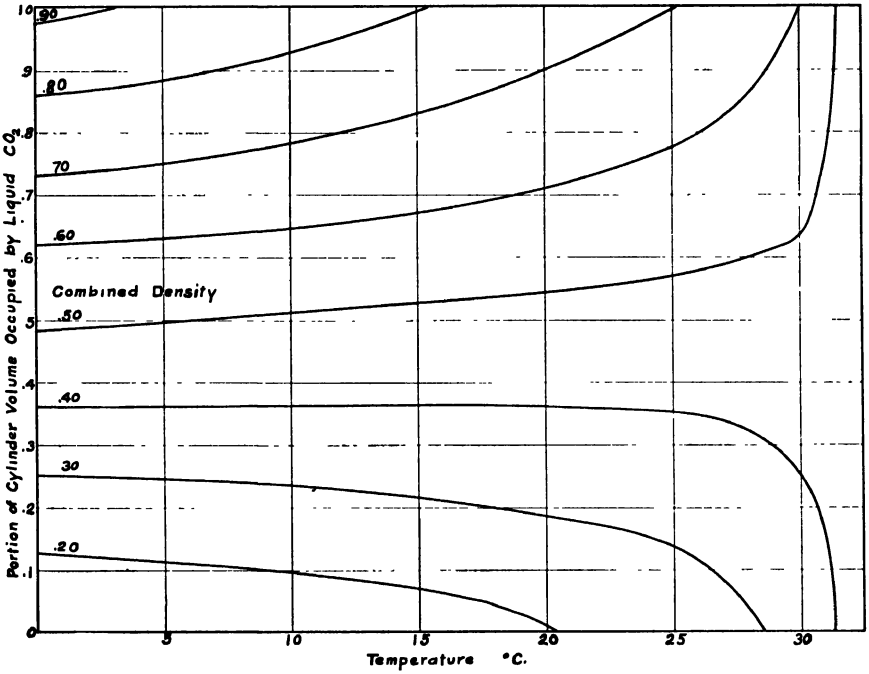


FIGURE 48. The Relative Proportion of Liquid and Gaseous Carbon Dioxide in Cylinders Under Different Degrees of Filling.

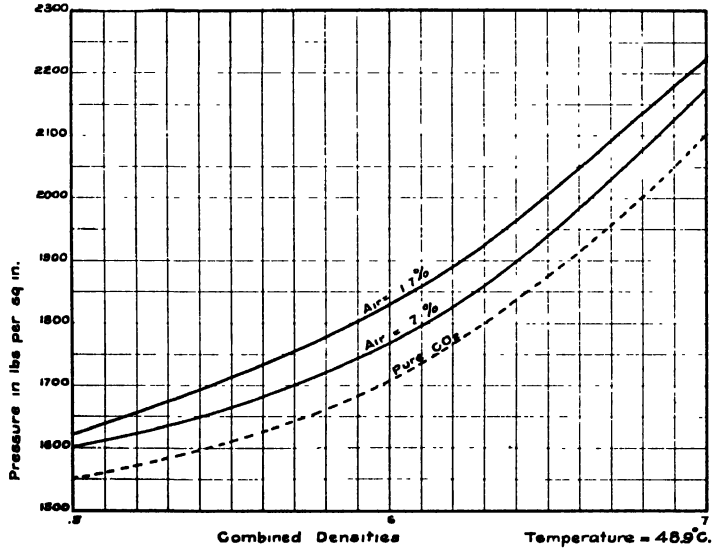


FIGURE 49. Showing how Impurities Affect the Pressure of Liquid Carbon Dioxide.

shows that if the combined densities of liquid and gas is less than the critical density (0.464) then the liquid will decrease in volume if the temperature is increased while if the combined densities is greater than the critical density then an increase in volume will result with an increase in temperature. In other words, if the cylinder is filled so that it is 50 per cent or more liquid then an increase in temperature will cause an increase in volume of liquid but with less than 50 per cent liquid in the cylinder a decrease in its volume will take place if the temperature is increased. Stewart considered that under normal conditions of use it is safe to fill a cylinder to 60 to 62 per cent of its volume with liquid. Fillings up to 75 per cent have been permitted but this high value is now considered unsafe. It might be added, that very strict regulations are made by the Bureau of Explosives for the filling and handling of all cylinders of carbon dioxide which are shipped by common carriers. Inspectors from time to time check on the weight and purity of gas found in manufacturing plants.

How gaseous impurities, especially air, affect the pressure exerted by liquid carbon dioxide is clearly shown by the curves in Figure 49. These curves, also by Stewart, are plotted so as to show the effect of various amounts of gaseous impurities and are plotted from the measured pressures found at different degrees of cylinder filling.

Chapter VII

Manufacture and Distribution of Solid Carbon Dioxide

Although carbon dioxide in the solid form has been applied to laboratory problems to some extent during the past century its industrial application for refrigeration extends back only a comparatively few years. Perhaps the first suggestion that solidified carbon dioxide might find application in commercial refrigeration is found in the patent specifications of Tichborne and Elworthy.[1] About the year 1907 Newth[2] made this most interesting comment concerning the solid carbon dioxide industry in England: " 'Carbonic acid snow,' as this substance is sometimes termed, is now an article of commerce, the compound being sent into the market in this form to avoid the cost of the carriage of the necessarily heavy steel bottles containing the liquid." In 1922 Reich[3] made some semi-commercial experimental batches of this material and proposed its use for railway refrigeration but no further commercial exploitation of the idea was then made. To Josephson and Slate must be accorded the credit of first realizing the advantages of solid carbon dioxide as a commercial refrigerant. In 1924 they proposed to sell and actually did commence to sell solid carbon dioxide in New York City for refrigerating ice cream. The ice cream industry also soon became aware of the many advantages of this refrigerant such as compactness, freedom from moisture, improved insulation efficiency and the changes in package and truck design possible, with the result that its use became gradually extended until today tremendous quantities of this solidified gas is being made and sold.

Before turning to a detailed description of the commercial manufacture of solid carbon dioxide, more popularly known as dry ice, it might be well to devote some attention to the relative importance of manufacture and distribution.

In general, it may be said that efficient distribution is a more important factor than efficient manufacture in the solid carbon dioxide industry of today. The fact that evaporation of solid carbon dioxide proceeds from the moment of its manufacture, introduces distribution problems not usually found in other commercial products. It is obvious that evaporation losses will be decreased as the point of production is brought closer to the point

[1] Tichborne, C. R. C., Brit. 13,684 (1891). Elworthy, H. S., U. S. 579,866 and Brit. 7,436 (1895).

[2] Newth, G. S., "A Text-Book of Inorganic Chemistry," page 307, Longmans, Green and Co. London (1907).

[3] Reich, G. T., *Chem. Met. Eng.*, **38**, 270 (1931).

of ultimate consumption. It is also evident that the evaporation loss depends upon the mass of material handled as a unit and that the smaller the unit the greater the percentage of material vaporized. It is also at once apparent that for each complete set of supply conditions an optimum container design can be reached in which the saving of evaporation loss gained through effective insulation and correct container construction, would be sufficient to justify the necessary investment. It is further apparent that the selection of the point in the distribution chain at which bulk is broken in each specific case is of vital importance.

The standard size for solid carbon dioxide blocks, in this country, is $10 \times 10 \times 10$ inches weighing from 52 to 55 pounds when freshly manufactured. Immediately on leaving the press or cutting saws these blocks are wrapped or bagged in Kraft paper and packed into shipping containers. For small requirements the blocks are shipped singly by express or truck in corrugated paper cartons augmented either with corrugated paper liners and pads, with fibrous insulation materials, or with multiple paper wrappings. Any one of these methods of packing is usually sufficient to reduce the evaporation loss under average summer conditions to 8 pounds or less per block during the first 24 hours. Such containers are usually discarded after one use, and hence their prime requisite is low cost. For regular shipments in larger quantities, boxes holding 2, 4, 6, 8, 12, 36, 45 and 120 standard blocks are commercially available. Some of these containers are illustrated in Figure 50.

The complication of the distribution problem and its paramount importance to the commercial success of the industry, has led to the growth of two schools of thought. One seeks to escape the heavy costs of evaporation losses and distribution by locating plants of minimum size as close to the market as possible, in some cases sacrificing the transportation saving by the added costs of producing on a small scale. The other school seeks to escape the heavy costs of small scale production by manufacturing in central plants of large daily capacity. This naturally necessitates shipment for longer distances in search of a market and in some cases sacrifices the saving in plant cost by higher evaporation and transportation costs. It is apparent that in any such situation generalities fail and local conditions determine the choice in each case.

It may be said that a rational consideration of a solid carbon dioxide manufacturing project should take the following order:

1. Thorough survey of markets and accurate mapping of tonnages expected to be sold in each, for each month of the year.
2. Calculation from (1) above of the probable evaporation losses and transportation costs. This enables a calculation of the number of extra tons which must be manufactured annually to cover losses and the probable burden of transportation costs which must be carried regardless of the merits of the source of carbon dioxide *per se*.
3. Survey of costs of power, water, labor and carbon dioxide at the proposed plant site.

4. Determination from these data whether the cost at the production point is low enough to bear the necessary burdens of evaporation and distribution costs.

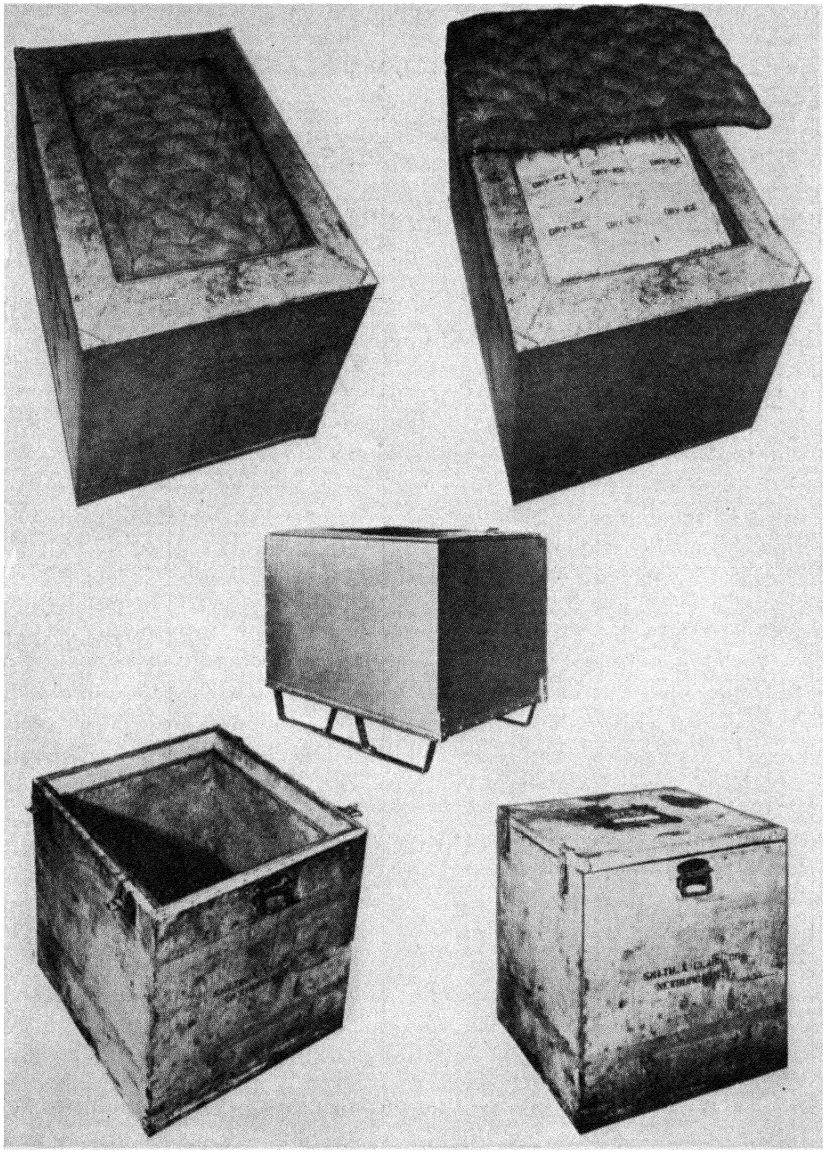


FIGURE 50. Shipping Containers for Solid Carbon Dioxide.

It is perhaps, quite evident that there is no best scheme for manufacturing solid carbon dioxide and that the selection of plant location and process

should be arrived at, in each instance, after thorough engineering study of all ascertainable facts bearing on the situation. It is well, however, to emphasize that the history of American ventures in solid carbon dioxide clearly indicates the importance of distribution and its ascendency over the chemistry and thermodynamics of solidification.

Refrigerating Cycles

Improvement in the refrigerating cycles, as applied to solid carbon dioxide production, has engaged the attention of refrigerating engineers for some time. Without doubt this interest has been stimulated largely by the fact that the refrigerating cycle affords the only opportunity in solid carbon dioxide manufacture for the specific exercise of the refrigeration art. These studies, however, have resulted in considerable advantage on the whole to the solid carbon dioxide industry.

The Simple Cycle. The starting point in the development of solid carbon dioxide manufacture is the simple cycle used for many years in the preparation of solid carbon dioxide for the laboratory. Liquid carbon dioxide, made by any of the methods already described, is expanded into a bag made of cloth or chamois leather and the heat of vaporization, taken largely from the liquid, converts part of it into "snow." The yield of "snow" obtained by this method naturally depends upon the initial temperature of the liquid and the efficiency of the heat transfer during the reaction. For all practical purposes commercial liquid carbon dioxide may be considered as a pure compound and in a saturated condition and it may be treated successfully in thermodynamical calculations for the determination of yields of solid. Therefore the amount of solid obtained by simple expansion or even a series of such expansions may be taken directly from the P-I diagram by assuming expansion at constant total heat.

A most convenient diagram prepared by Stickney[4] and given here as Figure 51, shows at a glance the yield of solid carbon dioxide obtainable from a definite weight of liquid or saturated vapor. Thus if one starts with 1 pound of saturated liquid at 70 atmospheres pressure and about 84° F. and expands it adiabatically to 1 atmosphere, a yield of 0.230 pounds of the solid will be obtained. If, however, the liquid carbon dioxide is first flashed to 20 atmospheres a yield of 51 per cent or 0.510 of liquid will be obtained at a temperature of about −2° F. Now if this liquid is again flashed to the triple point 0.297 pound of solid will be produced and on further decreasing the pressure to one atmosphere a yield of 0.230 pound of solid will remain.

It is evident from these figures that no matter what the intermediate processes may be the ultimate yield of solid will be the same in all cases. Therefore any advantages obtained by more elaborate methods such as will be described later, will be gained by returning the vapor to the compression system at pressures above atmospheric or by taking advantage of the cooling effect of the vapor from the snow machines.

[4] Stickney, A. B., *Refrigerating Eng.*, **23**, 334-42 (1932).

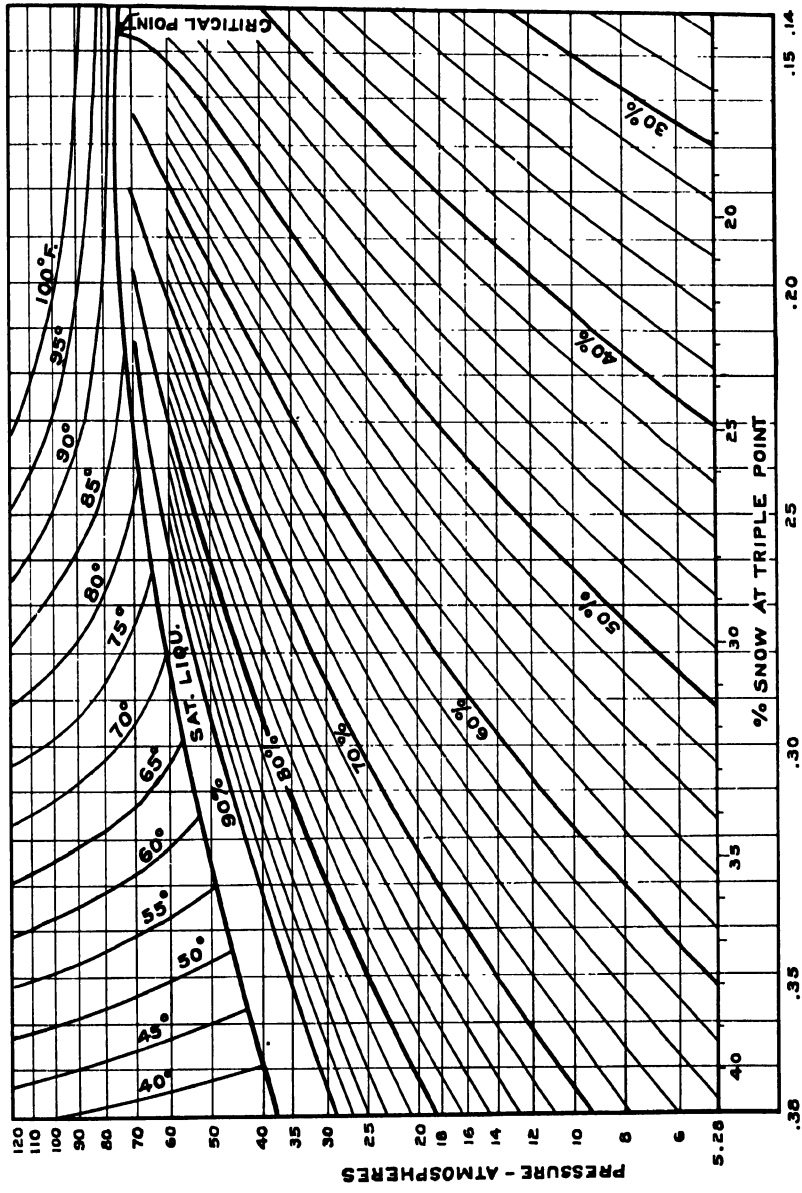


FIGURE 51. Yield of Solid Carbon Dioxide at Various Temperatures.
(According to Stickney)

Many of the small manufacturers of solid carbon dioxide today employ only the simple, inefficient and rather primitive refrigeration cycles, rather than the more complicated and refined systems described below. In most cases the savings from decreased leakage, easier regulation, greater safety, smoother operation, less investment and less expensive labor is more than adequate to offset the waste of power. In general, it may be said that only large capacity units operating with assurance of sufficient tonnage for sustained operation at heavy rates, can afford to entertain the more complicated and theoretically more efficient cycles.

Precooling Cycle.[5] The first improvement on the simple cycle was disclosed in the patents of Elworthy and Henderson,[6] who introduced a heat exchanger, by which a portion of the sensible heat of the liquid carbon dioxide leaving the condenser is transferred to the cold carbon dioxide gas leaving the solidification apparatus.

Bleeder Cycle. This cycle is so named because of the fact that some of the carbon dioxide vapor is bled from the system at some reduced pressure and returned to the compression system. If 1 pound of liquid at 70 atmospheres pressure and about 84° F. (as in the illustration given above) is run into a tank, called a flash tank, evaporator or accumulator, maintained at a pressure of 20 atmospheres, then 49 per cent of the liquid will evaporate. This vaporization will produce 0.490 pound of saturated vapor at a temperature of about −2° F. and a pressure of 20 atmospheres. This vapor can then be sent to the compressor and introduced at some intermediate stage for recompression.

This method of cooling liquid carbon dioxide by flashing from a higher to a lower pressure found its principal application and development in the mechanical refrigeration art and seems to have been first proposed by Linde and Lightfoot.[7] Windhausen[8] improved upon Linde and Lightfoot's system by the use of a dual effect compressor, equipped with two sets of suction ports through one of which high pressure vapor from the evaporator is passed. This made it possible to use one cylinder instead of two for compressing vapor received at two different suction pressures. This principle was further improved by Voorhees,[9] who arranged his auxiliary suction, receiving vapor from the primary evaporator, in the form of ports in the cylinder wall midway of the piston stroke.

Various devices have been used for automatically feeding the liquid carbon dioxide to the evaporators such as, for example, the float valve invented by Brier[10] and shown in Figure 52. These devices, however, operate more successfully on the carbon dioxide refrigerating machines

[5] The nomenclature of the refrigerating cycles given here and the general treatment of their comparative efficiency is based on the excellent paper by Stickney, *Loc. cit.*

[6] Elworthy, H. S., and Henderson, P. D., Brit. 7436 (1895).

[7] Linde, C., and Lightfoot, Brit. 1875 (1890).

[8] Windhausen, F., Brit. 9084 (1901).

[9] Voorhees, G. T., U. S. 793,864 and Brit. 4448 (1905).

[10] Brier, Henry, U. S. 1,452,999 (1918). Goosmann, J. C., and Zumbro, F. R., *Refrigerating Eng.*, **16**, 1 (1927).

than in the solid carbon dioxide manufacturing system because in the latter case the presence of water often seriously interferes with their operation. In the solid carbon dioxide industry hand regulation of the feed of carbon dioxide to the evaporators is the most usual practice.

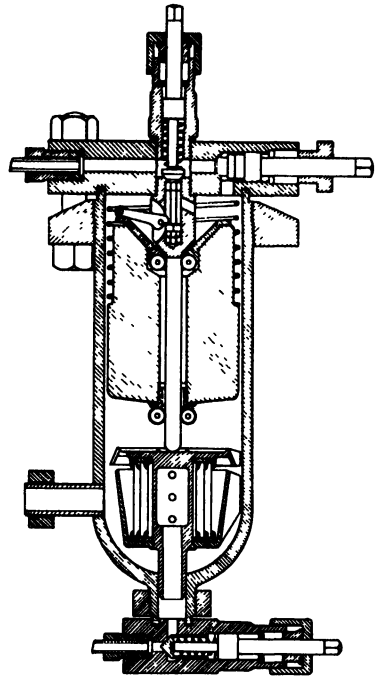


FIGURE 52.
Brier Evaporator.

Bleeder-Precooling Cycle. In both the "bleeder" and the "snow-making" cycles, liquid carbon dioxide is fed to the solidification machine under its own vapor pressure. When the liquid is fed to the snow-making machine at a temperature near its triple point considerable difficulty is encountered because of the clogging of the nozzles with solid carbon dioxide. This can be overcome by combining the bleeder and precooling cycles and delivering the liquid carbon dioxide to the expansion nozzles under a full condenser pressure. The liquid from the water cooled condensers is separated into two parts. One part of this liquid is expanded into heat exchangers, usually arranged in two units, and the resulting vapor is returned to the compressor system. The other part of the liquid carbon dioxide is sent through the inner coils of the exchangers where the temperature is lowered to any desired point.

Pressure Snow-Making Cycle. In many of the large solid carbon dioxide plants in this country, where automatic presses are used, the snow is made in the press chamber at the triple point and the pressure is reduced to atmospheric on the completed block. It is customary in plants of this kind

to have a separate compression system to handle the return vapor from the snow machine and the evaporators. This is often called the recompression system. The liquid carbon dioxide is expanded into the evapora-

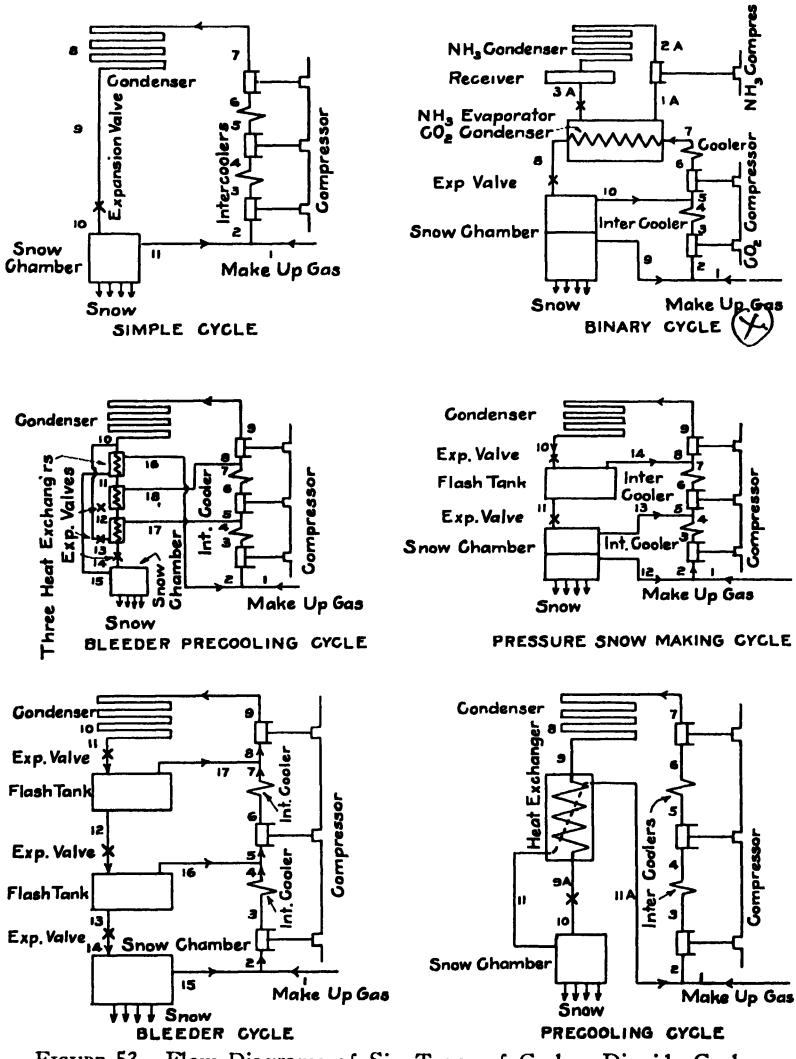


FIGURE 53. Flow Diagrams of Six Types of Carbon Dioxide Cycles.

tor where the vapor is returned to the recompressor and enters at the suction port of the high stage of a three-stage compressor, or when a four-stage machine is used, at a point where the suction pressure is approximately 250 pounds per square inch. The cooled liquid is then expanded into the snow chamber at a pressure below or at the triple point and after

the snow block is formed the return gas is sent to the suction of the low stage and the pressure above the block is reduced to atmospheric.

Binary Cycle. In this cycle the liquid carbon dioxide is cooled by means of an auxiliary refrigerating machine. When ammonia is used as the refrigerant considerable thermal advantage is gained over carbon dioxide. This is due to the fact that ammonia is a more efficient thermodynamic medium than carbon dioxide, over the range considered, because of the fact that carbon dioxide is working so near its critical temperature. The evaporator of the ammonia refrigerating machine serves as a condenser for the carbon dioxide system. It is thus possible to operate the entire system at a pressure below 25 atmospheres. Since ammonia leak detection is simpler and more reliable than carbon dioxide leak detection, the result is a system easier to operate with a minimum loss by leakage. Where a value must be assigned to the carbon dioxide, this becomes an important consideration. Indeed, where gas valuation is high, it is the controlling one.

These cycles are illustrated diagrammatically in Figure 53 which clearly distinguishes them. Other combinations are possible, of course, but these six types include all that have been used commercially to any extent, others being variations of detail following the same principles. Thus, the introduction of multiple effect compression may increase the stages of compression from three to six and the number of evaporators in the bleeder cycle from two to five but thus far such variations have had little appeal to manufacturers because of the added cost and complication.

For each of these six typical cycles, given a definite knowledge of the condenser pressure employed, and the temperature of the liquid carbon dioxide delivered by it, calculation of power consumption is readily made by the conventional formulas assuming adiabatic compression.[11] Power consumption can also be readily approximated by plotting the cycle in question on a temperature-entropy diagram and measuring the area included.

An interesting comparison of power consumption of the above described cycles was made by Stickney, based on the following assumptions:

(1) Three stage compression.
(2) Adiabatic compression in each stage.
(3) Make-up gas supplied at 1 atmosphere.
(4) Temperature of make-up gas same as temperature of liquid attainable by exchange with cooling water.
(5) Intercooling to 10° F. above the final liquid temperature.
(6) Terminal temperature difference in gas-to-liquid heat exchangers 20° F.

These comparisons are made in English units and are based on the thermal data of Plank and Kuprianoff.[12]

[11] Ford, J. M., "Compressor Theory and Practice," Constable (1923). Macintire, H. J., "Handbook of Mechanical Refrigeration," John Wiley and Sons, New York (1928).

[12] Plank, R., and Kuprianoff, J., "Die thermischen Eigenschaften der Kohlensäure im gasformigen, flüssigen und festen Zustand," Ges. f. Kältewesen, m.b.H., Berlin (1929).

Figure 54 shows the temperature-entropy diagrams for these cycles, each step in each cycle being readily understood by reference to Figure 53, the numerals corresponding throughout. Thus, in the simple cycle, the element between 2 and 3 in the flow diagram is obviously the first or low-pressure stage of compression, while the line 2-3 on the T-S diagram indi-

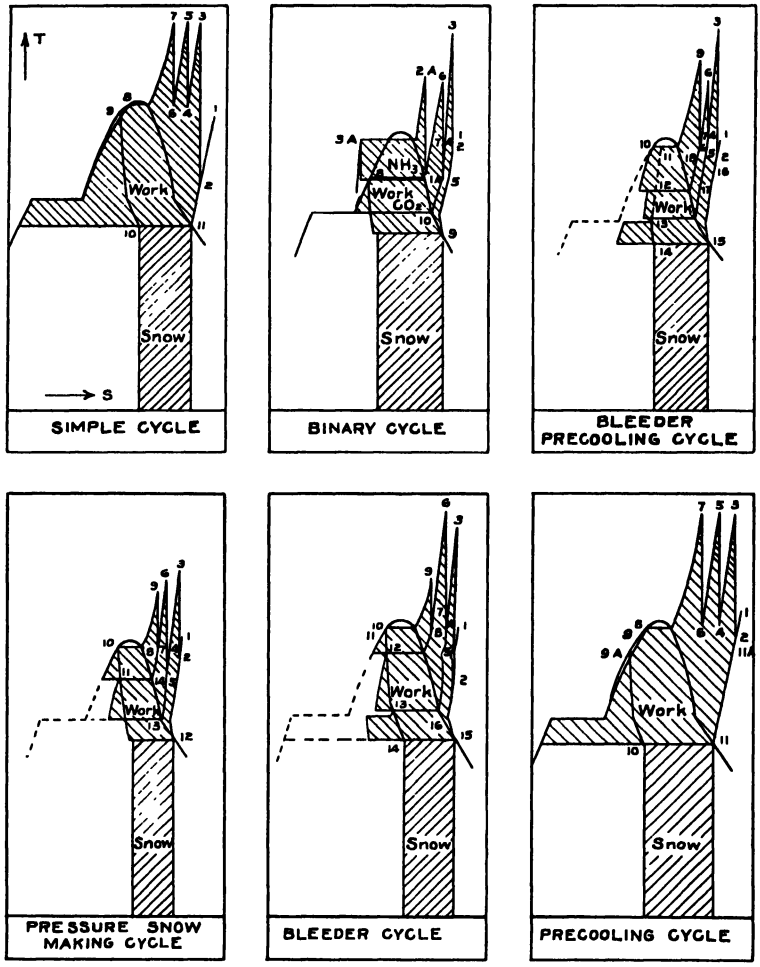


FIGURE 54. T-S Diagrams for Carbon Dioxide Cycles.

cates this operation, followed by 3-4 which on both diagrams in this instance indicates intercooling by water, 4-5 the second stage of compression, 5-6 the second intercooling, 6-7 the third compression stage, 7-8 the condensation and so on. Since all of the cycles may be clearly traced in this manner it does not seem necessary to traverse each one in detail.

It is obvious that for each of these cycles, the power consumption in manufacturing solid carbon dioxide will vary with the selection of intermediate and final pressures in the compressor system, with the temperature of the condensing water and the efficiency of the condensers.[13]

Stickney's calculations of the power consumption in each cycle are given in Figure 55. Here the power consumption in kilowatt hours per ton of solid produced is plotted against the liquid temperature. The diagram also shows the efficiency of each cycle in terms of per cent of Car-

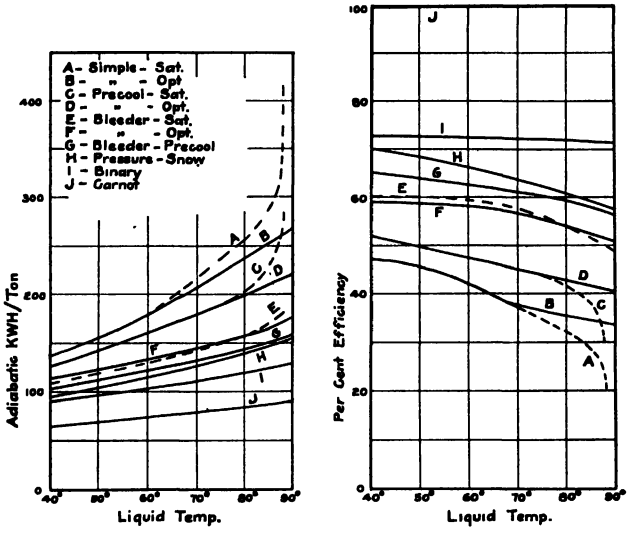


FIGURE 55. Efficiency of Carbon Dioxide Cycles.

not cycle efficiency as a function of liquid carbon dioxide temperatures. In the case of the simple, precooling and bleeder cycles two efficiency curves are given, one assuming that the head pressure on the compressor system is held to a minimum (i. e. saturation pressure) and the second assuming that higher head pressures are carried equivalent to theoretical optimum pressures as calculated by Stickney. Such higher pressures are sometimes loosely referred to as "follow-up" pressures.

PREPARATION OF CARBON DIOXIDE FOR SOLIDIFICATION

The purification of carbon dioxide for the liquid trade has already been considered and this operation in the solid industry adds no new problems. A plant manufacturing carbon dioxide for sale in cylinders can convert this liquid to the solid state without further treatment. There are, however, many plants manufacturing solid carbon dioxide as their only product and in such cases it is desirable to determine just how much purification is necessary.

[13] For a consideration of the factors affecting the selection of optimum head pressures, see Stickney, *Loc. cit.*

Removal of Permanent Gases. In all commercial plant operations known to the authors, the raw material for the solid carbon dioxide production is at least 99.5 per cent carbon dioxide, with one exception, the plant of Dry Ice Corporation in conjunction with the Commercial Solvents Corporation's operation at Peoria, Illinois. In this plant as has already been noted the carbon dioxide is furnished to the dry ice plant at approximately atmospheric pressure and containing from 4 to 5 per cent of hydrogen. A separation of the two gases is easily made by means of a fractionating column. There seems to be, however, little tendency to make use of this method for separating inert gases in other plants.

Removal of Water. In the consideration of methods of removing water from carbon dioxide in the manufacture of solid carbon dioxide, the first question to be determined is whether it is advisable to remove water at all. This is a question which can be decided only in the light of the conditions existing in particular plants and must be viewed from four general aspects:

(1) *Structure of Product.* There is considerable evidence to indicate that finely divided crystals of water ice dispersed through a block of solid carbon dioxide, modify its structure to a considerable extent. The water can be presumed to function as an intercrystalline impurity and no doubt exerts some bonding effect but more prominently it serves to interfere with the growth of the crystals of pure solid carbon dioxide so that an extremely dry product is considered more likely to become "sugary" from crystal growth. Josephson[14] claims definite advantages in the use of solid carbon dioxide refrigerant to which water has been deliberately added. Although the special properties of solid carbon dioxide containing considerable proportions of water snow have not proved desirable in commercial applications up to this time, there is no question that such a product behaves differently from dry solid carbon dioxide, and it is possible that these differences may prove desirable in some cases.

(2) *Corrosion.* Moist liquid carbon dioxide is an active corrosive agent in the presence of oxygen, but in the absence of oxygen is not appreciably corrosive. The best evidence of this fact is the use of mild carbon steel cylinders for the transportation of liquefied carbon dioxide and the fact that, due entirely to the limited supply of oxygen, corrosion is nominal in most cases even after these cylinders have been used for periods of as much as a quarter of a century as containers for moist liquid carbon dioxide. It seems probable that under these conditions corrosion continues until any free moisture present becomes saturated with ferrous bicarbonate, when corrosion ceases except to the extent that oxygen is available for its continuance.

A practical solution for the corrosion problem in solid carbon dioxide manufacture most often lies either in eliminating oxygen from the system, or in keeping any oxygen which may enter the system at the ice

[14] Josephson, W. S., U. S 1,873,131 and co-pending applications, *Refrigerating Eng.*, **19**, 25-6 (1930).

presses, separated from moisture which may enter with the supply of raw carbon dioxide. Where thorough drying is employed, however, corrosion is eliminated in all parts of the system reached only by dry product.

(3) *Stoppages.* It is obvious that, where temperatures below the freezing point of water exist in the refrigerating cycle, excessive quantities of water will cause difficulty with freeze-ups. This may cause serious interference with operation and necessitates careful drying where the more complicated low-temperature refrigerating cycles are employed. Many plants, however, adhere to the use of the simple cycle, or refrigerate their liquid carbon dioxide only to temperatures above 32° F. in cycles of the pressure snow-making type, thus escaping any necessity for the drying operation on the score of stoppage.

(4) *Odor Removal.* Where moist carbon dioxide gases such as fermentation by-product gas, are to be handled, removal of water vapor from the gaseous carbon dioxide generally results in condensing odorous material along with the water. This drying operation would naturally improve the quality of any gas containing any appreciable quantity of water-soluble odorous impurities.

The methods used for removing water from carbon dioxide in the manufacture of the solid differ in no essential way from those already discussed for drying liquid carbon dioxide. One method of interest, which perhaps is not practical in the liquid industry, is described in the patent of Jones.[15] In this process water is separated in the solid instead of the liquid phase by the evaporative cooling of liquefied carbon dioxide to temperatures below the freezing point of water and by the filtration of the resulting "sleet" through a filter bag, which retains frozen carbonated water ice and which permits relatively dry liquid carbon dioxide, still carrying a trace of dissolved moisture, to pass through it.

Structure of Solid Carbon Dioxide

Before proceeding to a discussion of the various devices for the commercial solidification of carbon dioxide it might be well to refer briefly to the structural form of the finished product. This is of importance, from a practical point of view, only to the extent that it affects the resistance of the product to mechanical injury and its behavior as a refrigerant on sublimation.

It is perhaps evident that a block of solid carbon dioxide to give satisfaction to the trade must be hard, compact and not too brittle. To attain this condition is not very difficult and is usually accomplished by giving attention to the pressing operation. It may be said that any method which places an evenly distributed charge of solid carbon dioxide in a chamber and compresses it to a desired predetermined density, will give a product which is entirely satisfactory if it is quickly utilized.

The differences existing between the various methods of manufacture, in so far as the structure of the product is concerned, become apparent

[15] Jones, C. L., U. S. 1,873,418 (1932).

only after extended storage or after shipping over considerable distances. As such conditions are found only in the United States it is not yet possible to make a comparison of the European methods and machines from this point of view.

Methods of Solid Carbon Dioxide Formation

The process of producing solid carbon dioxide merely consists of the removal of sufficient heat from the gaseous and liquid forms to reduce the product to a solid state. This may be accomplished by proceeding along any of the lines used for the solidification of other materials, if the availability of the necessary apparatus be presumed.

The general type methods may be classified as follows:

I. By transfer of heat to external refrigerating means.
   - A. By the freezing of liquefied carbon dioxide under pressure, heat being transferred from the carbon dioxide through the walls of its container to refrigerating means at temperatures below its triple point.
     1. With "follow-up" pressure on the liquid in order to fill voids caused by freezing contraction.
     2. Without "follow-up" pressure. The product in this case has a porous core.
   - B. By the freezing of carbon dioxide out of gas mixtures.
     1. By condensation on cold surfaces.
     2. By fractional condensation from gas mixtures by expansion.

II. By self-evaporative cooling, in which the solidification of a portion of the carbon dioxide is effected by the vaporization of the remainder.
   - A. Through evaporation of a bath of liquefied carbon dioxide withdrawing evolved vapor only from above.
     1. By very slow evaporation, adherent and fairly dense products may be made without subsequent pressing.
     2. In the more common practice, the boiling is conducted more rapidly to produce a porous mass of crystals which are subsequently pressed.
   - B. By expansion of liquefied carbon dioxide directly to pressures below or at its triple point to produce "snow," which is subsequently pressed or tamped to produce commercial blocks.
     1. By formation of snow in one apparatus and its removal, redistribution, and pressing in a second apparatus.
     2. In self-contained presses in which deposition and pressing take place in the same chamber.
   - C. By expansion of liquefied carbon dioxide with performance of external work for the purpose of increasing the yield of solid by more nearly isentropic expansion.
   - D. Deposition of solid progressively upon a filter or screen through which carbon dioxide gas is withdrawn partly or wholly downward through the mass already formed.

1. Pressure above the solid held below the triple point. The product in this instance is merely a dense snow more or less compacted by gas pressure and is of practical value principally in pellet machines, where the piece is so small that mechanical properties are comparatively unimportant.
2. Pressure maintained in the neighborhood of the triple point, involving production of so-called "moist" snow or "slush."
3. Pressure above the solid maintained in excess of the triple point, maintaining more or less liquid above the solid already formed, producing a mass of inspissated material in which crystal growth may readily be caused to proceed to lengths as great as 10 cm., but naturally limited in density by the necessity of sufficient downward permeability through the mass for continued escape of vapor.

It should be noted that not all of the above classifications are mutually exclusive. Thus it is theoretically possible to combine them in various ways, for example, snow may be deposited by expanding the liquid to pressures below the triple point as in II-B and then increasing the pressure and subjecting the mass of snow to downward flow of gas as in II-D-1, 2, or 3 to increase its density.

Again, it must be noted that the above type methods of solid formation bear no necessary relation to individual types of equipment. One type of press employed in American practice may be employed without physical alteration of the press construction for the performance of any desired one of the eight type methods listed under II and no doubt certain other presses among those described below would lend themselves, if desired, to operating under other solid formation technic than that recommended by the manufacturers of the devices as preferable.

For an extended theoretical discussion of certain of these general type methods, the reader is referred to the patent literature listed in the appendix of this book, and to Kuprianoff's discussion and report of small scale experiments.[16]

The description following will be confined to tracing the evolution of commercial solid-forming equipment now used in the solid carbon dioxide industry.

Development of American Press Equipment

The Snow Tank. The first machine employed by the DryIce Corporation, and indeed the machine in which all the solid carbon dioxide of commerce was manufactured for some time from the beginning of the industry, was the snow tank of Martin.[17] In this device, shown diagrammatically in Figure 56, a double sheet-metal tank is employed, with the inner tank closed at the top by a screen and filter cloth. Liquid carbon dioxide is expanded directly into the inner tank or can which is usually

[16] Kuprianoff, J., "Ueber die Herstellung von fester Kohlensäure," Gesellschaft für Kältewesen m.b.H., Berlin (1931).

[17] Martin, J. W., Jr., U. S. 1,659,431 (1928).

maintained at pressures below 10 pounds per square inch gage. The carbon dioxide snow resulting from this expansion is deposited below the screen while the evolved vapor passes through the screen, downwardly between the two shells and thence to the recompressor suction. Any one of the refrigerating cycles may be used in this process except the pressure snow-making cycle.

The device, commonly known as a "snow tank," is mounted on a scale, upon which reliance is placed for an indication of when the tank has been filled. A popular size has an interior tank capacity of 20 cubic feet and is filled to 500 pounds before opening. When the tank is filled it is disconnected, and the snow shovelled into open molds where it is tamped by

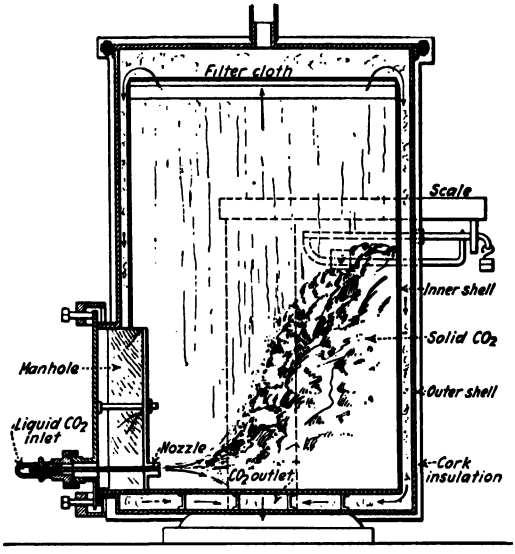


FIGURE 56.
The Snow Tank.

hand to secure approximately even distribution and pressed in open hydraulic presses at from 500 to 800 pounds per square inch pressure on the horizontal block faces. The optimum pressure is conditioned not only upon the mold wall friction and design but upon duration of pressure, density desired, moisture content and average crystal size of the solid carbon dioxide. Kuprianoff[18] has reported on laboratory experiments on snow pressing involving the relation of mold proportions to applied pressure and pressure duration. His results, however, do not consider varying particle size, nor varying moisture content, nor do they take account of variations in mold surface condition and frost-fouling which are unavoidable in practice. As a consequence, optimum pressure time relationships in pressing are usually worked out by empirical experiment in individual plants. In view of the number of variables involved, it is natural that they are by no

[18]Kuprianoff, J., *Loc. cit.*

means uniform, but there is little difficulty in adjusting the density of the product in particular plants to the demands of their specific trade. Kuprianoff's results are reproduced in Figure 57.[19]

The comparatively simple and crude snow tank method is still in use, and is much misunderstood. While it is ill-adapted for quantity production and involves from 3 per cent to over 10 per cent loss in transferring

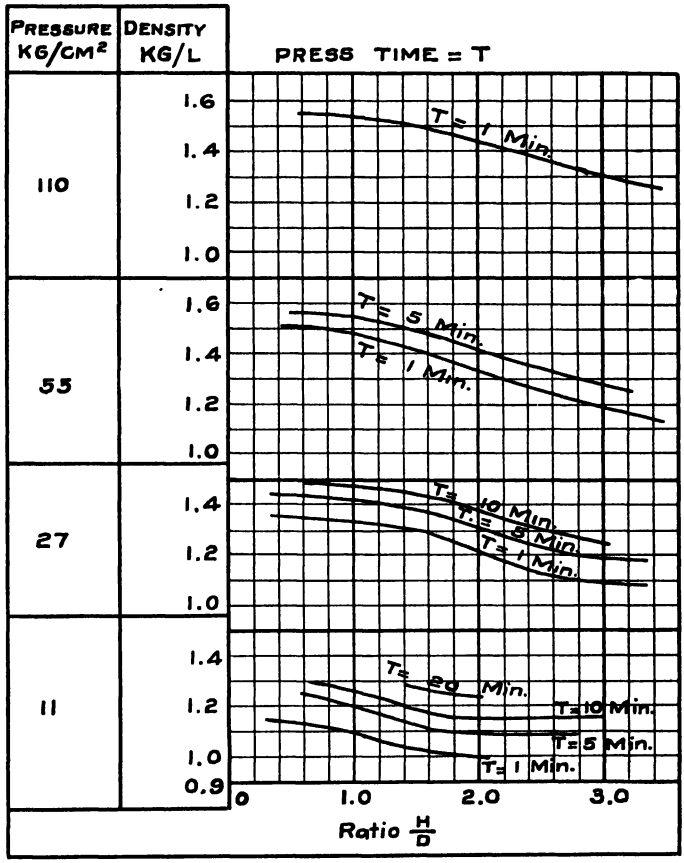


FIGURE 57. Relation Between Time, Pressure and Density of Solid Carbon Dioxide. (Data of Kuprianoff.)

the snow to open molds for pressing, it was designed for the purpose of exploring a market at minimum capital investment. For that purpose it has not yet been surpassed in the art.

Horizontal Presses. Following the snow tank, the earliest development in the direction of enclosed presses was the horizontal type press,

[19] It is to be noted that Kuprianoff's test data are for cylindrical molds pressed from one end only, while American practice is all but standardized on rectangular molds in which the design factor H/d=0.5 (H is the height and d is the diameter of the block) but owing to compressing the block from both ends instead of only one, the effective equivalent of H/d becomes 0.25.

known in the trade as the "Carbice" machine.[20] In this machine (Figure 59 A) snow is deposited by expansion of liquefied carbon dioxide directly to pressures at or below its triple point in a conical enclosed hopper stationed above the press chamber. The snow is fed to the pressing chamber by means of a screw, or more often, by a series of rabble arms mounted on a vertical shaft. Pressing is from one end only, the plunger moving horizontally. The principal weakness of this machine is the difficulty of obtaining uniform density in the product, owing to the fact that the snow dropping into the chamber is somewhat more densely packed along the bottom of the press, producing finished blocks of less density at the top.

This pressing difficulty is somewhat mitigated in the Solid Carbonic type of machine where the conical hopper and shaft are eliminated and the solid usually formed by evaporating the liquid directly in the press chamber. This produces a more uniformly distributed charge of solid prior to pressing. Employment of small hydraulic piston diameter, with

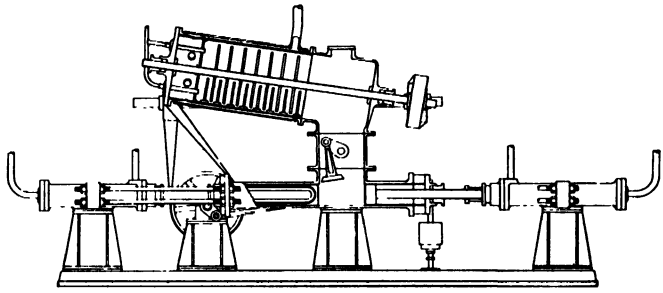


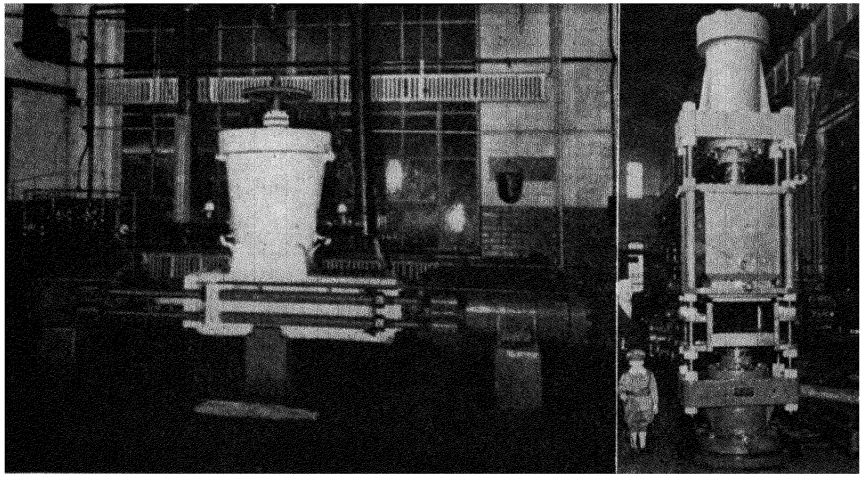
FIGURE 58. An Early Horizontal Press known as the "Carbice" Machine.

an adequate supply of high pressure (2000 lbs.) water, further gives extremely rapid pressing in this machine, the time per stroke not exceeding 3 seconds. It is believed that this rapid action violently "splashes" the solid in the chamber, thus redistributing it evenly across the transverse area and largely eliminating top to bottom density variations in the product.

Since pressing takes place entirely from one end, however, there is naturally a longitudinal density difference, the portion of the block nearest the platen being somewhat more dense than the closure end. A precise statement of the amount of this variation is impossible because of the many variables which influence it, but it is eliminated in practice by removing the pressed block, turning it end for end, reinserting it in the press chamber and pressing a second time.

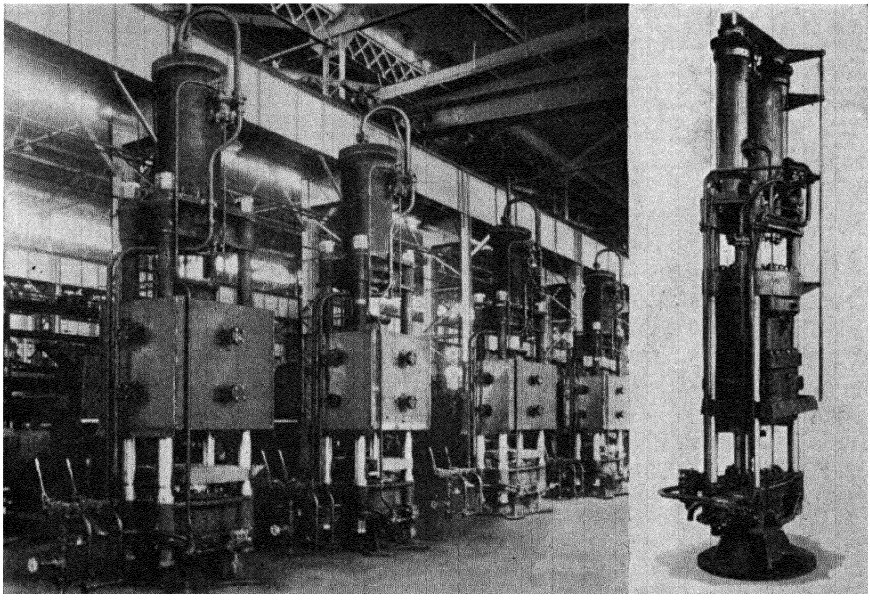
In both of the above machines the length of the block is not susceptible to precise control, since the weight of the charge in the press chamber is regulated only by time. These difficulties are eliminated in a more elaborate machine developed by the Dry Ice Corporation in 1928 and 1929,

[20] So called because developed by the Carbice Corporation, which at a later time became the Solid Carbonic Company, Ltd.



Courtesy, Baldwin-Southwark Corporation.

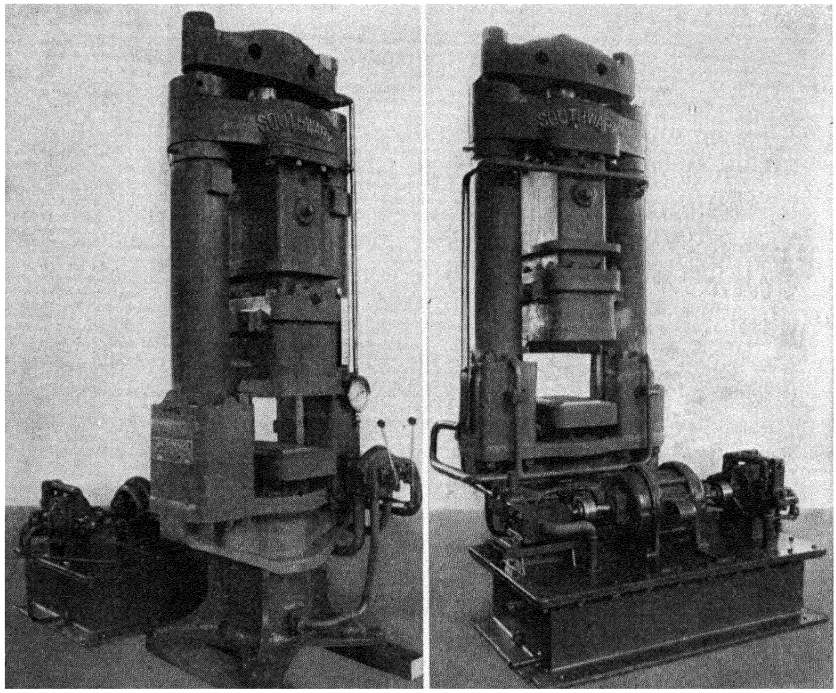
FIGURE 59. ("A" Left) An Early Horizontal Press and Snow Machine.
("B" Right) A Vertical Press of Cast Iron Construction. One of the Early Presses of the Dry Ice Corporation.



Courtesy, Baldwin-Southwark Corporation.

FIGURE 59. ("C" Left) A Battery of Double Acting Piston Type Presses. Designed to Permit Low Construction.
("D" Right) An Early Water-Operated Press of the Outside Pullback Type.

shown in Figure 58. In this device snow is deposited in an upper chamber from which it is advanced by rabble arms into a space in which a tamping device operates. The tamping operation distributes an even charge of snow in the pressing compartment of definite and adjustable size. The resulting snow is pressed from both ends and automatically discharged on a conveyor. When operated with snow of correct particle size, and at correct tamping and pressing rates, this machine turns out a product of exceptionally uniform density and size, and excellent storage and shipping characteristics. It has, however, been superseded in American practice by one variation or another of the simpler and much less expensive vertical press and well over 90 per cent of current world production originates in this type of press.



Courtesy, Baldwin-Southwark Corporation.

FIGURE 60. ("A" Left) Front View of a Modern Southwark Press with Pressing Cylinders on the Side.
("B" Right) Rear View Showing the Pipes and Oil Pump Arrangement.

Vertical Presses. Figure 59 A, B, C, D, and Figure 60, illustrate some of the steps taken in press development in this country. It will be noted that the various modifications of this type of press are similar in their general features. All involve a central press chamber of rectangular form, the lower end of which is sealed by a hydraulically supported

lower platen, except the Frick machine in which this arrangement is reversed by placing the chamber opening and its sealing platen on the top. Opposite the sealing platen, the chamber is equipped with a stuffing-box through which a piston or ram actuates the pressing platen. Details of the

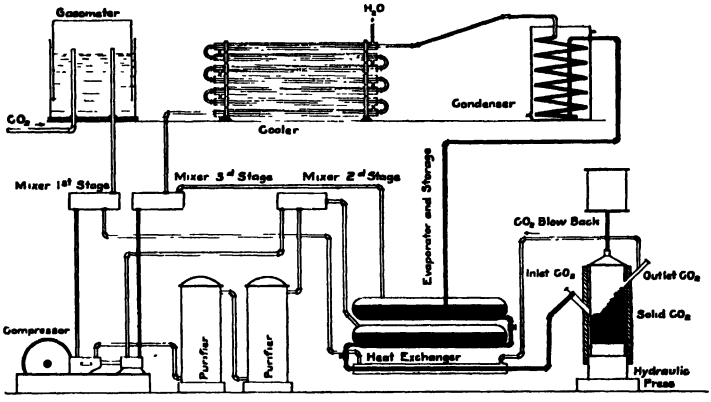


FIGURE 61. American Process for Making Solid Carbon Dioxide, Using a Frick Machine.

stuffing-box construction and insulating methods in segregating the cold and warm portions of the press are of prime importance in determining smooth operation and low maintenance costs.

EUROPEAN SOLID-FORMING APPARATUS

When it is considered that the bulk of United States production comes from a few plants of 40 to 250 tons daily capacity and that more than 95 per cent of it is manufactured in plants with a daily carbon dioxide output of 10 tons or more, and that there is not today in the entire world, outside of the United States and England, a single plant of as much as 10 tons daily solid carbon dioxide output, it is only natural that European solid forming equipment has evolved upon lines quite different from American practice.

The principal European methods developed are the Carba, Esslingen, Pegna, Agefko and Sürth procedures, each claimed by a company of corresponding name.

The Carba Process. Of the above-mentioned processes the Carba is perhaps the best known, since it has been licensed to the firm of G. A. Schütz, Germany's most widely represented exporter of carbon dioxide manufacturing machinery and since it is peculiarly suited to the conditions of severely limited demand and meager possible capital expenditures. Such conditions exist in many countries where the use of refrigeration in general and the consumption of ice cream in particular is not far advanced.

The principal advantage claimed by the Carba company is the elimination of the necessity of pressing the solid carbon dioxide. The elimination

of hydraulic pump, operating valves and hydraulic cylinders, has served to reduce the capital required for small plants and has turned out a product which serves very well indeed for supply in countries where demand is small and intermittent, and where long-distance transportation or long-time storage do not enter into consideration. In the United States, on the contrary, it has been found that these advantages are not available, since no way has been found to make a product adapted to mass production methods and suitable for storage and transportation without introducing the final step of pressing.

A diagram of the Carba apparatus is shown in Figure 62, supplemented by an enlarged view of the nozzle upon which reliance is placed for the operation of the principle. Briefly stated, this principle is the impingement of a moist snow or slush of liquid and solid carbon dioxide against a mat

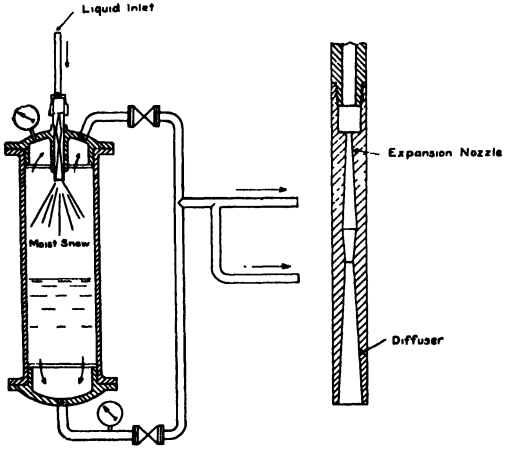


FIGURE 62.
Cross Section of the Principal Parts of the Carba Apparatus.

of solid already formed. The compacting action arises from the inertia of the impinged slush and the creating of a pressure difference through the mass of porous solid by withdrawing carbon dioxide vapor downwardly through the solid.

In operating this device, its bottom closure is secured and liquid carbon dioxide admitted through the nozzle situated in the upper portion of the apparatus and directed downward. It naturally requires a time interval before the pressure in the chamber is built up to the triple point, this time interval depending upon the rate at which vapor is being withdrawn during this initial stage. During this initial period, dry carbon dioxide snow is forced down against the screen by the vapor passing through it, building up a "filter mat" of dry snow in the bottom of the chamber. The quantity of such snow and hence the thickness of the dry snow layer may be nicely controlled by governing the time required to build up pressure to the triple point or the dry snow phase may be eliminated altogether by admitting vapor from elsewhere in the system to bring the device to the triple point pressure before liquid carbon dioxide is admitted.

Once the pressure in the device has been brought to or near the triple point, the special nozzle assumes its normal function, in which the Venturi action of the throat decreases the static head as the velocity head is built up in the narrower portions of the nozzle.

The actual flow conditions in this tube, when it functions according to the patent claims, must be very complex, since all three phases are present and the material must partake at the same time of the flow characteristics of a sludge (liquid and solid) and of a foam (liquid and gas). It is said, however, that in passing through the nozzle some solid is formed as the static pressure momentarily falls below the triple point and that this is violently thrown or impinged downward with the remaining liquid in the form of damp snow.

It will be observed that the behavior of the system is entirely dependent upon the relative magnitude of three flow rates:

1. Rate of liquid admission.
2. Rate of vapor withdrawal from the top of the apparatus.
3. Rate of vapor withdrawal from below.

If rate (2) becomes too great in relation to the other two, the pressure in the device will fall below the triple point and the apparatus will then function only as a snow tank. If rate (2) is cut to zero, withdrawing all the vapor from the bottom, the rate (3) will then be limited by the permeability and depth of the solid already formed, and unless the pressure is controlled by checking rate (1) the device will quickly rise above the triple point, after which the "damp snow" concept can no longer be operative. It will also be seen that when the rate (2) is adjusted to maintain effectively the desired pressure in the neighborhood of the triple point in the device, the nozzle dimensions being fixed, the moistness or "quality" of the snow will depend upon rate (1), which in practice is used to control this characteristic. It is said that maximum density of product is had when the percentage of liquid in the moist snow is thus regulated at 45 to 60 per cent, although the method of determining this percentage has not been stated. The precise value is not susceptible to direct determination, and must be surmised from relative values of rate (1). That is to say, if we know when all other factors are equal, that a given value of rate (1) produces dry snow and maintains a chamber pressure just below the triple point, while a second and higher value of rate (1) raises the pressure just above the triple point, and discharges only liquid into the chamber, it is presumed that a value of rate (1) midway between the two will deliver a mixture of 50 per cent liquid and 50 per cent solid. This method leaves much to be desired in rigidity, but no better one has apparently been advanced.

In operation, when a charge of loosely compacted moist snow has accumulated, as judged by timing, rate (2) is reduced, establishing a higher pressure difference across the mass in the device by the continued with-

drawal of vapor from below rate (3), and thus compressing the mass to increase its density, which may be raised as high as 1.5.

Since the amount of vapor which can escape through the bottom screen is limited to that which can pass through the pores of the block and between the solid and the wall of the container, it necessarily follows that when

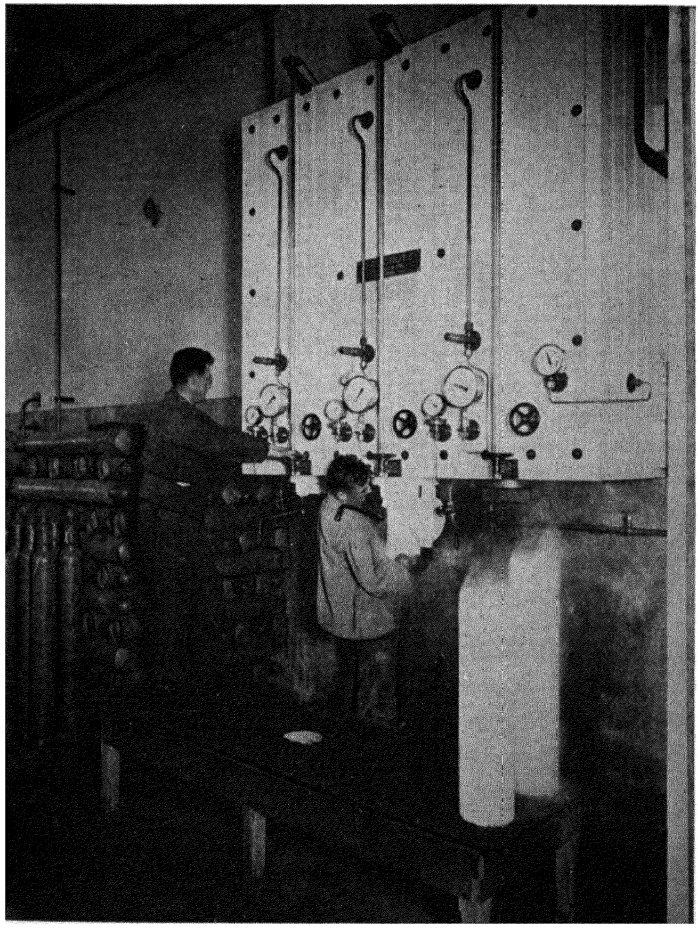


FIGURE 63. The Carba Plant at Bern, Switzerland.

a dense commercial product is made, most of the vapor must be taken out from the top, and only a minor proportion from below. This results in making the largest possible proportion of the vapor returned to the compressor system available at the highest possible pressure of solid formation (the triple point), which is very desirable from the viewpoint of power consumption.

The Carba snow-making device may be combined with any of the six type refrigerating cycles previously described, but the usual combination is with the "pressure snow-making" cycle, sometimes supplemented by a second evaporator whose position in the cycle corresponds to that of the flash tank 12-13-16 in the "bleeder" cycle in Figure 53. This additional flashing serves to somewhat simplify the operation by reducing the volume of top vapor which must be handled in the Carba device.

The precise consideration of the thermodynamic efficiency of the Carba procedure depends upon the moistness of the snow deposit, and on the ratio of vapor returned at the triple point to vapor returned to the compressor system at or near atmospheric pressure. These quantities naturally vary somewhat with the regulation of the device, but efficiencies are very close to the values given for the "pressure snow-making" cycle in the usual operation.

A typical installation of the Carba process appears in Figure 63, showing the generators of the Carba plant at Bern, Switzerland. In this case the generators are 180 mm. internal diameter and 1750 mm. long,[21] producing a "stick" of solid carbon dioxide weighing 60 kilograms, which is light enough to be removed by hand without special apparatus and cut into five cylindrical pieces of 12 kg. each. Five such generators are placed side by side and connected in parallel to liquid and gas manifolds. One generator is filled with moist snow while the other four are undergoing the final stage of solidification during which vapor is removed from the bottom while the block is compacting and being reduced from $-56°$ C. to $-78°$ C. This final solidification of the moist snow does not take place as rapidly as the first or filling stage, the filling requiring from 10 to 15 minutes, while the final solidification requires 50 to 60 minutes. Hence, for steady operation five such generators are required to give a capacity of 150 kg. per hour, or six to give a capacity of 200 kg. per hour. Although these figures tend to emphasize the special fitness of the method for small hourly production when contrasted with vertical press capacities in American practice commonly running twenty times the output per hour per machine, it must be noted in fairness to the Carba method that this time limitation is a question of depth of mass of solid rather than its transverse area. For this reason, were the process operated on the time cycle as given above, but employing the same horizontal section as the common American practice (20 in. by 20 in.), production of one half the American figure per machine would be a reasonable expectation, provided the resulting 1300 pound "ingots" could be handled at a reasonable cost. An alternative is, of course, the increase of transverse area, with a reduction of height, accompanied by more frequent opening and closing of the device, but the use of the procedure without the added step of pressing has not yet been applied to mass production successfully.

Figure 64 shows the schematic arrangement of the Carba apparatus.

[21] Salmony, A., "Über das Trockeneis," Verlag Ferdinand Enke, Stuttgart (1933).

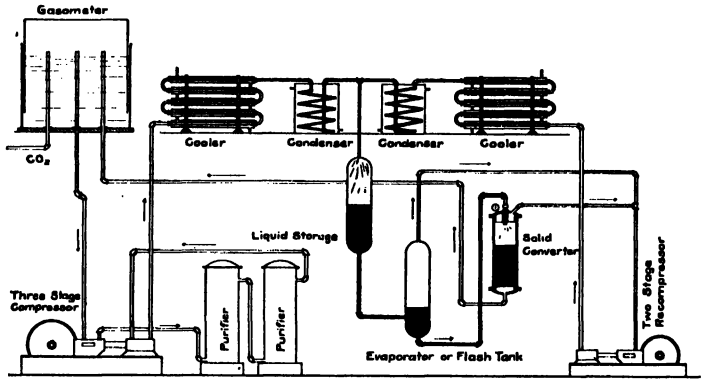


FIGURE 64. Carba Process.

The Linde-Sürth Process. This process[22] involves a procedure quite similar to the Carba in that it also removes the evolved vapor downwardly through the bottom of the solid-forming container or generator. In this generator the freezing cell, which constitutes the solid-forming chamber, is connected to the outside insulated casing by means of a diaphragm. In operation the freezing cell is completely filled with liquid carbon dioxide from a supply tank situated above, which furnishes the liquid at a pressure of about 6 atmospheres and a temperature of about $-53°$ C. A small part of the liquid in the freezing cell is permitted to expand through the porous diaphragm to the outside casing which is maintained at a pressure of about 1 atmosphere by means of the suction of the gas compressor. The temperature lowering caused by this expansion lowers the temperature of the liquid within the cell below the critical point and solid carbon dioxide is formed. This expansion and freezing process continues until all of the carbon dioxide is in the solid state after which the block of dry ice is discharged through an opening in the bottom of the cell.

The Agefko Process.[23] This likewise resembles the Carba process in claiming elimination of hydraulic presses, and in the use of a generator having a filter member at the bottom. In the Agefko procedure, the use of the Carba nozzle is foresworn, and the use of moist snow avoided by first injecting a charge of dry snow into the generator, and then admitting above it, preferably suddenly, liquid at 10 to 20 atmospheres, the higher value being apparently preferred. The relatively high pressure over the snow is said to compress it into a dense block, above which a charge of liquid is retained. Slight meltage along the walls affords an opening through which the liquid in this bath can penetrate downward, around, and into the compressed snow block, further increasing its density and welding it into a merchantable block. The bottom connection of the cham-

[22] German 581,727.
[23] German 599,367 and U. S. 1,925,041.

ber throughout the process is connected to the low pressure suction of the compressor system.

The Esslingen Apparatus. This is an interesting device, in which the manufacturer has endeavored to solve the problem of solid carbon dioxide manufacture for communities where the demand is too small to support a continuous operation, but where it is preferable to recover and purify carbon dioxide for 24 hours daily. This apparatus has as its essential feature one or more large vertical cylinders in which carbon dioxide snow is deposited as made, and where it remains hermetically sealed in storage until it is desired to press it into blocks. During this period, there is no loss of carbon dioxide except the leakage loss in the compressor system, and no cost of storage except the cost of the power required to compress the vapor evolved from the stored snow and the capital charges on the snow container, which are probably less in most cases than the capital charges on the extra capacity which would otherwise be required to make the product as required.

The pressing equipment is of conventional type, except that it is mounted horizontally in a traveling crane, which may be moved by hand to bring it under any desired snow container for work.

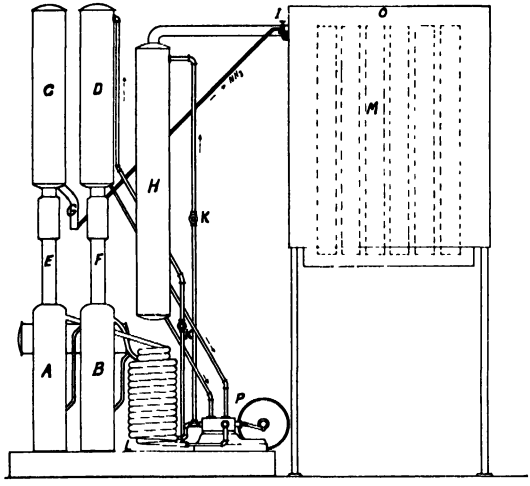
Blocks from 5 to 30 kilograms may be pressed, and machines are listed from 30 to 500 kilograms per hour capacity in steps of 50 kilograms. The size and capacity of the snow containers is varied to suit the individual plant conditions, but it is usual to provide sufficient capacity so that the carbon dioxide produced and converted to snow over 24 hours is pressed to blocks in one shift of 6 to 8 hours by a single man.

The Pegna Apparatus.[24] This is another variation of snow pressing apparatus where the snow is filled into a chamber below the triple point and is especially intended for the convenient preparation and handling of smaller blocks, pressed to high densities. It consists of an inner cylinder surrounded by an insulating jacket. The inner cylinder is closed with a cover which is held in place by the three hand clamps. The lower part of the cylinder is closed with a hydraulic piston which serves to compress the snow to a block after formation. The liquid carbon dioxide enters the cylinder against a pressure of 2 to 3 kg. per sq. cm. which is maintained in the snow chamber. The pressure inside is indicated by a gage. The carbon dioxide snow resulting from the expansion of the liquid forms a mat through which the gaseous carbon dioxide passes to a heat exchanger and thus back into the compression cycle again. A safety valve is provided to protect the apparatus from excessive pressures and a valve in the base serves quickly to reduce the pressure in case of need. A hydraulic pressure of 180 kg. per sq. cm. is employed and the manufacturer lays special stress on the high density of solid carbon dioxide blocks obtainable with it.

[24] Pegna, E. G., Pergine Valdarno bei Arezzo, Italy, D. R. P. App. 46,630 (1930).

The Maiuri Process.[25] This method of producing solid carbon dioxide is of considerable interest because of its similarity to the process ordinarily employed for the production of water ice. The carbon dioxide is frozen in cans or molds from which the heat is removed by means of an alcohol bath cooled with ammonia refrigeration. The low temperature necessary, is produced with an ammonia absorption refrigerating machine operated in such a manner that a temperature somewhere between −60° and −70° C. (−76° F. and −94° F.) is obtained.

Figure 65 shows the essential parts of the apparatus used to carry out this process. Liquid ammonia collected in receiver *G* is expanded through the regulation valve *I* into evaporation coils in the freezing tank *O*. The freezing cans *M*, submerged in an alcohol bath, transfers the heat from the



A. Boiler, high pressure
B. Boiler, medium pressure
C. Condenser
D. Absorber, medium pressure
E. Rectifier for "A"
F. Rectifier for "B"
G. NH_3 Collector
H. Absorber Vacuum
I. NH_3 Regulator
K. Water Regulator
L. Heat Exchangers
M. Freezing Molds for CO_2
O. Freezing Tank
P. Water Pump

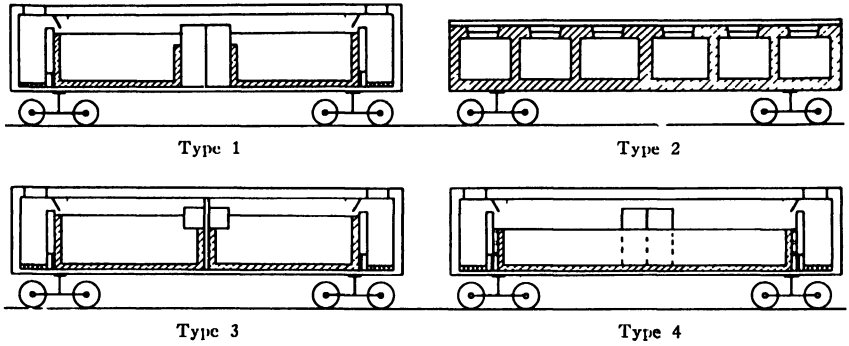
FIGURE 65. Maiuri Process for Solid Carbon Dioxide Manufacture.

carbon dioxide to the ammonia evaporating coils. The temperature of the alcohol bath, in this apparatus, can be held between −55° and −62° C. The ammonia vapor from the expansion coils passes through a heat exchanger (not shown in the diagram) where it removes heat from the gaseous carbon dioxide passing to the freezing cans and thereby becomes superheated. The vacuum absorber *II* then absorbs the ammonia vapor in an ammonia water solution of about 4 per cent concentration and builds it up to about 13 per cent ammonia at the bottom of the absorber. The ammonia vapor pressure in the evaporating coils can be lowered to between 2 and 3 lbs. per sq. in. absolute, with a properly constructed absorber. The strong ammonia solution is then pumped through a heat exchanger to the first stage boiler *B* where the ammonia is driven off at a temperature not exceeding 100° C. The vapor of ammonia from the boiler *B* is

[25] Maiuri, G., *Cold Storage and Produce Review*, Sept. 21 (1933).

passed through the rectifier *F* to the absorber *D*. In this absorber the ammonia is taken up in a weak ammoniacal liquor from the second stage high pressure boiler *A* and is built up to something like 34 per cent. In the second stage boiler *A* the temperature of the concentrated ammonia solution is increased to nearly 130° C. and the anhydrous ammonia thus obtained is collected in the condenser C from which it is sent to the freezing chamber again.

The gaseous carbon dioxide is furnished to the freezing cans under a pressure somewhat above the triple pressure, usually from 80 to 100 lbs. per sq. in. A heat exchanger cooled with the ammonia vapor from the expansion coils lowers the temperature of the incoming gas to approximately −30° C. On entering the cans the gaseous carbon dioxide quickly condenses to a liquid and the drops of liquid fall to the bottom of the can and freezes to a hard compact mass. Freezing is allowed to continue until



Types 1, 3, and 4 Standard Refrigerating Cars with Extra Insulation Crosshatched.

FIGURE 66. Typical Arrangements of Dry Ice Transportation Cars.

the cans are about half full, then the pressure is gradually lowered to atmospheric conditions and the blocks of solid carbon dioxide are removed from the bottom of the molds.

The time necessary for the freezing to take place will vary, of course, with the design of the apparatus. According to the inventor a small plant produced 12 blocks of 11 pounds each in a period of 6 hours. The ratio of weight of steam used in the generators to weight of solid carbon dioxide produced is said to be as low as 1.7 to 1. The density of the solid obtained by this process is about 1.48 or 92.35 lbs. per cu. ft.

TRANSPORTATION OF SOLID CARBON DIOXIDE

The problem of selecting suitable size and construction for transportation containers has already been briefly mentioned and some typical containers illustrated (Fig. 49). However, the movement of large quantities of solid carbon dioxide from one place to another is becoming quite general in America and this phase of the problem will be considered more in detail.

Car Transportation. Railroad cars of the refrigerator type are being used for the large scale transportation of solid carbon dioxide in ever increasing numbers. In some cases, these are ordinary standard refrigerator cars remodeled to fit the conditions encountered in moving this type of refrigerant, while in others special cars have been constructed for this purpose. The arrangement of four types of these cars are shown in Figure 66.

In arranging cars for transportation of solid carbon dioxide two factors must be considered; first the proper insulation of the car body and second the proper sealing to prevent gas loss. The former simply follows general insulation practice, the insulating material being cork, some commercial refrigerator car insulant or occasionally Balsa wood. Insulation thickness ranges from 4 inches to 10 inches depending upon the type of service to which the car is to be put. Sealing to prevent gas leakage may be accomplished by several methods but two of the most effective are the employ-

FIGURE 67. Latest Type Ten-wheel Model AUTOCAR Truck for Long Distance Transportation of Product. Dry Zero and Cork Insulation.

ment of an all steel car shell, and the insertion inside the shell, but outside the special heat-insulating material, of a metal sheath of roofers' tin or sheet copper, with all seams locked and soldered. In the peak summer season standard refrigerator cars are often used for peak load requirements of short duration. In general, the "settled" loaded car loss averages 0.75 per cent per day (loading and unloading excepted) for type 3, while type 1 averages approximately 1 per cent and type 4 averages 1.25 per cent.

Truck Transportation. Truck bodies designed for the transportation of solid carbon dioxide are insulated and sealed in much the same manner as railroad cars. Figure 67 shows a photograph of a new truck made especially for the transportation of this refrigerant.

Transportation Losses. A mathematically rigid treatment of the transit evaporation loss problem cannot be undertaken here with any hope

of achieving practical significance because of the variation introduced in practice by evaporative cooling. There are, however, certain factors bearing on the problem which perhaps are worth discussing in some detail.

Figure 68 represents a plot of solid carbon dioxide temperatures versus the volume percentage of carbon dioxide in the air in equilibrium with it. This will be recognized at once as merely a form of vapor pressure curve, but it is immediately noted that reduction of the surrounding atmosphere (i. e. the atmosphere at the evaporating face), for example, to 65

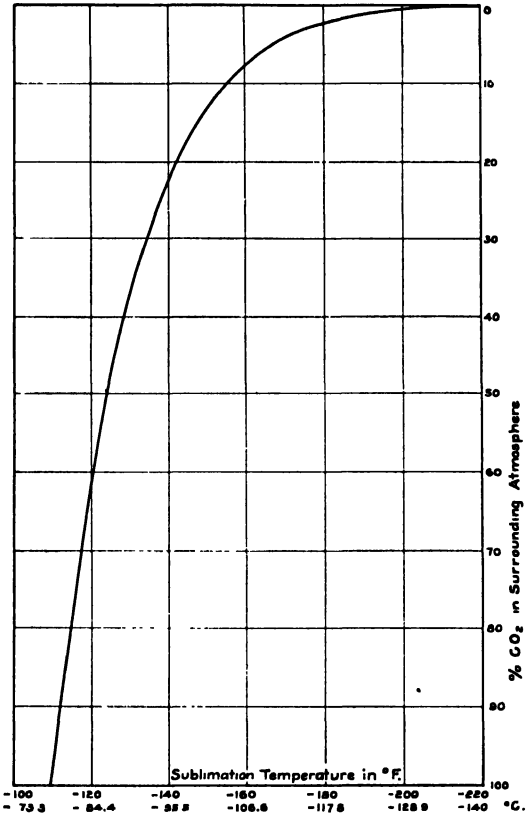


FIGURE 68.

Solid Carbon Dioxide Sublimation Temperature versus Carbon Dioxide Content of Surrounding Atmosphere.

(According to Plank and Kuprianoff)

per cent, reduces the temperature of the carbon dioxide more than 5° C. by evaporative cooling. Figure 69 expresses the additional refrigerating effect of the remaining "supercooled" solid carbon dioxide in terms of per cent excess refrigeration capacity referred to the total cooling effect per pound of solid at −78.52° C. changing to a vapor at 0° C. and atmospheric pressure, due to sensible heat removed from the remaining solid.

When the block of solid carbon dioxide, made by whatever process, is first exposed to the air, whether for cutting, for wrapping, or merely for transfer from one vessel to another, evaporative cooling commences, and

the block is chilled below its normal sublimation temperature in pure carbon dioxide. The result is temporarily increased sublimation rate, with increased refrigeration available per pound of remaining refrigerant. Such decrease in temperature has the effect of discounting subsequent losses, for when the supercooled block is then placed in a car, truck, or shipping box,

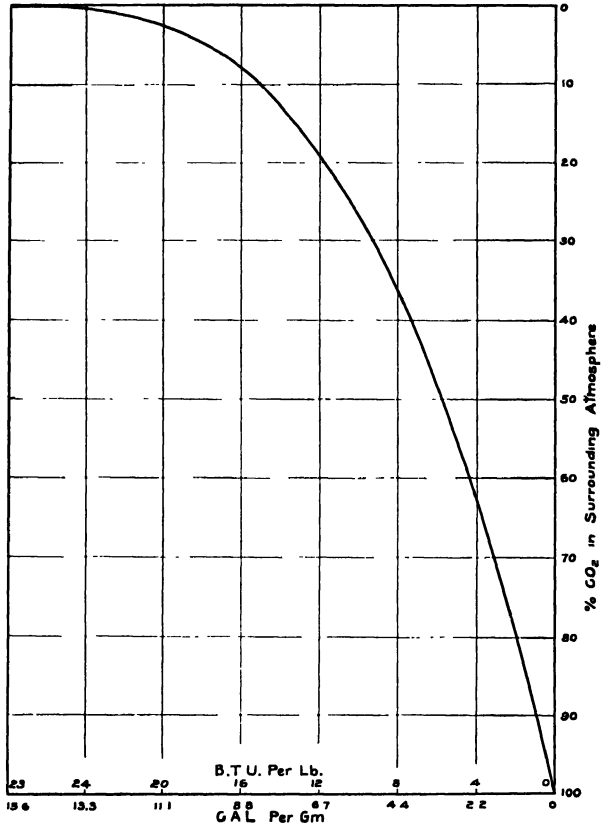


FIGURE 69. Solid Carbon Dioxide Excess Refrigeration Capacity Over Solid at −78.52° C. Versus Carbon Dioxide Content of Surrounding Atmosphere.

(According to Maass and Barnes and Plank and Kuprianoff.)

it finds itself protected from the air and surrounded by an atmosphere richer in carbon dioxide. If the sealing is good enough to maintain the carbon dioxide around the block at 100 per cent, the block will warm up again to −78.52° C. by absorption of heat before the evaporation loss in weight can approach a normal value calculated from the heat leakage of the box or other structure and the normal refrigerating effect of solid carbon dioxide.

This discounting of loss will obviously vary with the time and nature of the air contacts and the purity of the carbon dioxide atmosphere maintained in the container, and in practice it robs many loss test figures determined under trade conditions of much of their significance, since it is not a constant factor and all the variables are rarely, if ever, known in commercial tests. In the trade, however, the phenomenon works consistently for the customer and against the seller, since the seller must handle, and sometimes saw and wrap his product before weighing it for sale. During this period is it supercooling, and when sale is made by weight, the purchaser then receives a product of slightly more than normal refrigerating effect per pound. If he then places the block in a tight storage box, his loss will be somewhat reduced because discounted by the excessive loss previously suffered. In practice this effect will amount to any value from none at all up to 4 per cent by weight of the solid made, depending on conditions of exposure.

Season Storage of Solid Carbon Dioxide

The problem involved in season storage of solid carbon dioxide can be best understood by considering that it has the general economic aspects of seasonal water ice storage, and the following additional features not encountered in water ice storage:[26]

Economic Problems. (a) Although water ice plant capacity may be installed for as low as $1000 per daily ton of output, solid carbon dioxide plant capacity (for gas and solid) costs from $2000 to $15,000 per daily ton, depending upon the process used and its location. The capital charges on the idle peak load capacity are hence greater, and the incentive to use a moderate amount of storage capacity and limit the plant capacity is accordingly greater.

(b) In specially favorable instances it is possible to place in storage solid carbon dioxide that has been manufactured from waste by-product gases, where no value is assigned to the gas employed because it would otherwise have no market. In this case the evaporation loss would be reduced to the cost of labor, power, water and supplies used in the manufacture of the evaporated material. In addition there should be added also the capital charges on a portion of the storage structure loaded with material not marketed, and the expense incurred for purification of unmarketable product. Each of these values is, of course, peculiar to each specific plant location.

(c) By all odds, the most difficult problem is involved in the comparative newness of the industry, and the great difficulty in forecasting markets accurately. Competitive plant capacity is likewise an important factor, and in seasons where the American enthusiasm for building new plants outruns demand by too wide a margin, all incentive to store is naturally removed.

[26] For a typical analysis indicating the economic factors bearing on season storage of manufactured water ice, see Macintire, "Handbook of Mechanical Refrigeration," page 427.

(d) In cases where by-product gas is used, and the seasonal demand fluctuation for the main product does not correspond to the seasonal demand curve for the by-product, season storage affords a logical means of bringing the variations into harmony.

(e) The amount of season storage employed will determine to a considerable extent the economic significance of such storage. Thus, if only sufficient material is stored to care for peak load demands of the highest week's summer sales, it is apparent that the manufacturer preferring to construct additional plant capacity would have to assess the carrying charges on his additional plant for fifty-two weeks against one week's production. When it is considered that the capital cost of well-constructed season storage per ton of material available for sale has already been reduced to less than $30 in storages of 3000 tons net capacity, it is apparent that economic justification is merely a question of moderation in the use of storage and its limitation to a relatively small output in comparison to plant capacity.

Trade Problems. (a) Since no economical, dependable mechanical refrigeration cycle is available for continuously maintaining temperatures below −78° C. in a large storage space, storage thus far constructed has relied upon the evaporation of a part of the stored material to preserve the remainder. This results in the rounding of blocks stored near the walls of the storage space. Such rounded blocks are entirely suitable for industrial applications, car refrigeration, and most types of motor truck refrigeration, but are not salable to the portion of the ice cream trade desiring to cut dry ice into cakes. Since railway and industrial outlets still take only a small tonnage in proportion to ice cream manufacturers and are not yet in a position to absorb sufficient off-size material, the construction of season storage from this point of view has been premature.

(b) Changes in crystal structure taking place on long-time storage are not yet well understood. Indeed, the only adequate method yet known of determining whether or not a given product will stand long time storage is to store it and examine it afterward. It can be stated with assurance that the differences among the various patented manufacturing methods have less to do with such changes in storage than the character, amount and dispersion of traces of impurities. At all events, some of the material that has been stored has emerged in a very sugary condition, earning a bad reputation in the trade for itself, while other material has been held for periods as great as six months and sold to the most exacting trade without being distinguished from fresh product. Much work on the effect of traces of impurities on structure changes in storage remains to be done.

Engineering Problems. (a) It is imperative that the gaseous atmosphere in season solid carbon dioxide storage be maintained as nearly stagnant and as nearly of constant carbon dioxide content as possible, since changes of composition induce temperature variations due to evaporative

cooling, as has been discussed above. Such temperature variations cause evaporation of some parts of the charge and condensation of the carbon dioxide on material that has been supercooled by evaporation in a gas of lower purity. Because of this phenomenon, it is not uncommon to remove blocks from storage weighing as much as two pounds or 4 per cent heavier than when loaded into storage six months earlier. Such exchanges naturally render weight changes of individual blocks quite devoid of any value in indicating the merit of the storage as a whole.

(b) Owing to the low temperature maintained, it would be very costly indeed to maintain a large storage space refrigerated throughout even when only a small proportion of its volume is occupied with stored material. This problem has been met by the use of a floating insulated roof, which is elevated once a year during the loading process, and lowered during unloading. The space above the floating roof is not refrigerated, and is in fact quite warm as a rule during the summer season, uncomfortably so at times.

(c) In time the heat abstracted from surroundings will, of course, freeze the bearing soil under the structure. This must be provided for by mounting the storage on a suitably reinforced mat, preferably underfilled with gravel or porous filling, and provided with adequate drainage.

(d) Opening the storage space for loading or unloading, even though complicated air-excluding devices are used, at best involves some loss of carbon dioxide and entrance of heat. This is minimized by mounting the floating roof (familiarly known as a "pancake") so that it may be rotated, and providing a loading slot through which the dry ice is handled. The exposure is thus limited to a narrow radial portion of the stored material where loading or unloading is actually in progress.

(e) The importance of high carbon dioxide purity around the solid and minimum leakage through the structure, already pointed out, virtually necessitates a gas-tight shell, which has been cared for by employing only steel-shelled structures in which all joints have been electric welded and carefully tested for leakage.

(f) While many insulating materials might be applicable, it is desired to hold the movement of gases in the pores of the insulation to the lowest possible value, and vegetable cork is hence preferred, supplemented by aluminum foil covering to minimize possible convection at imperfect joints.

Present Storage Structures. Up to the present time only two season storage structures have been erected. The first, illustrated in Figure 70, was built by the DryIce Corporation at its Elizabeth, New Jersey, plant. It is 47 feet internal diameter by 50 feet high, insulated with 12 inches of vegetable cork, and has a capacity of 3000 short tons of solid carbon dioxide, loaded in standard wrapped $10 \times 10 \times 10$ in. cubes.

The second, illustrated in Figure 71, was erected in 1931 at the Peoria, Ill., plant of DryIce Corporation of America, and is 40 feet in diameter,

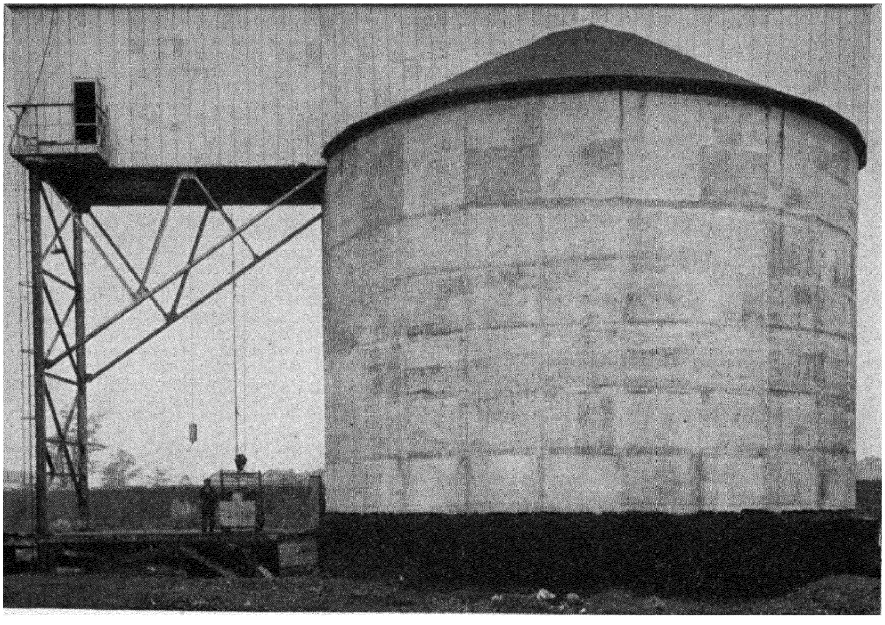


FIGURE 70a. Storage Structure for Solid Carbon Dioxide at Elizabeth, N. J.

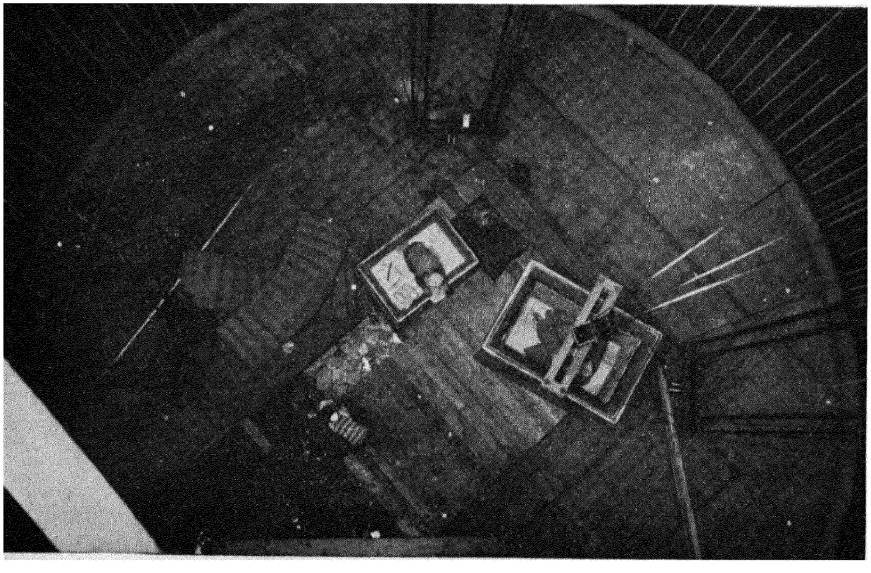


FIGURE 70b. "Pancake" Floating Roof of Storage Structure at Elizabeth, N. J.

75 feet high, with a capacity of 4000 short tons. At the present writing this structure has been filled only once.

Evaporation losses in these structures on a daily basis are almost without meaning, largely because of the supercooling factor. The season losses on complete operation usually extending from early February to late August vary from 20 to 40 per cent, according to the loading and unloading times and rates. In all probability, figures below 20 per cent can be readily reached if trade conditions ever permit rapid and continuous loading late in the spring season, and complete unloading not later than July.

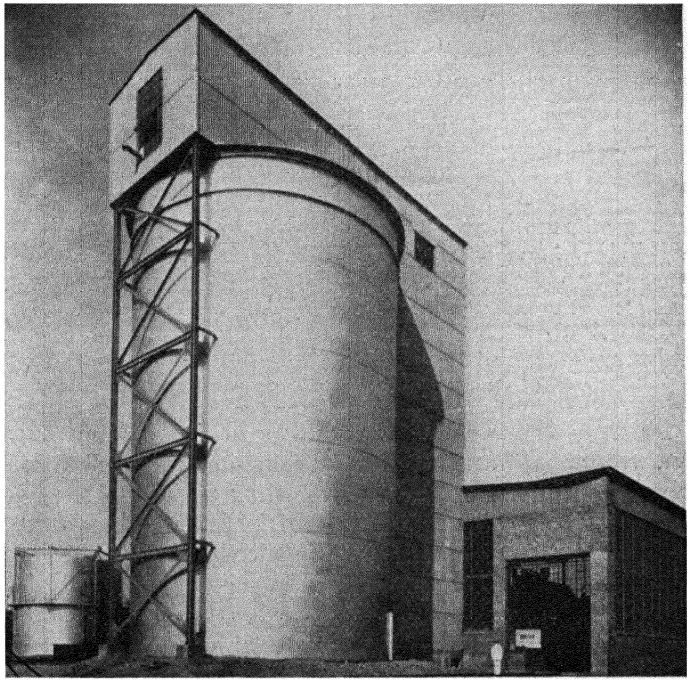


FIGURE 71. Storage Structure for Solid Carbon Dioxide at Peoria, Ill.

It is as yet entirely too early in the development of the solid carbon dioxide industry to evaluate the commercial possibilities of season storage accurately, or to venture any prediction as to trends in design. The storages described served to re-establish the confidence of the trade in the adequacy of peak season supply at a time when there was a shortage of plant capacity, but now seems quite likely to lie idle for so long as plant capacity continues in its present condition of unneeded excess. Perhaps the future trend will be determined by the seasonal characteristics of the markets developed for solid carbon dioxide as much as by any other factor.

Chapter VIII

Uses of Commercial Carbon Dioxide

In discussing the uses to which carbon dioxide in any of its three phases, may be put, attention here will be directed principally to those uses which are or have been of some commercial importance. As with other industrial material, the commercial uses may be divided into three classes:

1. Industrially important uses which absorb the bulk of the material produced, and which are economically feasible under the conditions of cost and volume of market existing.
2. Proposed and tentative applications as well as minor uses, which because of cost, time required for development, small size of the consuming industry, or other limiting factors, are of small importance at any given time, but may increase in volume when factors of price and service available permit expansion.
3. Intermittent or obsolete uses in which the trend of the consuming industry has been away from the use of the product or towards a reduction of its consumption.

It should be understood at the outset that the uses of commercial carbon dioxide clearly falling in the first class are limited to two; the carbonation of beverages, which is largely accomplished by the use of the liquid form transported in steel cylinders and the refrigeration of ice cream, which naturally requires the solid form, more familiarly known as dry ice.

Smaller markets have been developed in such promising fields as meat, fish, and frozen food refrigeration, charging compression refrigeration systems, mining coal, fire extinguishing, special low temperature operations and the packing of food products in inert atmospheres as well as larger volume applications in which the carbon dioxide is essentially an "intermediate" such as urea manufacture, but the existence of the carbon dioxide industry of today rests squarely upon the two applications first mentioned.

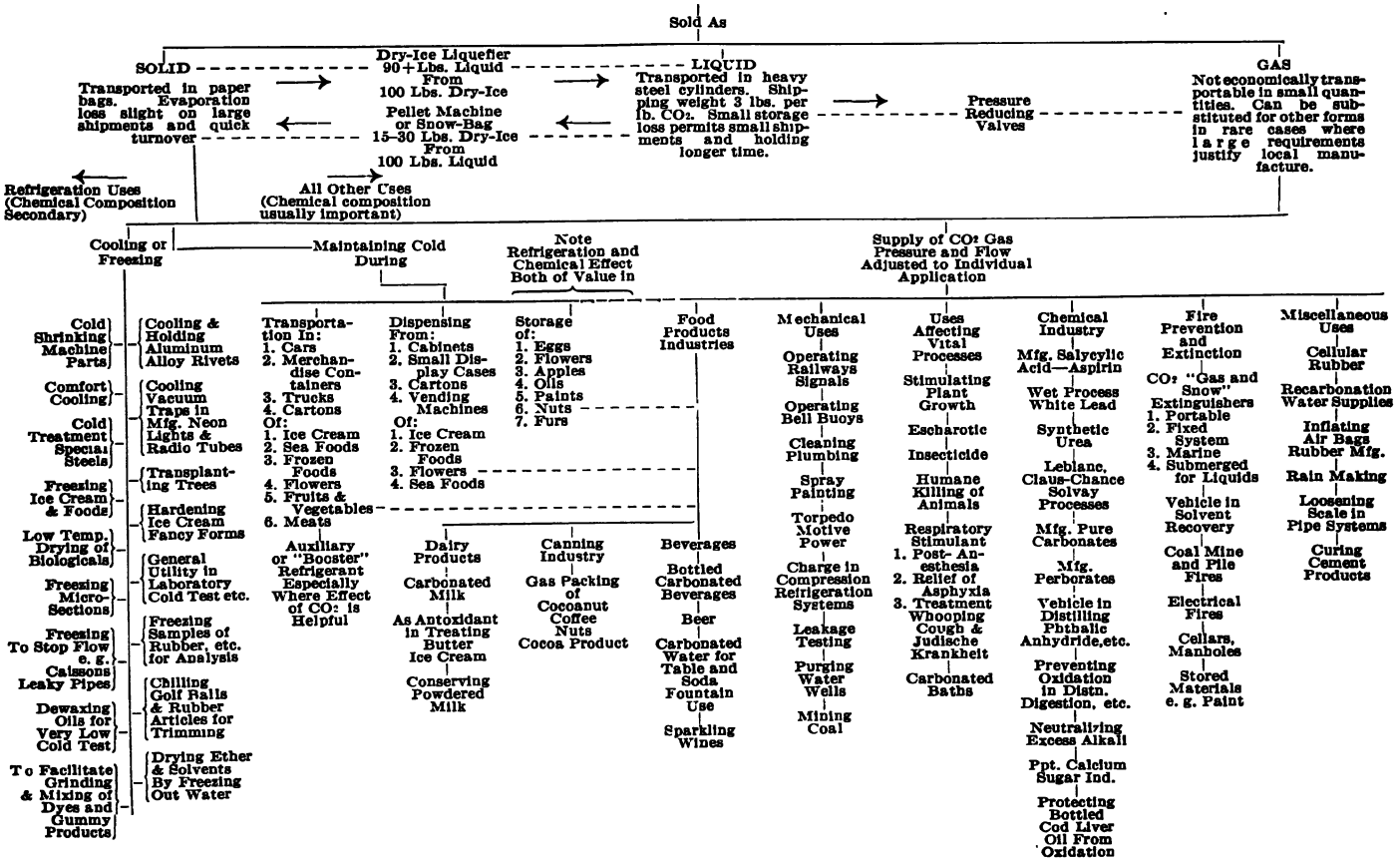
In discussing the uses of carbon dioxide an attempt will be made to list the applications, as far as possible, under the general headings of solid, liquid and gas. To assist in visualizing the outlets for this product more clearly, a chart of uses[1] has been prepared and is given here as Table 69.

Uses of Solid Carbon Dioxide

Refrigeration. By far the most important industrial application of carbon dioxide is the direct use of the solidified product as a refrigerant.

[1] Jones, C. L., *Chem. Met. Eng.*, 40, 76-9 (1933).

TABLE 69.—*Uses for Carbon Dioxide.*



The first suggestion of the possibility of commercial application of solid carbon dioxide appears to have been contained in the patent of Elworthy[2] who says, "By the improved means of preparing and transporting solidified carbon dioxide this material will be rendered available for all or nearly all purposes for which ice is now used, as well as for any other purposes for which ice is unsuitable. By placing a small quantity of solidified gas in a small box, preferably made of silver or aluminum, and which box may also contain ether or alcohol, and immersing the box in any liquid or solution the latter may be cooled without contact with the gas, and in this way the delicate bouquet of wines and other liquors is preserved."

Commercial application, however, did not immediately follow, and as a matter of fact, has not yet followed the lines of Elworthy's suggestion. The availability of water ice at low cost made it essential that solid carbon dioxide find collateral advantages to justify its higher cost.

These were first found in the ice cream industry, where compactness, freedom from drip, ability to produce low enough temperatures, and lack of residue, combine to render solid carbon dioxide peculiarly suitable for the refrigeration of ice cream.

Package Refrigeration. Solid carbon dioxide must be credited as the first means available to the ice cream manufacturer of refrigerating ice cream in throw-away paper containers. These are classified as "carry-home," "home-delivery" and "shipping" containers. "Carry-home" containers are those refrigerated by the dispenser, and sold with sufficient dry ice to preserve the cream as a rule from four to eight hours. "Carry-home" package trade is naturally in small units, the one-quart size being most widely used.

"Home-delivery" packages refer to those used for party and catering service, where the ice cream may be either in brick form or in molded fancy forms, and is provided with sufficient dry ice to hold until the expected time of consumption. Because of the character of service, the usual size package is somewhat larger than in "carry-home" trade, ranging from two quarts to two gallons. For express and truck shipments to dispensers at some distance from the ice cream plant, cartons carrying two and one-half and five gallons of bulk ice cream in tin or paper cans are usual practice in the United States.

The essential features of all such packages are:

1. Sufficient dry ice for the desired time of transit.
2. Insulation around the package as a whole.
3. Insulation between the dry ice and the ice cream.
4. Proper distribution of the refrigerating effect.

It is obvious that when a small piece of solid carbon dioxide is brought into direct contact with ice cream, the cream in contact with the solid carbon dioxide will be over-refrigerated, while the remoter portions will

[2] Elworthy, H. S., U. S. 579,866 (1895).

be relatively warm. This tendency is obviously overcome by the use of sufficient insulation on the package as a whole, together with a proper degree of insulation between the solid carbon dioxide and the ice cream.

In practice, the packages used are economic compromises in which somewhat less than the ideal amount of insulation is used in order to reduce package cost, and skill in packing. The education of the consumer to temper the ice cream properly after delivery, is relied upon largely to overcome the usually faulty temperature distribution in the package. Package design and practice varies so much with the time of year, climate and type of trade, that no single standard can be said to exist. However, the use of corrugated paper containers is common and Figure 72 shows the

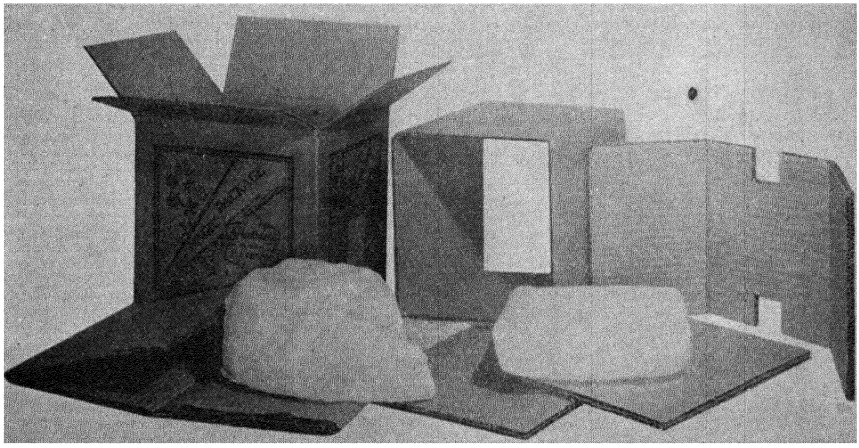


FIGURE 72. The Common Type of Ice Cream Package.

ordinary package. Figure 73 shows the proportions commonly employed in making up such packages, although proportions are varied somewhat according to conditions by experienced packing crews in some of the more successful plants.

Truck Refrigeration. Following the development of a market for solid carbon dioxide in refrigeration of packaged ice cream, its use for refrigeration of ice cream trucks next engaged wide attention, and is now in general use.

The competitive standing of solid carbon dioxide as an ice cream truck refrigerant varies with the locality, since availability and low cost of solid carbon dioxide are important factors, and these are naturally at their best in the larger centers of population.

Solid carbon dioxide has, however, firmly established its position as the lightest of all refrigeration methods permitting maximum pay load on a given chassis. Of all refrigeration methods, it has also established a position quite beyond question as the cheapest to install per gallon of truck

capacity, a factor of great importance in a seasonal business. It also possesses in the highest degree the factors of simplicity and dependability, sharing with water ice the familiar catch phrase: "A block of ice cannot get out of order."

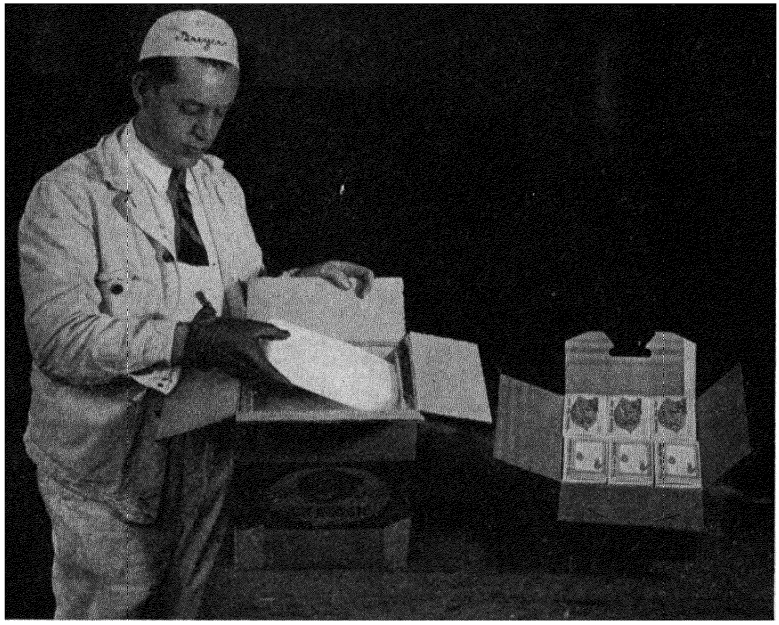


FIGURE 73. The Usual Method of Packing Ice Cream.

Because of these advantages, solid carbon dioxide refrigeration is now accepted standard for ice cream truck refrigeration in the larger cities of the United States. Its application is extending to smaller centers more gradually as economical distribution of the necessary refrigerant to the more sparsely settled districts is developed.

Figure 74 shows several types of truck refrigeration systems in successful use. Generally speaking, the simpler types have been found to suffice in this field, and the use of temperature control devices is not general. The proper proportioning of the equipment and proper hardening room and loading practice are usually sufficient to deliver the cream to the dispenser in a satisfactory condition.

Ice Cream Dispensing Equipment. In dispensing of ice cream, solid carbon dioxide has made possible sweeping changes familiar to most residents of larger cities. The general characteristics of development in this market have been first, the necessity for limiting the use of solid carbon dioxide to very small and very efficiently insulated containers during the introductory period of small volume and high cost, and second a gradual

shifting of the balance toward larger and less expensive types of dispensing containers as the cost of the refrigerant was lowered.

Thus, the earliest type of dispensing was limited entirely to the retailing of ice cream novelties from vacuum jars. Initially only the one-gallon size was used, requiring approximately one pound of solid carbon dioxide daily for sufficient refrigeration. In this instance, a double-walled, wide-mouthed, silvered vacuum flask of Pyrex glass was employed, in which it was customary to have the residual gases between the walls largely carbon dioxide instead of air.[3]

The next step from the one-gallon container is the dispensing box or basket, carried over the arm. This type was originally developed for train and ferry-boat service, but has found application for roadside sale of ice cream novelties.

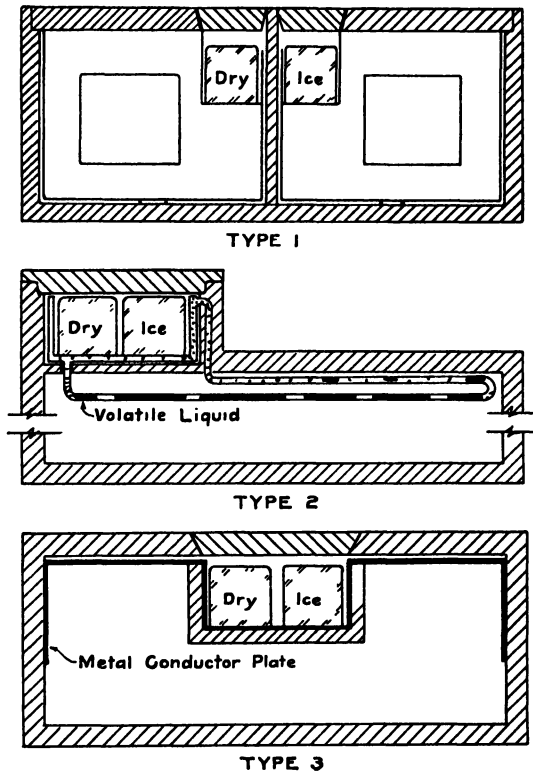


FIGURE 74.
Typical Truck Body Cooling Systems.

The next step upward in size leads to the ice cream dispensing cabinet. Here the problem becomes a little more complicated, inasmuch as solid carbon dioxide must meet the competition of other refrigeration methods which are much better adapted to dispensing cabinet use than to truck,

[3] Deuvil, C. O., *Refrigerating Eng.*, 20, 223 (1930).

package, or counter-dispenser design. It is further necessary that ice cream cabinets be satisfactory in most locations for the refrigeration of bulk ice cream, which means that the temperature must be controlled within a range corresponding to satisfactory dipping condition of the cream. A number of such cabinets have been introduced, and they are in successful use, although at this writing it is too early to state how far it may be possible for solid carbon dioxide cabinets to penetrate this important field.

Of particular interest is a classification of the methods used for controlling temperature in the devices thus far offered. It will be understood that it is general practice to insulate the solid carbon dioxide container sufficiently to prevent the temperature of the cabinet from going below the desired point, permitting a normal heat leakage through the insulation around the solid carbon dioxide bunker sufficient only to care for the minimum refrigeration demand, and conveying the variable portion of the heat load to the dry ice in one of the following ways:

I. By fluid circulation.
   a. By thermal circulation of a liquid, usually acetone, methanol or butanol, in a closed circuit, the flow being interrupted by a thermally operated valve.
   b. By thermal circulation of gas in a path controlled by thermostatic means.
      1. The atmosphere in the refrigerated space is circulated, cooled by means of a surface, usually provided with fins, which is in turn cooled by solid carbon dioxide.
      2. The gas around the solid carbon dioxide is permitted to escape directly into the refrigerated space through a thermostatically operated valve, thus establishing gas circulation in direct contact with the solid carbon dioxide.

II. By evaporation and condensation.
In this method a secondary refrigerant is permitted to boil in an evaporator, and condensed in a condenser cooled directly by the solid carbon dioxide, the flow through the circuit and hence the temperature of the refrigerated space being controlled by any of the conventional types of valve used in the mechanical refrigeration art. The choice of refrigerants is naturally limited to those not frozen to a solid by the solid carbon dioxide.

III. By variation in the thermal conductance of the paths of heat flow from the refrigerated space to the solid carbon dioxide.
   a. By wrapping the solid carbon dioxide.
   b. By placing the solid carbon dioxide on insulating pads, whose thickness and material are varied to produce the desired result.
   c. By varying the degree of contact between a cold surface directly refrigerated by the solid carbon dioxide, and a second surface in heat-conducting relation to the space refrigerated.
      1. By thermostatically operated "make-and-break" solid contact.
      2. By thermostatically flooding and draining a gap between the two conductors, for example, with alcohol.

IV. By interposing a layer of freezable liquid between the refrigerant and the space refrigerated, such as an eutectic brine, the temperature being obtained by adjusting the melting point of the brine to the desired point.

The commercial application of solid carbon dioxide to ice cream cabinets is as yet in its infancy, and it is quite impossible to say which of the above schemes will survive the test of time. Indeed, a number of the cabinets now in apparently satisfactory use can boast of no temperature control

more advanced than wrapping the refrigerant in paper when the ice cream seems too hard.

Refrigeration of Meat and Fish. While the development of this type of refrigeration has been somewhat slower than in the case of ice cream it has been found that express shipments of meat and fish can often be made cheaper when solid carbon dioxide is used for refrigerating instead of the less efficient water ice. Such shipments are usually made in containers such as are illustrated in Figure 75 and Figure 76.

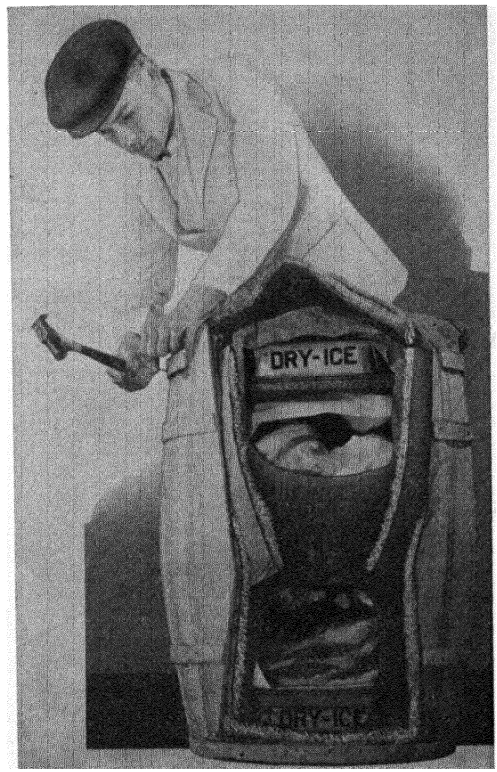


FIGURE 75.

Packing Meat with Solid Carbon Dioxide for Refrigerant.

Both meat and fish are also transported in motor trucks employing solid carbon dioxide as the refrigerant, and the practice is a growing one among wholesale meat peddler trucks in the larger cities where solid carbon dioxide may be obtained cheaply and conveniently. The design of such trucks follows the same general lines as those employed in the ice cream industry.

Railroad Transportation of Perishables. In 1924 the Canadian National Railways and the Dominion of Canada Bureau of Fisheries made an experimental shipment of fresh fish from Halifax, N. S., to Montreal. A standard refrigerator car was used and the solid carbon dioxide, formed into cylindrical blocks and made by the expansion of liquid carbon dioxide from

cylinders, was interspersed throughout the load. The fish arrived in Montreal in good condition, and the shipment received such favorable comment that it was freely prophesied that the time was not far distant before this new refrigerant would completely revolutionize the refrigerator car industry.

During the spring of 1926 further experiments were conducted to determine the feasibility of refrigerating carload shipments with dry ice, in which fillets were shipped from the Atlantic seaboard to points in

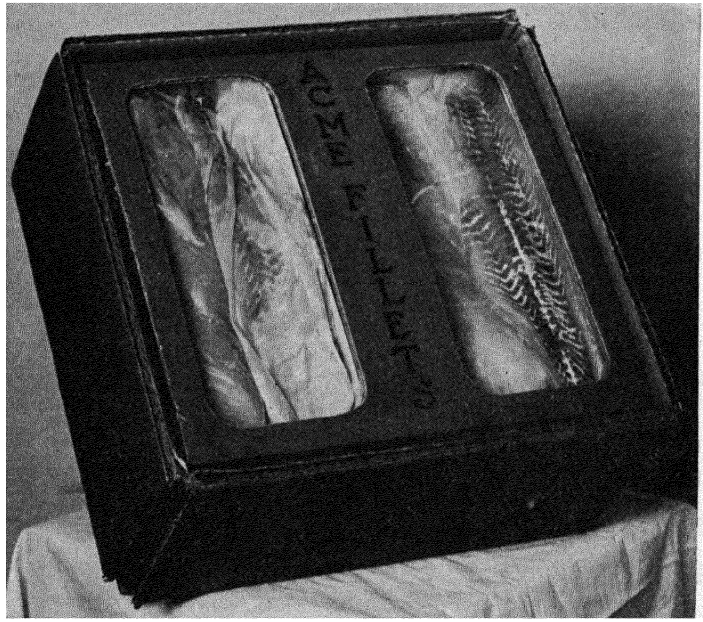


FIGURE 76. Fillets of Fish Refrigerated with Solid Carbon Dioxide.

the middle west with varying amounts of dry ice placed directly in contact with the load in standard water ice refrigerator cars.[4]

In 1929 the construction of refrigerator cars especially designed to utilize the properties of solid carbon dioxide was undertaken. The first cars so constructed, however, were not well enough regarded by their builders to have had their design details published in the literature. About a year later practical experiments were undertaken by modifying the construction of water ice refrigerator cars and testing their actual performance in a constant temperature room, with a view to evolving a workable construction for a dry ice refrigerated car.[5] In Figure 77 is shown diagrammatically the arrangement of refrigerant, air flow, and thermostatic control

[4] Martin, J. W., Jr., *Railway Age*, **85**, 1239-41 (1928).
[5] Jones, C. L., *Railway Age*, **90**, 363 (1931).

in a resulting car. Such cars are in service in parts of the United States, and have transported successfully more than 100 carloads of dressed hogs and pork products, many shipments of fresh eggs, and numerous carloads of frozen foods. King[6] has described such cars and outlined the results of their operation.

Solid carbon dioxide has also been applied to the refrigeration of carload shipments as a supplement to the customary refrigeration with water ice. When so used it is commonly referred to as a "booster" or "auxiliary" refrigerant. The factors involved in this use, with particular reference to the shipments of fruits and vegetables, have been investigated by Brooks and his associates[7] who found that the gas evolved by 300 to

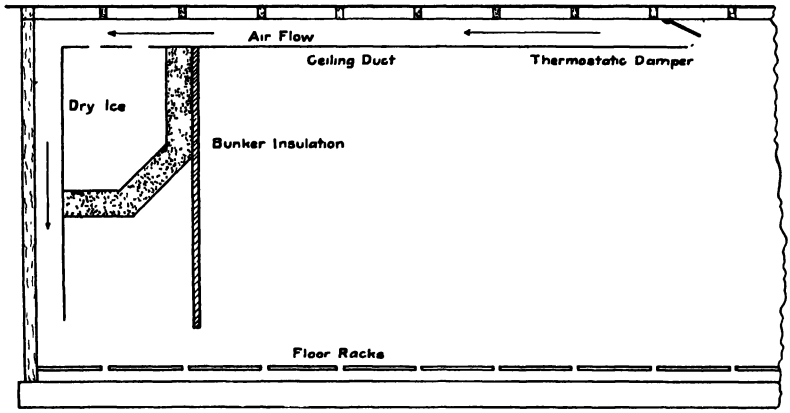


FIGURE 77. Controlled Refrigeration of a Refrigerator Car with Solid Carbon Dioxide.

1000 pounds of solid carbon dioxide placed above loads of strawberries, peaches, and dewberries is usually as effective as 21° F. lower temperature during the first 36 hours in prolonging the life of the produce. This type of application has also been used in the shipment of meats, in which it is customary to hang from 50 to 300 pounds of solid carbon dioxide from the ceiling of a refrigerator car cooled by the ordinary ice and salt practice. The reduction of temperatures by such a small amount of added refrigeration is not impressive, but owing to slightly lower humidity or to the effect of carbon dioxide on the meat, the practice is reported to result in better appearance of the delivered product.

Some study has also been given to the use of solid carbon dioxide as a refrigerant in cooling smaller unit containers for rail shipments. Church[8] has described such a unit container cooled by means of a metal bunker having an extended or finned cooling surface.

[6] King, C. W., *Ice and Refrigeration*, **84**, 343-6 (1933).

[7] Brooks, Charles, Miller, E. V., Bratley, C. O., Cooley, J. S., Mook, Paul V., and Johnson, H. B., "Effect of Solid and Gaseous Carbon Dioxide Upon Transit Diseases of Certain Fruits and Vegetables," *U. S. Dept. Agr., Tech Bull.*, **318**, 1-59 (1932).

[8] Church, *Refrigerating Eng.*, **23**, 33 (1932).

Cooling and Freezing Uses. In the preceding discussion emphasis was placed on the application of solid carbon dioxide for holding material, chiefly foodstuff, at a reduced temperature to prevent spoilage. It is now well to consider another field in which the refrigerating effect of solid carbon dioxide is used to produce low temperatures or to extract heat from certain substances in order to freeze them.

Shrinkage of Machine Parts. One of the most interesting uses of solid carbon dioxide in this field is the cold shrinking of machine parts, both as a substitute for the older brine-shrinking method, and to take the place of press fits. The study of the use of liquid air for shrink fitting[9] naturally led to focussing attention on the possibility of shrink fitting with the cheaper and more available, though less frigid, solid carbon dioxide.

Among the first such uses was the insertion of bronze liners into the cylinders of hydraulic machinery, where it has been found sufficient to pack the interior of the liner with crushed solid carbon dioxide. Care is taken to make the insertion rapidly to avoid loss of temperature gradient, and it is usual to slush the outer surface of the liner with kerosene or alcohol to avoid the formation of frost from atmospheric condensation. It is said that slightly higher shrinkage allowances than with ice and salt cooling have been used with success.

A somewhat more elaborate arrangement is employed in shrinking cast-iron cylinder liners into engine blocks, shown in Figure 78.[10] In this instance the cylindrical liner is placed on an aluminum spindle cooled by conduction to a block of solid carbon dioxide in a rotary cooling cabinet. Rotation of the cooling element by means of a pedal serves to bring a fresh liner in position for removal, and it is found that twenty minutes in the cabinet suffices to chill the liners to approximately −65° C. At this temperature they may be inserted into the cylinder block by hand, replacing a press-fitting operation, with the elimination of a press and some saving in time since it is not necessary to position the cylinder block accurately to insert the liners.

A very similar arrangement has been used for the production chilling of heat-resistant alloy valve seat rings in automotive engines. In this instance, however, the rings feed by gravity through a chilling chamber cooled by solid carbon dioxide, emerging at a temperature permitting them to be dropped into their places in the engine block without further treatment. Still other special shrinking operations have been performed by immersing the parts directly into a freezing mixture of solid carbon dioxide with kerosene or methanol.

Generally speaking, it is found possible to obtain shrink fits approximating 0.1 per cent of the linear dimensions of the shrunk part in working with steel. The coefficient of expansion of the metal in question and the shape and size of the parts as well as the temperature of the warm part

[9] David, E. V., and Farr, W. S., *Power*, **74**, 506 (1931).
[10] Herb, C. O., *Machinery*, **39**, 305 (1933).

must be taken into consideration. The method is too young as yet to appraise its full possibilities in the metal working industries, but has already achieved recognition as the cheapest and most convenient method of accomplishing certain assembly operations.

Chilling Aluminum Alloy Rivets. It is well known that the rate at which the so-called air hardening alloys of aluminum age is a function

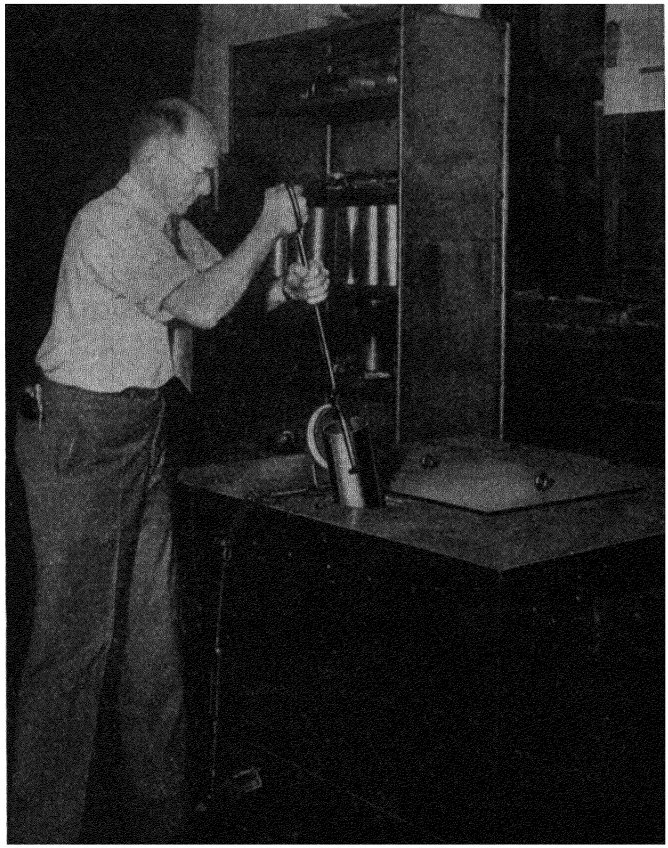


FIGURE 78. Rotary Cooling Cabinet for Cooling Cylinder Liners for Engine Blocks, Refrigerated with Solid Carbon Dioxide.

of temperature. Unfortunately, some of the strongest alloys age so rapidly at room temperatures that rivets made from them quickly become unworkable, requiring either that they be re-annealed just before they are to be driven, or that the aging phenomenon be retarded.

It has been customary for some time to retard the hardening of such rivets by refrigeration using water ice, but solid carbon dioxide offered the advantages of adaptability to small unit chilling boxes in which a local

supply of soft rivets could be maintained at each working position in an aluminum fabricating shop. Solid carbon dioxide is now the accepted and all but universally used refrigerant for storing such rivets in airplane construction shops.[11] Figure 79 illustrates a Balsa wood box of the type commonly used at each work place to hold a supply of soft aluminum alloy rivets.

Cold Treatment of Special Steel. Luerssen and Greene[12] have investigated the properties of certain silicon steels which are hardened by chilling to subzero temperatures by means of solid carbon dioxide. The method is

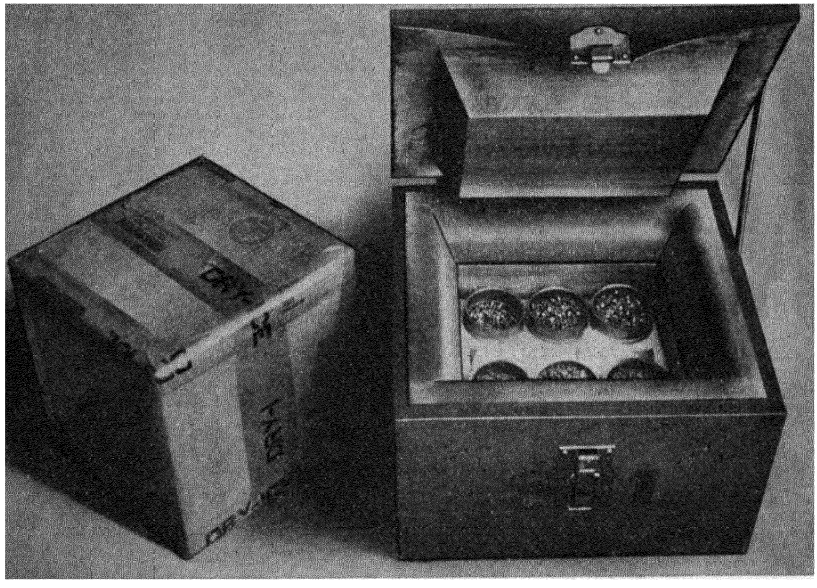


FIGURE 79. Balsa Wood Container for Refrigerating Aluminum Alloy Rivets with Solid Carbon Dioxide.

not yet applied commercially, but offers interesting advantages arising from the fact that parts may be machined and then hardened cold with complete freedom from any question of warpage or oxidation.

Laboratory Uses. Solid carbon dioxide finds many uses as a low temperature refrigerant in laboratory work. Killeffer[13] has pointed out its adaptability to the dehydration of organic solvents, and states that ether may be dehydrated by freezing out moisture with solid carbon dioxide rapidly and economically.

It is convenient in controlling the consistency of sticky and gummy materials for sampling and grinding. Thus, rubber samples may be packed

[11] *Refrigerating Eng.*, 22, 182 (1931); *Iron Age*, 78, 337 (1932); *Metals and Alloys*, 2, 165 (1931).
[12] Luerssen, G. V., and Greene, O. V., *Trans. Am. Soc. Steel Treating*, 501-52 (1932).
[13] Killeffer, D. H., *Ind. Eng. Chem., Anal. Ed.*, 3, 386-7 (1931).

with crushed solid carbon dioxide and ground in a chilled mortar, facilitating solution of the ground sample, and simplifying its handling. Similar advantages attach to the grinding of other gummy or plastic materials, as it will be found that few substances exhibiting such properties at room temperature fail to become quite brittle when chilled to the temperature of solid carbon dioxide.

The fact that vapor evolved from evaporating solid carbon dioxide is extremely dry, its dew point being at most the sublimation temperature of the solid carbon dioxide, leads to drying applications where oxidation is regarded as undesirable. Thus, biological serums are occasionally concentrated by low temperature evaporation in this manner.

Freezing of sections for histological work has long been accomplished by means of solid carbon dioxide. Dunn[14] has described a convenient apparatus especially designed for this purpose which is illustrated in Figure 80.

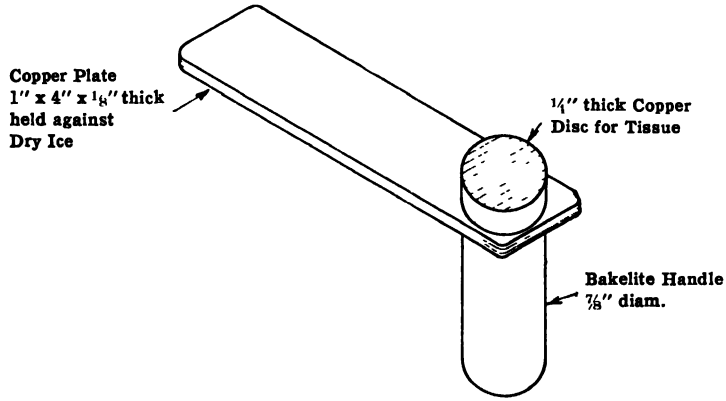


FIGURE 80. Microtome Attachment for Freezing Sections of Tissues with Dry Ice.

Solid carbon dioxide is also useful in the laboratory for low temperature tests of the properties of materials. Thus, many laboratories use it in making cold tests of lubricating oils, and it has been employed to cool special test spaces in the investigation of gasoline engine performance at low temperatures, the study of the behavior of building and especially roofing materials at low temperatures, and in perfecting the design of a cold weather windshield-wiping device.

Many of these laboratory applications have their counterparts on a little larger scale in industry. Thus, the cooling of vacuum traps for the protection of laboratory vacuum pumps from volatile materials find a direct parallel in the cooling of similar traps in the manufacture and repair of neon and other gas-filled tubular signs. Indeed, the sign industry probably employs the cheaper and more available solid carbon dioxide today on a wider scale than the liquid air formerly used for the purpose.

[14] Dunn, F. L., *J. Lab. Clin. Med.*, **16**, 627 (1931).

Likewise the laboratory application in chilling rubber and gummy materials for grinding finds a parallel in the grinding of aniline dyes, in which some operators prefer grinding of solid carbon dioxide in small amounts directly with the dyestuff to other methods of cooling. This refrigerant ground with the dye is obviously applied in the most efficient manner, since the refrigeration is applied directly inside the mill. It seems possible that the gas evolved may help prevent "balling" and "gumming" in the mill by aerating the product and providing for rapid adsorption of a gas film on freshly formed surfaces.

Freezing to Stop Flow. There is occasional use of small quantities of solid carbon dioxide for freezing off flow in pipes where other shut-off facilities are not available and it is necessary to make repairs.[15] This method probably has a wider usefulness than has yet appeared, since solid carbon dioxide has not always been available when emergencies occurred, and it has hence not been used in many instances where it might have been helpful. At least one case is on record, however, of a water main being shut off by filling a trench around a section with solid carbon dioxide. Such use of any refrigerant naturally presumes a speed of freezing sufficient to freeze the material through to the center of the pipe, involving not only the question of diameter, thickness, and material of which the pipe is made, but the latent heat of fusion of the liquid in the pipe, and its temperature, heat capacity and rate of flow past the point which is to be frozen off.

A similar case of emergency freezing is to be found in the disposal of dangerous materials under pressure in leaky or dangerous containers. Thus, a case has been recorded in which it was necessary to dispose of a ton container of chlorine the valve of which had become badly corroded and had commenced to leak. It was considered dangerous to tamper with the valve, or to move the container, which was in a congested area. Solid carbon dioxide was packed around the container until the vapor pressure of the chlorine was reduced below atmospheric pressure, as judged by the fact that the leak ceased to exhaust chlorine, and commenced to draw in air. It was then found easy and safe to replace the defective valve.[16]

Of somewhat similar character is the discovery that when chlorpicrin is mixed with solid carbon dioxide, its vapor pressure is reduced to such a low value that the mixture may be handled in open buckets without the necessity of the operator wearing a gas mask. The application of this fact to the use of chlorpicrin in fumigation is obvious, although the use to date has been very limited. The possible application of the same phenomenon to the safe transportation of noxious materials in large quantities during war time is of the greatest importance, holding out the possibility of large savings in the decreased number of pressure containers required, and reducing the use of approved pressure containers possibly to the handling

[15] Laughton, W. M., *Chem. Met. Eng.*, **37**, 643 (1930).
[16] Anon., *Ind. Eng. Chem., News Ed.*, **9**, 197 (1931).

of small unit quantities at the scene of action. It would thus be possible to effect bulk shipments from the manufacturing plants to the filling stations near the arena of war in open insulated boxes, reliquefying the products at the filling station and separating the carbon dioxide, in order to fill the noxious material into approved pressure containers for further shipment to the front in smaller unit shipments. Composite products made up of solid carbon dioxide mixed with volatile noxious organic materials have been made on a small scale and the practicability of their safe transportation in insulated sheet-metal boxes has been established, but there is no present commercial demand justifying wide use of this method of transportation.

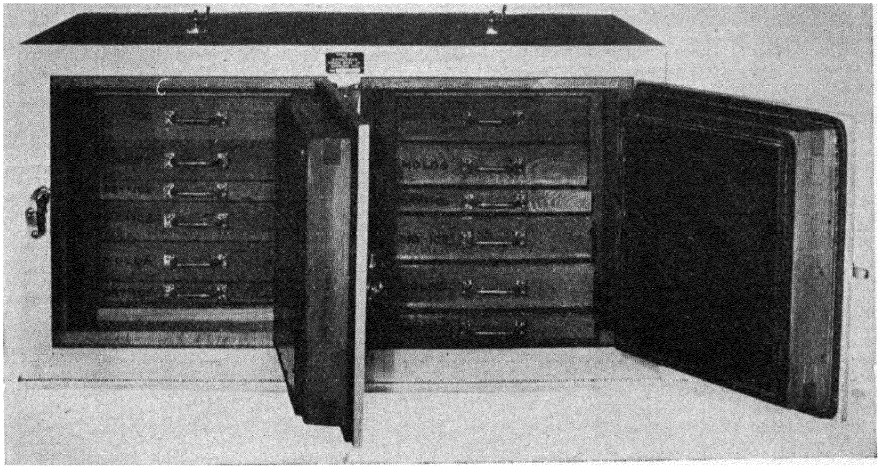


FIGURE 81. Cabinet for Hardening Fancy Forms of Ice Cream, Refrigerated with Dry Ice.

Chilling Golf Balls. Solid carbon dioxide has been applied to refrigeration in the manufacture of golf balls in two ways. The centers have been chilled prior to winding, not only insuring that they hold their shape during the winding operation, but no doubt causing a little added tension by reason of the later expansion as the center warms up. It has also been the practice in at least one plant to chill the finished balls with solid carbon dioxide rendering any scarf at the junction of the mold sufficiently brittle to be readily removed by merely breaking off.

Somewhat similar to this use is the chilling of crepe rubber for trimming to size. In this case trouble previously experienced in trimming crepe rubber, for sound-proofing airplane cabins, accurately to size was eliminated by chilling the sheets to brittleness between metal sheets refrigerated with solid carbon dioxide, then cutting to size when the chilled rubber sheet had warmed up approximately to the cutting consistency of pasteboard.

Freezing Food Products. It is sometimes found desirable to use solid carbon dioxide for freezing food products in cases where the convenience of the refrigerant outweighs the disadvantage of cost. Pedlers sometimes operate devices mounted on trucks for freezing custard or ice cream. Also manufacturers often use this refrigerant to harden "fancy forms" of ice cream in cupboards such as that illustrated in Figure 81.[17]

For small scale experimental freezing, several devices employing solid carbon dioxide have been used. Burke[18] has offered a small unit for such work, in which motor-driven agitation of a brine bath cooled with solid carbon dioxide affords apparatus for laboratory freezing operations under close thermostatic control. Similar and quite as efficient is the laboratory type cooler developed by Dry Ice Corporation.[19] A somewhat different construction has been employed by the Georgia Experiment Station.[20] Goosmann[21] has proposed the freezing of food products by direct contact with liquefied carbon dioxide at low temperatures, and it would seem that if suitable apparatus is developed, this method should possess advantages in its great speed, its freedom from oxidizing influences, its complete freedom from deformation of products, and its indifference to shape and size.

Producing Liquid Carbon Dioxide. While most of the solid carbon dioxide is employed for its refrigerating properties, some is also used for its carbon dioxide content. The great difference in selling price between solid and liquid carbon dioxide is responsible for the development of evaporators or converters for the conversion of the former into the latter state. This conversion may be accomplished in evaporators designed for employing the refrigerating effect of the solid and then making use of the resulting gas or it may take place in a simple container in which solid carbon dioxide is placed and the gas taken from the top after liquefaction has resulted from the transfer of heat from the surrounding atmosphere. Because of its simplicity and the fact that the gas and refrigeration are not always needed at the same point the tendency at present seems to be towards the simple evaporator.

In liquefying solid carbon dioxide the fact should be kept in mind that for equal weights, liquid carbon dioxide requires more space than the solid. While the solid at −75° C. occupies a volume of 0.0105 cubic feet per pound (theoretical cf. Table 82) the liquid requires almost twice that volume or 0.01689 cubic feet at 25° C. Even with the less dense commercial solid carbon dioxide the change will be practically of the same order. Liquefiers must therefore be designed to withstand the extremely high pressures which will result if they are to be completely filled with

[17] Houlton, B. F., *Ice Cream Trade J.*, **27**, 56 (1931).
[18] Anon., *Ice and Refrigeration*, **79**, 219 (1930).
[19] U. S. Patent 1,873,130 (1932).
[20] Woodroof, J. G., *Ga. Exp. Sta. Bull.*, 163, (1930).
[21] Goosmann, J. C., *Ice and Refrigeration*, **81**, 56 (1931).

the solid. It is better, however, to charge the liquefiers with only sufficient solid to permit expansion on melting.

Figure 82 shows diagrammatically two forms of liquefiers according to Goosmann.[22]

Solid Carbon Dioxide for Rain Making. The distribution of finely divided solid carbon dioxide has been proposed as a means of assuring fair weather for important events on foggy or misty days by promoting

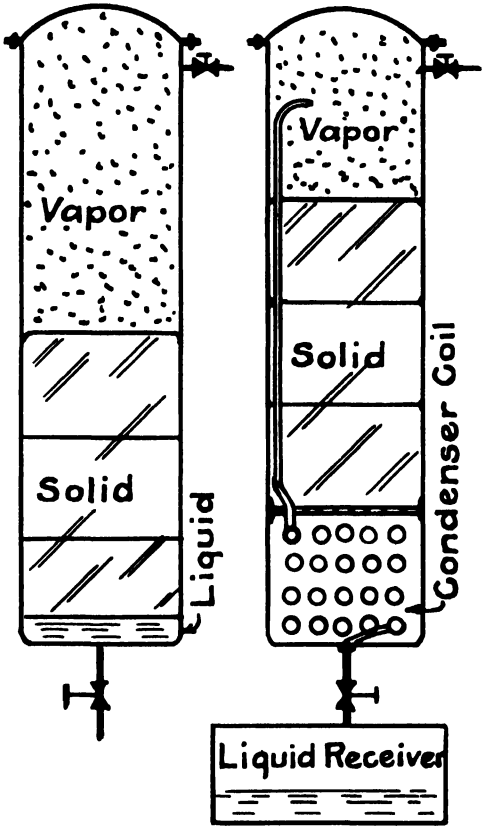


FIGURE 82.

Solid Carbon Dioxide Liquefiers.

Unit at left having sufficient space to allow for the expansion of the solid on melting.

Unit at right provided with condensing coil below the solid.

precipitation over a small area. For this purpose a trial was conducted in Holland in 1930 in which three aeroplanes were employed to distribute powdered solid carbon dioxide over the clouds. The results[23] are said to have shown promise, and there is no question that sufficient quantities of solid carbon dioxide used in this manner will cause precipitation, but sufficient detail is not furnished on the results obtained from the trial to support any judgment as to the possible practical significance of the method.

[22] Goosmann, J. C., *Ice and Refrigeration*, **79**, 134 (1930).
[23] *Ice and Refrigeration*, **79**, (1930).

Uses of Liquid Carbon Dioxide

In Mechanical Refrigeration. The oldest use for carbon dioxide in the refrigeration field is in the recharging of compression refrigerating systems employing carbon dioxide as the refrigerant. Inasmuch as the thermal properties of carbon dioxide utilized in such machines have been reviewed in preceding chapters, and the literature of compression carbon dioxide refrigeration deals largely with mechanical detail, it will suffice here to refer to more comprehensive works on mechanical refrigeration.[24]

Due to the fact that the critical temperature of carbon dioxide is very near ordinary room temperature it has not received much favor as a refrigerant where condenser water temperatures are high, but in climates where cool water is available, and more particularly in places where safety has been highly regarded, the carbon dioxide machine has had wide recognition. These refrigerating systems probably exceed in number all other types in marine work, where dependability and freedom from hazard to operators in case of leakage or loss of charge are essential. In theater cooling many carbon dioxide machines are in service, presenting the advantage that leakage into the air of the ventilating system, should it occur, could occasion no panic and in all probability would not even attract the notice of the patrons. For similar reasons many carbon dioxide systems are found in hospitals and other public places.

The use of liquid carbon dioxide here is confined to providing the original charge for the system, and making up losses by leakage from time to time. The principal requirements are that the substance must be as pure as possible, present commercial products for the purpose analyzing over 99.7 per cent carbon dioxide, and that it must be dry, since moisture in the system occasions difficulty with expansion valves, and tends to accumulate in the evaporator, where it naturally interferes with both flow and heat transfer if sufficient quantities accumulate.

The Cardox Blasting Device. This is a device in which the expansive force of liquid carbon dioxide is used for blasting down coal. The process has many advantages over ordinary explosives and is rapidly taking its place as an essential to the coal mining industry.

The Cardox cartridge, shown in Figure 83, is an alloy steel tube closed by caps on either end, which is filled with liquid carbon dioxide, which at the proper time is vaporized by the application of heat, the force being allowed to escape at a predetermined pressure by the shearing of a mild steel disc. Heat is applied to vaporize the liquid carbon dioxide from within the cartridge through the combustion of a mixture of chemicals in a paper tube known as a heater. The heater is a paper tube averaging 15 inches in length and $\frac{5}{8}$ inch in diameter. One end of this tube is closed with a wood plug through the center of which projects the positive terminal

[24] Pratt, J. H., *Ice and Refrigeration*, 65, 141 (1923); Macintire, H. J., "Handbook of Mechanical Refrigeration," John Wiley and Sons, New York (1928).

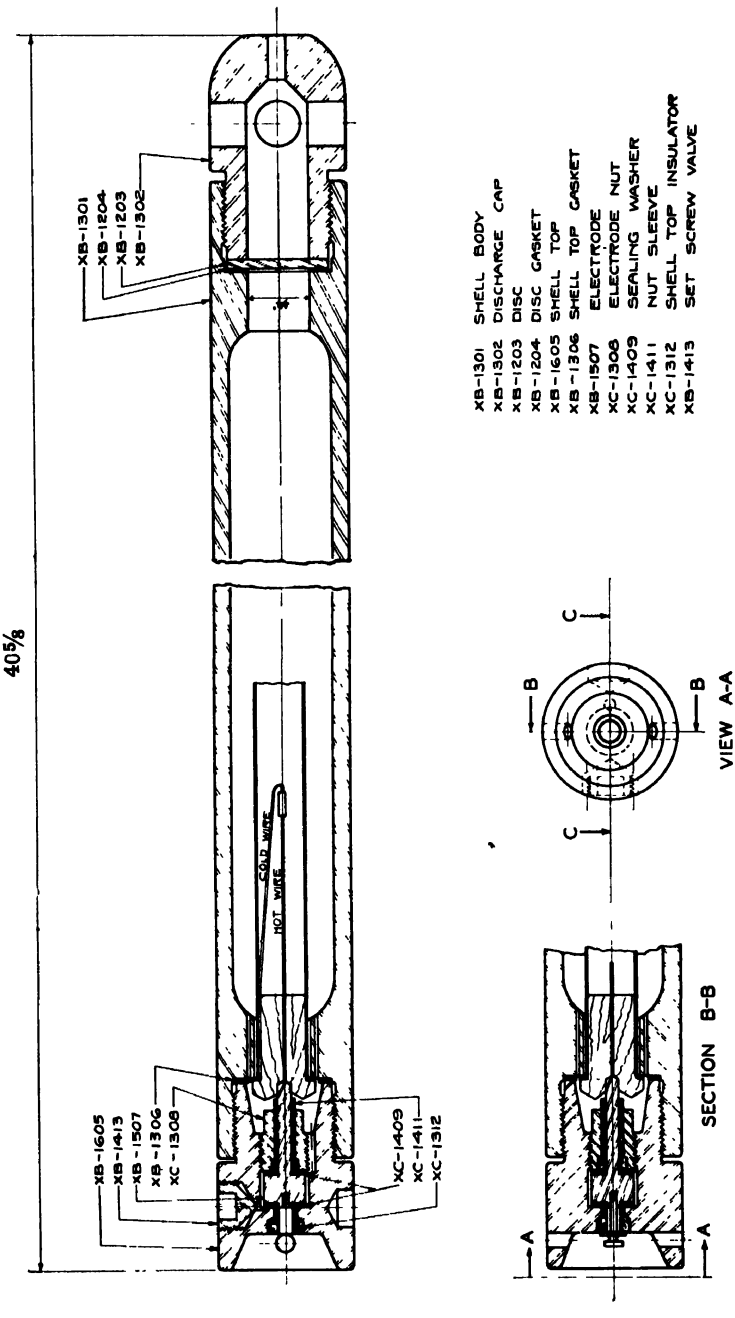


FIGURE 83. Details of Cardox Blasting Cartridge.

wire of an electric match. The negative terminal wire comes out under the shoulder of the plug. When the heater is placed inside the cartridge the negative terminal wire makes a ground contact against the inner wall of the steel cartridge while the positive terminal wire is engaged by an insulated electrode in the terminal cap. The heater tube contains, besides the match, a powder mixture known as the heating compound. This compound comprises an intimate mixture of potassium perchlorate, aluminum and carbon, so balanced as to provide an excess of oxygen in the reaction. The reaction is started by ignition of the match by an external source of electric energy. The thermal value of this compound is about 1600 calories per gram of mixture.

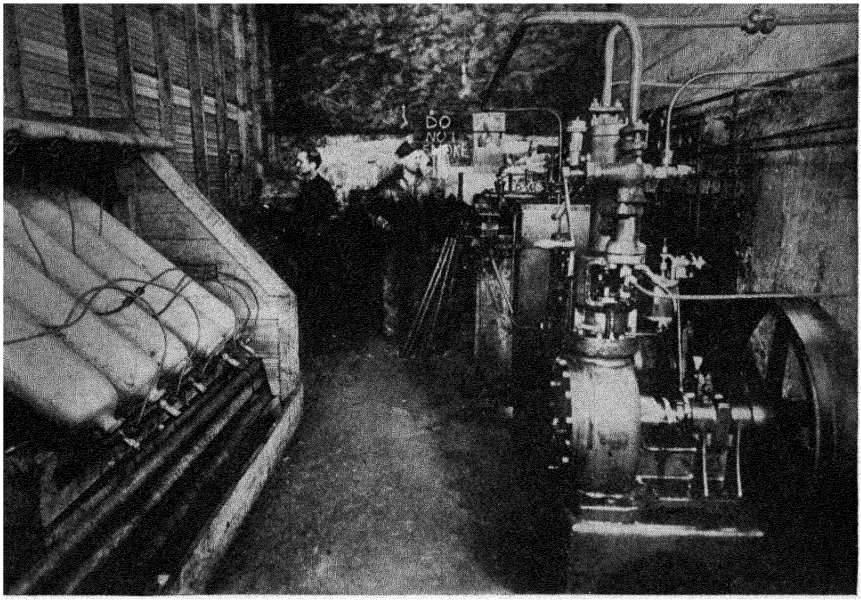
The temperature of the gases in the cartridge just before the discharge is approximately 350° C., which is safely below the ignition temperature of any mixture of natural gas, coal dust and air. Upon release, the expansion has a natural refrigerating action so that the final temperature of the released gases at atmospheric pressure is lower than the normal mine temperature. The air in a room that has just been shot with Cardox is perceptibly cooler after the shots are fired.

The pressures at which the shearing discs fail vary with the diameter of the orifice and the thickness of the discs and are maintained between a minimum of 10,000 pounds and a maximum of 30,000 pounds per square inch.

The cartridges have screwed caps at each end, one of which confines and holds the shearing disc while the other contains the filling valve and the electric contacts. After the discharge the cartridges are recovered from the coal and returned to a charging plant located usually at the mine, where the charge and disc are renewed for the next service. These cartridges are used daily over a period of years, requiring only a few minutes each for renewal of the charge. They are safe to handle and to transport and cannot be discharged except by application of an electric current through properly insulated contacts. They are of various sizes, ranging from $1\frac{3}{4}$ inches to $2\frac{9}{16}$ inches in diameter and from 20 inches to 47 inches in length. The weight varies from 9 pounds to 35 pounds, according to size. Their use in the drill hole at the face of coal is similar to that of explosives. They are inserted in the drill hole, tamped in place, connected to the usual shotfiring cable and discharged by a pocket type blasting generator or a dry cell battery. After having been discharged the cartridges are returned to a charging plant where the caps are removed and a new disc and heater inserted and the caps replaced. The cartridge is then placed in a charging clamp and by operation of a packed wrench the filling valve is loosened. Liquid carbon dioxide is allowed to flow through this valve until the cartridge is filled, after which the valve is reseated and the cartridge is removed from the clamp. The weight is checked and the electric circuit is tested. Then the cartridge is ready to be returned for its next service at the face. Carbon dioxide is drawn from standard shipping

cylinders and delivered in liquid form at about 30° F. to the charging clamp (Fig. 84). For this service a standard type of carbon dioxide refrigeration plant is used, which has a capacity of ¾ ton of ice in 24 hours. A 5-horsepower motor and a single-stage compressor are used with double pipe coolers and condensers and a liquid receiver having about 3 cubic feet capacity.

Cardox costs somewhat more than black powder or permissible explosives. There must therefore be other attendant advantages to justify its use. The safety of Cardox permits the convenience of its use during the



Courtesy, Safety Mining Company.

FIGURE 84. A Charging Plant at a West Virginia Mine where Cardox Cartridges are filled with Liquid Carbon Dioxide.

working shift. A more tangible advantage is an increase in the percentage of coarse sizes of coal in the mine-run product.

Coal prepared with Cardox is said to be stronger in structure and does not break up so much during shipment as that blasted with permissible explosives.

Thus far it has not been possible for these advantages to be made available without an increase in the operating costs; hence all factors are analyzed as thoroughly as possible in the case of each individual mine before the system is installed and new installations are made on a trial basis until the various factors are established and evaluated.

Some of the large mines in Franklin County, Illinois, are using the Cardox method of mining. Since these mines are only a few miles apart

and are connected with good roads, a central charging station has been established from which the mines are served, the loaded cartridges being delivered daily to the mines and returned to the central plant for recharging.

In the State of Utah it happens that there is a well which produces carbon dioxide in such quantities and at such a pressure that it is possible to fill these cartridges without refrigeration or compressing equipment. Despite this advantage, however, the present practice is to ship the liquefied gas to the mines and fill the cartridges as already described.

The Cardox method is being extended rapidly in Great Britain and tests are now under way leading to prospective development in France and Canada.

Liquid Carbon Dioxide as a Power Producer. The history of carbon dioxide is filled with references to its use as a power generator for operating various mechanical devices. Among these applications one finds reference to its use as a motive power for operating flying machines,[25] for propelling torpedoes,[26] the elevation of ladders on hook-and-ladder fire trucks,[27] and many others.

Operation of Bell Buoys. Liquid carbon dioxide is also used as a convenient and reliable decentralized source of power in the operation of bell buoys. The buoy at the entrance of Chesapeake Bay is operated from a cylinder containing 100 pounds of liquefied carbon dioxide, which filters from the cylinder through an asbestos-packed check valve until 19 atmospheres pressure is built up in a chamber, when it is released to operate a bell striker. Sufficient carbon dioxide is placed in the buoy to strike the bell 800,000 blows, or enough to last for a period of four months without attendance.[28]

Operation of Railway Signals. Somewhat similar to the operation of bell buoys is the application of liquid carbon dioxide for operating railway signals in isolated spots. This use, however, has survived only on one American railroad system, and the forward strides in developing reliable storage battery-operated devices for such service has thrown some doubt on the necessity of resorting to gas pressure systems for such work.

The Power Bottle. More recently the advantages of liquefied carbon dioxide as a source of power have been exploited in this country in the so-called "Prest-Air" power bottle, a small cylinder of carbon dioxide adapted to be carried in automobiles, and accompanied by a lifting jack in which a pressure piston is raised by admitting carbon dioxide to the jack cylinder. The device did not meet with wide acceptance and is today little used, although quite large numbers were placed in service in 1922 and 1923.[29] In Europe power bottles are used considerably for producing

[25] *Z. ges. Kohlensäureind.*, **2**, 507 (1895).
[26] Hill, Walter, "Liquid Carbonic Acid," Newport (1875).
[27] *Carbonic Acid*, **4**, 48 (1906).
[28] Anon., *Engineering News-Record*, **93**, 783 (1924).
[29] Anon., *Scientific American*, **130**, 181 (1924).

far-reaching sound signals (Tyfon System of Krupp), for railway repair groups, for emergency or fire signals in small towns, motor boats, etc.

Airplane Starters. Recent studies indicate the possibility of constructing carbon dioxide pressure starters for airplane motors more compact and of lighter weight than electric starters, and naturally more convenient than starters which must be operated from outside the pilot's position.

Leak Testing. Small quantities of liquid carbon dioxide are regularly used in leakage testing, where carbon dioxide is especially favored for gas pressure tests of vessels that have been used in storing or manufacturing inflammable or explosive materials. While safe practice demands the cleaning of such vessels as thoroughly as possible before repair work is undertaken, the use of carbon dioxide eliminates all combustion explosion hazard in a fool-proof manner. An allied application is the clearing of obstruction from plumbing, where a cylinder of carbon dioxide affords a convenient portable means used by plumbers to generate sufficient pressure to dislodge obstructions not moved by gentler means.

Cleaning Water Wells. A new and apparently unpublished use for carbon dioxide has been found in the cleaning of water wells. In this case, however, it is the solid form which is used to generate the pressure instead of the liquid. The well is closed off and solid carbon dioxide is dropped into it permitting the melting or vaporization of the substance to build up a pressure, which must be relieved through the water-bearing strata, thus dislodging obstructions in its path, and providing for increased well flow. The incidental effect in loosening and partially dissolving deposits of carbonate scale or scale having a carbonate binder may be of value, although precise information is not available. The depth of the well, character of the water-bearing strata, size of casing, temperature distribution, possibility of escape from other points than through the points to be cleaned, and amount and size of the pieces of solid carbon dioxide used would seem to be some of the factors involved in practicing the method successfully, and the precise effect of these factors does not seem to have received research attention, although the method has been successfully used in a number of instances. The judgment of the practical man supervising the cleaning appears to be sufficient in many cases to obtain a desired result. Further study would seem to be indicated and justified.

Operating Paint Guns. An interesting mechanical use of carbon dioxide is its employment in place of compressed air for the operation of spray-painting equipment.[30] Compressed air has become so easily and cheaply available that carbon dioxide is now regularly used for this purpose only in the sign-painting trade, where the use is so intermittent and for such comparatively small painting jobs that many operators do not consider the first cost of compressor equipment justifiable.

For Raising Beer. This application is of considerable importance to the carbon dioxide industry. A rather large proportion of the liquefied

[30] Sturcke, U. S. 1,294,190; 1,277,269; 1,303,987; 1,210,500; 1,283,823.

gas now sold, especially in this country, is used for this purpose. This application depends upon two factors. First, the pressure of the gas on the surface of the beer which forces it from a container usually located at a point lower than the dispensing tap. And second, the property of the gas to keep the beer fully carbonated at all times. Other mechanical devices have been developed for this purpose but the carbon dioxide cylinder still holds its place remarkably well.

Uses for Gaseous Carbon Dioxide

In this section the applications of carbon dioxide will be considered which depend to a considerable extent upon the chemical nature of the gaseous compound. It is perhaps obvious that such a classification is somewhat artificial because in many applications involving the use of gaseous carbon dioxide the liquid and solid also play some part.

Carbonating Beverages. When carbon dioxide gas is dissolved in water the resulting solution contains besides the dissolved gas, a compound resulting from its combination with water and the ions produced from this compound. The result is a sparkling liquid with a characteristic taste for which the public has developed a liking. While this carbonated water is often consumed as such, it is more often mixed with syrups and flavoring materials to produce products sold under the names of "soda water," "pop," "tonic" and others. The bottling industry is a large and important part of our industrial structure and uses a very high percentage of the liquid carbon dioxide of commerce.

The principal operation in the bottling industry in which carbon dioxide gas is used is the process of carbonating water. This is accomplished by means of automatic machinery which admits the gas under pressure to a carbonating chamber and brings about its solution by agitation. Many types of machines are used but the principle of operation is the same in all of them.

Carbonated Milk. An interesting proposed use for carbon dioxide which has not been successfully commercialized is the proposal for the preparation of carbonated milk.[31]

Fire Extinguishing. The advantages of carbon dioxide gas for fire extinguishing have long been known but it was not until the growth of the extensive telephone system in the United States that attention became focussed upon the special fitness of carbon dioxide for certain types of fire extinction.

As early as 1914, the Bell Telephone Company of Pennsylvania recognized the desirability of avoiding damage to wiring by extinguishing agents, and installed a number of 7-pound capacity hand extinguishers. These were steel cylinders of the conventional type (I.C.C. No. 3) equipped with the ordinary valve ($\frac{1}{8}$ inch bore), and provided with a rubber hose and

[31] Van Slyke, L. L., and Bosworth, A. W., *N. Y. Agri. Expt. Sta. Bull.*, 292 (1907).

nozzle taken from soda and acid extinguishers to facilitate directing the gas toward the fire. This crude device, despite its tendency to freeze and clog, and despite the fact that it entrains considerably more air than carbon dioxide, is quite effective on small telephone switchboard fires and remained in use in Pennsylvania for over a decade with fairly good results.

At about this time there was also introduced in Europe a system for extinguishing fires in the holds of vessels known as the Gronwald system. Gronwald employed commercial cylinders of carbon dioxide, with a heating device which required warming up at the time of a fire before the cylinders could be exhausted, and used valves of such small bore the rate of discharge of the carbon dioxide was very limited.[32]

In the decade following the World War, however, renewed activity was shown in this field, and the use of liquefied carbon dioxide in extinguishing fires was greatly extended. The increased importance of carbon dioxide in this field can be attributed largely to the following general developments:

1. Recognition of the necessity for employing either a siphon tube as proposed earlier by Camus or inverted cylinders as described by Luhmann in order to conduct liquid rather than gaseous carbon dioxide from the cylinder.
2. The employment of larger valve openings promoting higher rates of discharge, with less likelihood of stoppages.
3. The development of several types of dependable quick-opening valves suitable for the service. The requirement of a reliable quick-opening valve which would at the same time insure against leakage has been met by combining the functions of rupturable safety disc and valve. There are two general types: (a) Valves in which copper or gold-plated copper discs having a bursting pressure of 2350 to 2950 lbs. per sq. in. are used, combined with devices for punching a portion of the disc, shearing out a circular portion, punching out a star-shaped portion, or pulling through a piercing member from inside the disc by means of a pull wire soldered through the disc itself. (b) Valves in which a special light disc is employed, so light that it will rupture under normal cylinder pressure. The center portion of the disc is supported by a movable spud which prevents rupture of the disc until the extinguisher is to be discharged. Discharge is accomplished by merely removing the support from the disc, which bursts, releasing the discharge.
4. The development of nozzles suitably designed to prevent freezing or formation of carbon dioxide or water snow in a manner that would clog them.

[32] The broader subject of marine fire extinguishing systems employing combustion gases is not treated here, since the purpose of such systems is primarily to obtain gases low in oxygen, the carbon dioxide *per se* playing a minor rôle. For an extended description of such systems see *Trans. Inst. Marine Eng.*, **24**, 354-423 (1913). For a description of similar systems intended for use on land see *Chem. Met. Eng.*, **25**, 513 and 729 (1921). On the application of flue gases and occasionally pure CO_2 as well to mine fires, see *Mines and Minerals*, 505 (1908); *Trans. Inst. Min. Eng.*, **17**, 181 (1900); *Colliery Guardian*, 505 (1916); *Bull. Am. Inst. Mining Engrs. (London)*, **55**, 186 (1916); *Coal Industry*, 292 (1923); *Quarterly Natl. Fire Protection Assoc.*, **17**, 42-51 (1923).

5. The development of entrainment shields, usually of conical or cylindrical form, to limit the amount of air or other gases entrained by the carbon dioxide at the point of discharge.
6. The development throughout the fire extinguishing field of devices for automatically discharging extinguishers. These are arranged for immediate or delayed discharge, actuated either locally or remotely, and responsive to temperature, pressure, time, or rate of rise in temperature.

A typical carbon dioxide hand extinguisher is shown in Figure 85. It has a carbon dioxide capacity of 7 or 15 pounds and is designed to dis-

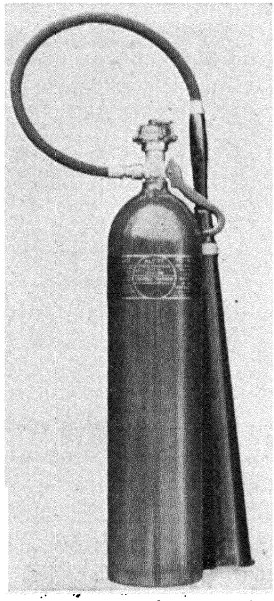


FIGURE 85.
Typical Hand Fire Extinguisher Using Liquid Carbon Dioxide.

Courtesy, American-LaFrance-Foamite Corporation.

charge its contents of liquid in well under 1 minute, extending the discharge of the high pressure gas remaining in the cylinder after the liquid is gone for another 2 or 3 minutes. The discharge consists of a mixture of carbon dioxide gas and snow. The latter is thrown upon the fire, tending to chill it to some extent, and rendering the extinguisher considerably more effective than would be the case if carbon dioxide were used in gaseous form only.

This type of extinguisher has become standard for the protection of telephone switchboards, and is widely used for first-aid fire protection in electrical hazards, inflammable liquids, small boats, garages, and the like. It has gained for itself an important place in fire protection engineering, suffering principally from two limitations—its cost is somewhat higher than older forms of first-aid fire appliance, and its range is quite limited,

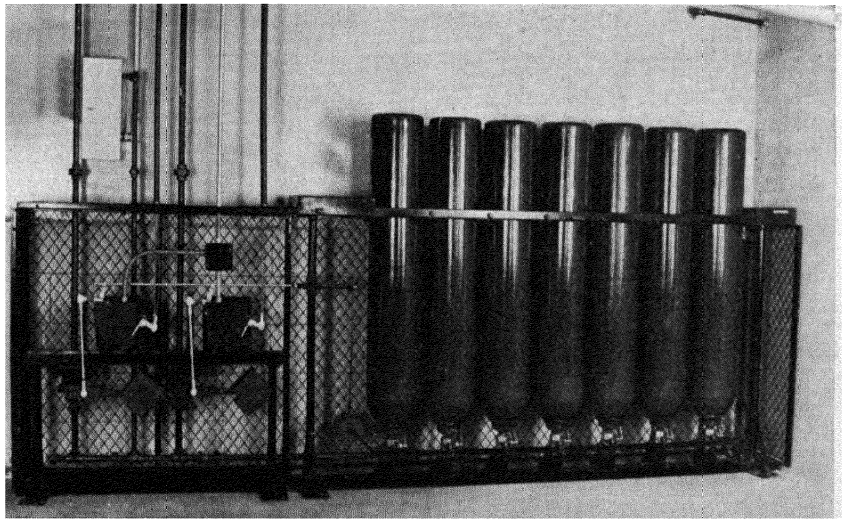
Courtesy, American-La-France-Foamite Corporation.

FIGURE 86. Carbon Dioxide Fire Extinguisher.

requiring that it be employed not more than five feet from the fire. Offsetting these disadvantages, it has the great advantages that its operativeness can be checked by simply weighing, that there is no deterioration of the charge, no necessity for periodic recharging, and no damage or hazard of any kind connected with the fire-extinguishing medium.

Figure 86 shows the so-called "direct hose" apparatus in which the carbon dioxide is taken from cylinders of 50 or 100 pounds capacity.

When fire protection is desired for ships, electrical machinery and spaces containing inflammable materials, a system is employed in which carbon dioxide is conducted, from a battery of steel cylinders, through



Courtesy, American-LaFrance-Foamite Corporation.

FIGURE 87. Battery of Carbon Dioxide Cylinders and Automatic Releasing Mechanism for Fire Extinguishing. A General Application of the Alfite System for an Industrial Hazard.

permanent piping to the space to be protected. Automatic release of the carbon dioxide is usually provided for and the discharge nozzles carefully placed to direct the gas to the points best suited for obtaining the greatest efficiency. Figure 87 shows such a battery of carbon dioxide cylinders and the automatic, electrically operated, releasing mechanism. In Figure 88 is shown a typical installation for the protection of a space containing inflammable vapors.

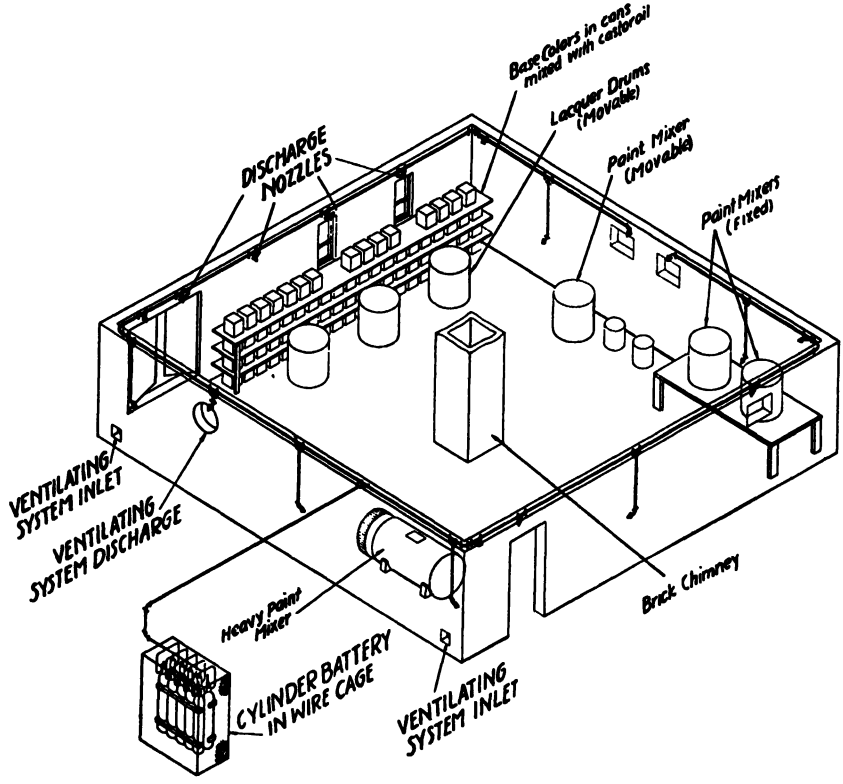


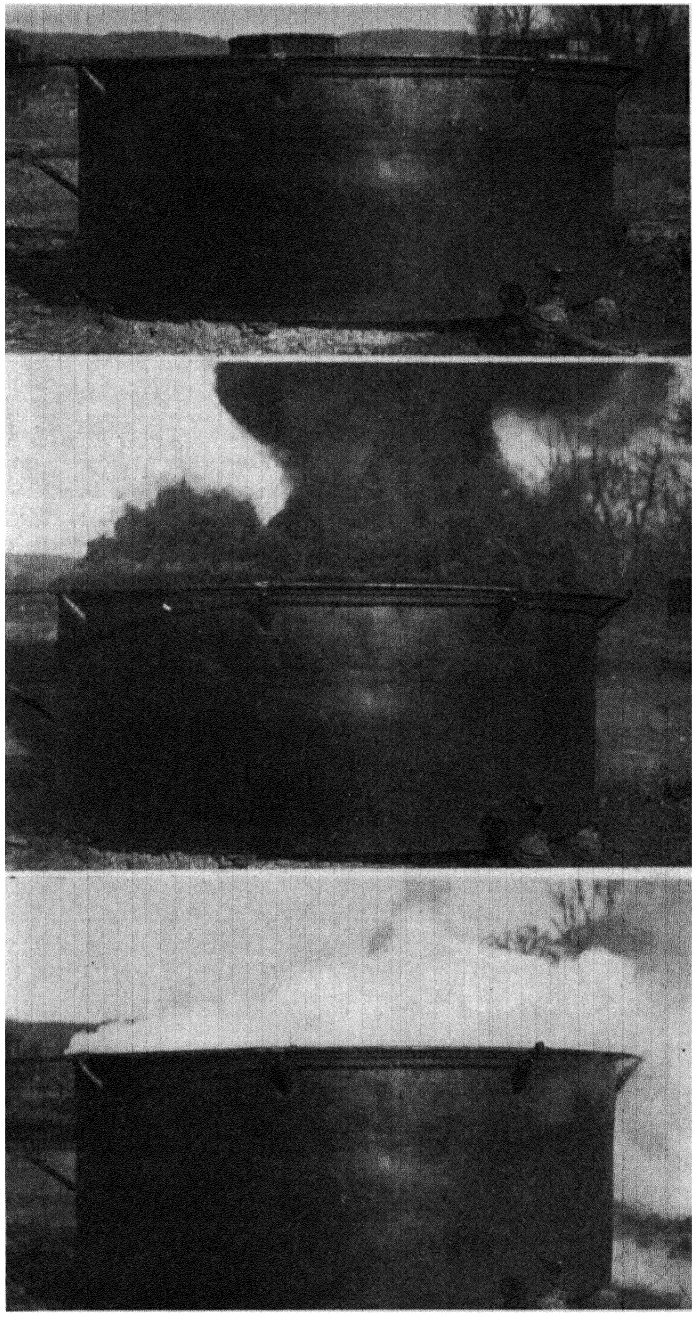
FIGURE 88. Typical Installation of Carbon Dioxide Fire Extinguishing Apparatus for Protecting Space Containing Inflammable Vapors.

Figure 89 shows a test of a system in which the carbon dioxide is liberated below the surface of burning oil in an open tank. In this case the tank had an area of 400 square feet.[33]

For a more extended discussion of both theory and design, as well as records of successful performance of carbon dioxide extinguishers on fires, the reader is referred to the special literature on the subject.[34]

[33] *Quart. Natl. Fire Protection Assoc.*, 157 (1928).

[34] See "Regulations of the National Board of Fire Underwriters for Carbon Dioxide Fire Extinguishing Systems," obtainable from National Fire Protection Association, 60 Batterymarch St., Boston, Mass.; Jones, C. L., *Quart. Natl. Fire Protection Assoc.* (1924); Moulton, R. S., *Ibid.*, 145-60 (1928); *Ibid.*, 271-288 (1930).



Courtesy, American-LaFrance-Foamite Corporation.

FIGURE 89. Testing Carbon Dioxide System for Extinguishing Oil Tank Fires.

Another application of liquid carbon dioxide to fire extinguishing differs somewhat from that just discussed as it depends more upon the power available from the liquid than upon the chemical properties of the gas itself. In this country and especially in Europe many thousands of small fire extinguishers are in use where small power bottles of liquid carbon dioxide eject extinguishing liquids or powders, as for instance, bicarbonates or carbon tetrachloride.

Mention perhaps should also be made of the very important use of liquid carbon dioxide for the instantaneous extinguishing of the arc of high voltage switches.

Preservation of Foods and Flowers. It is a pretty well established fact that atmospheres containing various amounts of carbon dioxide furnish environments in which bacteria do not thrive. Studies extending back for many years indicate that the carbon dioxide in carbonated beverages retards to varying degrees the development of bacteria which would otherwise find favorable conditions for growth. Recently much interest has been shown in the action of gaseous carbon dioxide to prevent spoilage of foods in general and especially to its preservative action on fruits, vegetables and meats.[35]

Preservation of Fruits. Brooks[36] found that it was possible by the use of solid carbon dioxide to secure a carbon dioxide content of the atmosphere in a railway car within 30 to 60 minutes which checks rotting and softening of warm fruit as much as would a 30° to 40° drop in temperature. It is necessary, however, that the gas escape within 18 to 24 hours to prevent injury to the flavor of the fruit, especially peaches, red raspberries and strawberries. Dewberries, blackberries, cherries and plums are more resistant to injury. Grapes, sweet corn, peas and beans offer the greatest promise of beneficial action of carbon dioxide in storage without harm to the product.[37] Harmful concentrations of carbon dioxide on certain types of vegetables under various conditions of gas storage have also been determined by Thornton.[38] Trout[39] discovered that an atmosphere containing 2 per cent of carbon dioxide retarded the ripening of pears and did not harm the fruit although the flavor was slightly affected. Kidd and West[40] conducted storage experiments on Lane's Prince Albert apples which showed that the optimum conditions for preservation were 4° C. in an atmosphere containing 2.5 to 5 per cent carbon dioxide. Under these conditions the commercial storage life of the fruit was twice as long as that in air at the same temperature and nearly twice as long as that in air at

[35] Valley, G., *Quart. Rev. Biol.*, **3**, 209-24 (1928). This paper gives a general review of the literature up to that date.

[36] Brooks, Charles, *Phytopathology*, **21**, 103 (1931).

[37] See also, Brooks, C., Miller, E. V., Bratley, C. O., Cooley, J. S., Mook, P. V., and Johnson, H. B., *U. S. Dept. Agr., Tech. Bull.*, 318 (1932).

[38] Thornton, N. C., *Contrib. Boyce Thompson Inst.*, **3**, 219-44 (1931).

[39] Trout, S. A., *J. Pomology Hort. Sci.*, **10**, 27-34 (1932).

[40] Kidd, F., and West, C., *J. Pomology Hort. Sci.*, **11**, 149-70 (1933).

1.11° C. Miller and Brooks[41] found that peaches, corn and peas withstand treatments with 35 to 47 per cent carbon dioxide at 5° C. for 4 to 5 days without impairment of flavor. Treatment at higher temperatures produced a characteristic ripe flavor in 1 to 2 days.

Preservation of Meat and Fish. Killeffer[42] tabulated the changes in pH on meat surfaces exposed to carbon dioxide, and gave data on experimental reduction of bacterial infection by exposure to the gas. He concluded that meat and fish can be kept fresh longer when refrigerated in a carbon dioxide atmosphere than in air. Lea[43] showed that the tainting of fat stored at 0° C. was greatly retarded in an atmosphere of carbon dioxide. The inhibiting effect of carbon dioxide was greater when the fat was stored in the carbon dioxide atmosphere at once and when the humidity was reduced from 100 per cent to 90 per cent. It has also been found[44] that the retarding effect of carbon dioxide on meat-attacking fungi is greater on growth than on germination of the mold spores. Thus in a 10 per cent carbon dioxide atmosphere at 0° C. the growth rate was reduced to about 50 per cent of the value in air.

Gas storage of fresh fish has been investigated by Coyne[45] who found that various types of fish could be kept in carbon dioxide at 0° C. for periods up to 28 days without serious deterioration, while controls stored in air were inedible after 12 to 14 days. Air containing 40 per cent carbon dioxide was as satisfactory as pure carbon dioxide.

Preservation of Flowers. Thornton[46] has made a very thorough study of this field as well as the gas storage of fruits and vegetables. Table 70 gives the results of a tabulation of considerable importance. Although this table expresses the effect in terms of carbon dioxide concentration causing injury, it is to be noted that many of the products investigated show benefits when treated with less than injurious quantities. Thus, rosebuds removed to warm air after a period of storage in 15 per cent carbon dioxide for 7 days at 3.3° C. or 10° C. lasted as well as untreated roses which had been in cold storage without carbon dioxide for 3 days—a possible gain in shelf life of 4 days.

Preservation of Eggs. The storage and shipment of eggs presents a special problem, since the carbon dioxide concentration in the air surrounding an egg determines the equilibrium pH in the white of the egg. It has been found desirable to maintain a pH approximating as closely as possible that of the eggs when laid, and commercial carbon dioxide in both liquid

[41] Miller, E. V., and Brooks, C., *J. Agr. Research*, **45**, 449-59 (1923).

[42] Killeffer, D. H., *Ind. Eng. Chem.*, **22**, 140-3 (1930).

[43] Lea, C. H., *Dept. Sci. Ind. Research Dept. Food Investigation Board* 1932, 39-43 (1933), also *J. Soc. Chem. Ind.*, **52**, 9-12 T (1933).

[44] Moran, T., Smith, E. C., and Tomkins, R. G., *J. Soc. Chem. Ind.*, **51**, 114-16 T (1932); Tomkins, R. G., *Ibid.*, **51**, 361-4 T (1932).

[45] Coyne, F. P., *J. Soc. Chem. Ind.*, **51**, 119-21 T (1932); *Ibid.*, **52**, 19-24 T (1933).

[46] Thornton, N. C., *Ind. Eng. Chem.*, **22**, 1186-89 (1930); *Am. J. Botany*, **17**, 614-26 (1930); *Contrib. Boyce Thompson Institute*, **3**, 219-44 (1931); **5**, 371-402 (1933); **5**, 403-18 (1933); **5**, 471-81 (1933); **6**, 395-402 (1934); **6**, 403-5 (1934).

TABLE 70.—*Effect of Various Concentrations of Carbon Dioxide on Fruits, Vegetables, and Flowers Stored at Different Temperatures*

Material	Period Tested, 1929	Time of Storage *Days*	% CO_2 Concentration at Which No Injury was Observed at:						% CO_2 Concentration at Which Injury was Observed at:					
			32° F.	38° F.	50° F.	60° F.	70° F.	77° F.	32° F.	38° F.	50° F.	60° F.	70° F.	77° F.
Apple:														
Dutchess	August	6–7	25	25	[a]			[a]	50	50	28			25
Gravenstein	August–September	7	46	30	[a]			[a]	64	50	27			25
Delicious	January–March, October–November	7	83	67	50				[a]	78	70			26
McIntosh	February, October–November	6–7	48	25	25			25	65	50	50			50
Banana	February–May	7			[a]	33	33				25	40	40	
Grapefruit:														
Walters	February-April	7	25	25	25	25			50	50	50	50		
Foster pink	April	7	50	50	50	50			65	65	65	65		
Thompson seedless	April	7												
Orange:														
King	April	7	[a]	30	30	[a]			27	52	52	30		
Common Sweet	February–April	7	50	50	50	50	50		64	64	64	64	64	
Valencia	April	7	50	50	50	50			63	63	63	63		
Peach, Georgia Belle	August–September	4	20	20	10			[a]	30	30	20			10
Pear:														
D'Anjou	January-March	7	42	25		[a]			62	49		30		
Bartlett	August–September	7	10	10	10			[a]	28	28	28			12
Strawberry	April–June	3	15	15	15				25	25	25			
Tangerine	April	7	25	25	25	25			50	50	50	50		
Asparagus	May–June	3	28	28	28	28			50	50	50	50		
Bean, stringless	May–June	3	[a]	18	18	[a]			18	30	30	18		
Carrot (root)	June	5	80	80	80	25			[a]	[a]	[a]	50		
Cauliflower	June	7	25	25	25	[a]			50	50	50	27		
Celery	January–March	7	25	25	[a]	[a]			50	50	25	25		

[a] Not determined.

TABLE 70.—*Effect of Various Concentrations of Carbon Dioxide on Fruits, Vegetables, and Flowers Stored at Different Temperatures*

Material	Period Tested, 1929	Time of Storage *Days*	% CO_2 Concentration at Which No Injury was Observed at:						% CO_2 Concentration at Which Injury was Observed at:					
			32° F.	38° F.	50° F.	60° F.	70° F.	77° F.	32° F.	38° F.	50° F.	60° F.	70° F.	77° F.
Lettuce	January–March	7	7	7	[a]	[a]			13	13	[a]	[a]		
Mushroom	February–April	4	15	15	15	[a]			25	25	25	[a]		
Pea	April–May	4	19	19	30	[a]			30	30	40	18		
Radish (root)	June	7	50	50	25	25			70	70	50	50		
Rhubarb:														
Stalk	June	7	80	80	80	80			[a]	[a]	[a]			
Dry leaf	June	7	50	27	27	27			70	50	50	50		
Spinach	January, March, and June	4	25	[a]	[a]	[a]			30	20	20	20		
Tomato	August–September	4	6	6	6				10	10	10	6		
Cosmos	July–August	4		15	15					25	25			
Dahlia:	September													
Jersey's Beauty		5	[a]		10						15			
Clarissa		5			[a]						15			
"Fern:"	September–October													
Aspidium spinulosum		7			15						25			
Asparagus plumosus		5			80						[a]			
Gladiolus:	July–August–September													
Salmon pink		4		15	15					25	25			
Rose pink		4		15	15					20	20			
Rose:	July–December, incl.													
Briarcliff		2–3–7	15	15	15				20	20	20			
Pierson		2–3–7		15	15					20	20			
Talisman		2		40	40					48	48			
Talisman		3		37	37					45	45			
Talisman		7		30	30					40	40			
Snapdragon	July–August–September	4			15						25			

[a] Not determined.

and solid forms has been used for introducing the gas into the air of the storage rooms.[47]

Uses in the Canning Industry. Rector[48] has developed a method for canning food products in an atmosphere of inert gas. In this process the can is evacuated, and inert gas, usually drawn from steel cylinders, is injected. While the process is applicable with either carbon dioxide or nitrogen to any powdered or shredded food product subject to oxidation, such as coffee, nut-meats, powdered milk, cocoa products and the like, the best known commercial use is in the gas-packing of sweetened shredded cocoanut, where the lower pH maintained through the use of carbon dioxide in the can is of material assistance in controlling spoilage.

Uses in the Chemical Industry. The most general use of carbon dioxide in the chemical industry is in the formation of carbonates. Large quantities are used in the Le Blanc, Claus-Chance, and ammonia-soda processes, more especially in the last named. In these reactions, however, as well as in the familiar Dutch process for manufacture of white lead, pure forms of commercial carbon dioxide need not be employed, and never are. It is hence customary to supply the necessary gas for carbonation in impure form, usually by burning lime. Since these arts are well developed and have a considerable literature of their own, they need not be considered further here.[49] The use of kiln gases in carbonating beet sugar solutions is also well covered in the literature pertaining to that industry.

Manufacturing Carbonates. Small quantities of commercial carbon dioxide are used for the manufacture of certain carbonates such as chalk. A proposed use of commercial carbon dioxide of considerable interest to the manufacturers is in the production of wet or Carter process white lead, for which improved yield and quality of product are claimed. The price of the product has apparently never been sufficient to support the use of commercial grades of pure carbon dioxide for this purpose, yet the suggestion of manufacturing wet process white lead in commercial carbon dioxide plants during the slack winter season to improve annual load factors of plant operation has been seriously advanced, though not yet applied commercially.

Kolbe Synthesis. Commercial liquid carbon dioxide was formerly employed to some extent in the manufacture of salicylic acid and aspirin from sodium phenolate. For economic reasons a large amount of the carbonic acid now required for this purpose in the United States is produced by the calcination of carbonates. One large chemical company in New Jersey is now obtaining its carbon dioxide supply from liquefiers charged with the solid. It is said that this practice is rather common in Great Britain.

[47] Sharp, P. F., *Ice and Refrigeration*, **78**, 253 (1930). Shutt, F. T., *Dept. Agr. Canada, Rept. Dominion Chemist for Year Ending March 31, 1930*, 121 (1931).

[48] Rector, T. M., "Scientific Preservation of Foods," John Wiley and Sons, New York, (1925).

[49] *See* Hou, T. P., "The Manufacture of Soda with Special Reference to the Ammonia Process," New York Chemical Catalog Co., Inc., **1933.**

Controlling Acidity. An interesting application of commercial carbon dioxide is in the control of pH, in which its usefulness lies in the ease of controlling its application to produce slight changes in pH. The principal point of application is to refrigerating brines.[50] The suggestion has also been advanced of using carbon dioxide to control the pH during the drying of sensitized film, where the control of concentration of carbon dioxide and ammonia in the air of the drying room affords a ready means of adjusting the pH to any point desired.[51]

As an Inert Gas. Perhaps the most obvious property leading to commercial application of carbon dioxide is to be found in the fact that it is the most readily available and least expensive commercial gas that may be regarded as "inert" or at least "non-oxidizing" in virtually all ordinary chemical operations. This is the basis of its use in deodorizing cod-liver oil and in supplying a non-oxidizing atmosphere in the containers in which it is handled.[52] Small quantities are sold for use as a vehicle in the distillation of phthalic anhydride and resort to the use of carbon dioxide for similar operations in the laboratory is not uncommon. Of interest also in this connection is the patent to Bacon,[53] in which a current of carbon dioxide is relied upon to drive traces of sulfur dioxide out of fruit juices preserved by means of it, in order that there may be no sulfur dioxide in the finished product. There appears to be no published record of its commercial use for this purpose. It has also been proposed as an non-oxidizing gas in the handling of phosphorus, and preparation of phosphorus alloys.[54] Lewis suggests its use in the manufacture of zinc oxide, using the gas as a non-oxidizing diluent to decrease particle size.[55]

As a Cheap Acid. The possible application of carbon dioxide as a mineral acid in neutralizing operations, and the fact that when shipped in solid form it is the only cheap, available, non-corrosive acid anhydride which may be shipped without special containers and handled easily and safely, does not seem to have engaged the attention of industrial researchers to any great extent. When it is considered that the material is now available in a range of cost competitive with sulfuric acid in cost per pound of hydrogen ions, and that its shipping weight per pound of hydrogen ions is less than half that of the commoner mineral acids, it would seem likely that further applications to neutralizing operations will be found. Methods for rapid graphic calculation of such operations have been published,[56] and it is, of course, true that carbon dioxide may be regarded as a substitute for other acids in such operations as carbonation in beet sugar refining.

[50] Bush, R. J., *Ice and Refrigeration*, **81**, 296-7 (1931).

[51] Morse, S., U. S. 1,493,000 (1924).

[52] Nitardy, F. W., British 214,238 (1923); Heyerdahl, P. M., U. S. 1,368,148; Hamilton, U. S. 1,745,851.

[53] Bacon, R. F., U. S. 1,305,244 (1919).

[54] Millring, E. R., U. S. 1,501,356 (1924).

[55] Lewis, W. K., U. S. 1,442,265 (1923).

[56] Dittmer, J. C., *Chem. Met. Eng.*, **23**, 1179 (1920).

Carbonic acid is a sufficiently strong acid to hydrolyze starch and sugar solutions, and has been proposed for commercial use, although no published record of such use appears to exist. The reaction is of great importance in explaining the rapid inversion of sucrose in carbonated beverages, however, and in that sense may be considered to be in daily use.[57] The rôle of carbon dioxide as a mineral acid is also found in the conversion of sodium chromate to bichromate under pressure.[58]

Carbonation of Water Supplies. This might well be considered as a chemical use, inasmuch as the purpose in every case is strictly chemical. The recarbonation of lime-softened domestic water supplies is either to reduce the pH of the treated water to a point less conducive to precipitation of carbonates, or to neutralize excess lime usually used in the process. It is almost always necessary in the lime-softening process, when it is desired to produce low alkalinity water, to use from 2 to 4 grains of lime per gallon of water treated, in excess of the molecular relation of lime to the hardness compounds. This excess lime, or high causticity, if left in municipal supplies, is objectionable because it increases the hardness and gives the water an alkaline taste. Excess lime is readily neutralized by carbon dioxide and its introduction into caustic settled softened water produces a secondary insoluble precipitation of calcium carbonate which can readily be removed by settling or filtering. The combined use of excess lime and carbon dioxide makes it possible to reduce carbonate hardness to the lowest permissible degree.

The solubility of mixed precipitate of calcium carbonate and magnesium hydroxide, the precipitate resulting from the lime reaction, is about 17 p.p.m. and it is possible to reduce the carbonate hardness of water to this extent. Before the adoption of carbonation a reduction of carbonate hardness to 50 or 60 p.p.m. was considered to be about as good as could be attained and still have good tasting water. Practice has shown, however, that if the carbonate hardness is reduced to less than 30 or 35 p.p.m., corrosion in pipe lines and hot water systems is apt to result; therefore, 35 p.p.m. seems to be the lowest permissible limit to which carbonate hardness should be reduced.

In practice, since the amount of carbon dioxide per volume of water is very small, it is customary to produce the carbon dioxide in the treating plant by combustion, using coke, natural gas, or in some small installations, kerosene; then scrubbing the flue gas to reduce the content of sulfur dioxide, dust, or products of incomplete combustion that might impart a taste to the water and finally pumping the flue gases through diffusers or perforated pipes submerged in the water. While the method may be somewhat wasteful from the point of view of carbon dioxide recovery, it is comparatively inexpensive and is in successful use in more than a score of American cities. It is considered amply justified by the greater reduction in hardness made

[57] Dewey, M. A., and Krase, N. W., *Ind. Eng. Chem.*, 23, 1436-7 (1931).
[58] Neumann, B., and Exessner, C., *Z. angew. Chem.*, 43, 440 (1930).

possible, the savings effected through prolonged life of sand filters, increased flow through mains, and decreased trouble with incrustation throughout the water system, and it is reasonable to expect increased use of the method.[59]

Because of the steady requirement, the comparatively large daily demand, and the possibility of absorbing carbon dioxide directly from flue gases, commercial liquid or solid carbon dioxide has not yet been applied successfully to city water recarbonation. Their use, however, has been proposed, and it is believed that they may find some place in the field at a price in view of the certain purity and greater convenience of application for small installations.

Removal of Scale with Carbon Dioxide. Closely allied to the recarbonation use is the occasional use of commercial liquid or solid carbon dioxide in removing deposits of scale already formed in water systems. Such action is, of course, an incidental benefit from the reduction of pH when recarbonation is installed in a city where incrusted mains already exist, but the concentration of carbon dioxide applied to city water is naturally insufficient to effect the rapid emergency removal of scale from an industrial pipe system that has become too badly clogged with scale for further use.

The removal of scale deposits by means of carbonated water appears to have been proposed by Greenhorne.[60] Cross and Irvin[61] further developed the idea, and made some practical trials. They described a method of determining the applicability of the scheme by treating samples of the deposit to be removed with carbonated water in pressure bottles and conclude that the method is more satisfactory on deposits composed largely of silicates, having a binder of calcium carbonate than on deposits consisting largely of the carbonates themselves.

A practical application of the method to the removal of scale from an obstructed line in the Duquesne works of the Carnegie Steel Company is described by Jones.[62]

Carbon Dioxide in the Rubber Industry. The use of carbon dioxide in the rubber industry today is limited to the filling of air bags used to support tires during vulcanization. This application has been developed by Minor,[63] who has proposed a method of using a combination of steam and carbon dioxide for inflating such bags. It is said that this method gives an increased life to the bag together with a close temperature control and increased vulcanization speed.

[59] *Eng. News-Record*, **90**, 671 (1923); *Eng. Contr.*, **61**, 1092 (1924); *J. Am. Waterworks Assoc.*, **11**, 393-408 (1924); *Ibid.*, **11**, 718 (1924); *Chem. Met. Eng.*, **35**, 230 (1928). For more extensive discussions of results in particular installations, see the Annual Reports of the Ohio Conference on Water Purification, obtainable from the office of the Secretary of State, Columbus, Ohio.

[60] Greenhorne, T. R., U. S. 1,135,684 (1915).

[61] Cross, R. J., and Irvin, Roy, *Power*, **55**, 422-23 (1922).

[62] Jones, C. L., *Power*, **60**, 578-9 (1924).

[63] Minor, H. R., *India Rubber World*, **49**, 17 (1923).

Hardening of Cement Products. The relation of moisture and carbon dioxide from the air to the setting of Portland cement has been investigated,[64] and it is recognized that carbon dioxide plays a part by neutralization of the free alkali in the cement. The calcium carbonate thus formed strengthens the final product, and increases its density somewhat, naturally increasing the weight by the amount of the carbon dioxide absorbed.

In contrast to this, when uncarbonated cement is submerged in water deficient in carbon dioxide, the free lime is removed by solution, leaving a lighter and more porous final product.

Few Portland cement products are of sufficient value to justify the use of commercial carbon dioxide for their improvement, and hence the commercial use is limited to the carbon dioxide hardening of precast specialties on a restricted scale. For this purpose the formed pieces are placed in a curing room where a moisture content near saturation and a high carbon dioxide content is maintained. Increased use of the method, however, awaits only the reduction of the cost of carbon dioxide curing to a point commensurate with the value of the improvement obtained.

Drying and Testing Cables. In Great Britain it has been found that carbon dioxide drawn from commercial steel cylinders is a more efficient drying agent for telephone cables than is calcium chloride dried air. The practice of drying out cables after laying does not seem to be favored in the United States; hence neither expedient is used, and no carbon dioxide is sold in this country for this purpose. According to Gibbons,[65] field drying is accomplished about 25 per cent faster and at about half the expense with carbon dioxide as compared with dried air.

Carbon dioxide finds some application in testing lead-sheathed cables for leakage. Obviously, if a gas is admitted under pressure at one end of a uniformly built cable and discharged at the other end, assuming no leakage, the pressure drop per unit of length from the admission point to the leak will be greater than that from the leak to the exhaust end, and greater than the average for the entire length. By the use of this principle and suitable pressure measurements along the cable, it is possible to locate leakage approximately without going over the entire cable.

Chemical Control. A most interesting application to which carbon dioxide has been put in at least one case is for controlling the inflation of a metalclad air ship.[66] The high density of gaseous carbon dioxide and the ease with which it is chemically separated from other gases, especially helium, makes it especially adapted to this process.

The inflation of the metalclad airship, the ZMC-2, was conducted in two stages. In the first stage the air in the hull was displaced by passing carbon dioxide into the bottom of the ship at a rate of about 10,000 cubic feet per

[64] Meyers, S. L., *Concrete*, **18**, 128-30 (1921).

[65] "Recent Developments in Underground Construction," Paper read before London Centre, Institution of Post Office Electrical Engineers, obtainable from Engineer-in-Chief Office, G. P. O. (West), E. C., London, England.

[66] Carr, A. R., and Good, A. C., *Ind. Eng. Chem.*, **22**, 227 (1930).

hour. The displaced air was exhausted from the top of the hull. In the second stage helium was run into the hull at the top at a rate of about 10,000 cubic feet per hour and the displaced carbon dioxide was discharged from the bottom. When the helium content of the escaping carbon dioxide reached about 48 per cent the gas was scrubbed with a caustic solution and the separated helium returned to the ship.

Appendix

List of Patents on Manufacture, Storage and Distribution of Solid Carbon Dioxide and Tables of Physical Data Calculated to English Engineering Units

SATURATED LIQUID AND VAPOR

Table No. 71 Vapor pressure of Liquid
72 Specific Volume of Liquid
73 Specific Volume of Vapor
74 Density of Liquid
75 Density of Vapor
76 Enthalpy of Liquid
77 Enthalpy of Vapor
78 Heat of Vaporization of Liquid
79 Entropy of Liquid
80 Entropy of Vapor

SATURATED SOLID AND VAPOR

81 Vapor pressure of Solid
82 Specific Volume of Solid
83 Specific Volume of Vapor
84 Density of Solid
85 Density of Vapor
86 Enthalpy of Solid
87 Enthalpy of Vapor
88 Heat of Sublimation of Solid
89 Entropy of Solid
90 Entropy of Vapor

LIST OF PATENTS

Dealing with Solid Carbon Dioxide

I. Manufacture of Solid Carbon Dioxide
(Methods and Apparatus)

United States:

No.		
579,866	Elworthy, H. S.	March 30, 1897
1,018,568	Julius, H. P.	February 27, 1912
1,546,681	Slate, T. B.	July 21, 1925
1,546,682	Slate, T. B.	July 21, 1925
1,600,308	Blanchard, G. B.	September 21, 1926
1,643,590	Slate, T. B.	September 27, 1927
1,659,431	Josephson, W. S.	February 14, 1928
1,659,434	Martin, J. W., Jr.	February 14, 1928
1,659,435	Martin, J. W., Jr.	February 14, 1928
1,727,865	Dehottay, H.	September 10, 1929
1,735,094	Slate, T. B.	November 12, 1929
1,768,059	Hassensall, L. W.	June 24, 1930
1,795,772	Goosmann, J. C.	March 10, 1931
1,806,240	Donald, J. R.	May 19, 1931
1,810,989	Smiley, O.	June 23, 1931
1,814,195	Thomas, N. R.	July 14, 1931
1,818,816	Rufener, H. and Eichmann, T.	August 11, 1931
1,822,788	Stoffels, J.	September 8, 1931
1,843,397	Marcus, D. A. and Ogier, W. W., Jr.	February 2, 1932
1,861,328	Small, N. M.	May 31, 1932
1,863,263	Belt, J. S.	June 14, 1932
1,863,287	Small, N. M.	June 14, 1932
1,863,377	Lockwood, E. J.	June 14, 1932
1,864,396	Zumbro, F. R.	June 21, 1932
1,869,346	Comer, W. T.	July 26, 1932
1,870,691	Rust, R. R. and Jones, C. L.	August 9, 1932
1,875,164	Schlumbohm, P.	August 30, 1932
1,876,266	Weston, B. H.	September 6, 1932
1,877,180	Jones, C. L.	September 13, 1932
1,879,463	Petrequin, F. J.	September 27, 1932
1,884,313	Small, J. D.	October 25, 1932
1,887,692	Martin, J. W., Jr.	November 15, 1932
1,893,850–1–2	Sullivan, E. G.	January 10, 1933
1,894,892	Small, N. M.	January 17, 1933
1,895,886	Lockwood, E. J.	January 31, 1933
1,903,167–8–9–70–1	Cordrey, A. J.	March 28, 1933
1,912,443	Goosmann, J. C.	June 6, 1933
1,914,337	Belt, J. S.	June 13, 1933
1,919,698	Hessling, W.	July 25, 1933
1,920,434	Prescott, F. L.	August 1, 1933
1,925,041	Auerbach, E. B.	August 29, 1933
1,925,619	Zumbro, F. R.	September 5, 1933
1,927,173	Jones, C. L. and Small, J. D.	September 19, 1933
1,943,232	Zumbro, F. R.	January 9, 1934
1,949,179	Pierce, R. C.	February 27, 1934
1,949,730	Shoeld, M.	March 6, 1934
1,950,180	Jones, C. L. and Small, J. D.	March 6, 1934

United States:

No.		
1,965,922	Fievet, H.	July 10, 1934
1,968,318	Seligmann, A.	July 31, 1934
1,969,169	Eichmann, T.	August 7, 1934
1,969,703	Cribb, G. D. G. and Witby, W. H.	August 7, 1934
1,971,106	Hasche, R. L.	August 21, 1934
1,972,240	Rufener, H. and Eichmann, T.	September 4, 1934
1,974,478	Weber, G.	September 25, 1934
1,974,681	Maiuri, G.	September 25, 1934
1,974,791	Belt, J. S. and Cady, H. P.	September 25, 1934
1,976,777	Goosmann, J. C.	October 16, 1934
1,978,508	Reich, G. T.	October 30, 1934
1,979,556	Jones, C. L. and Fitzpatrick, W. H.	November 6, 1934
1,981,675	Stapp, P.	November 20, 1934
1,984,249–50	Chamberlain, J. R.	December 11, 1934

Austria:

114,103	Lejune, F.	March 15, 1929
119,947	Hamburger, Hermann and Hamburger, Hugo	June 15, 1930

Belgium: (Includes distribution and storage).

353,014	Hessling, W.	July 23, 1928
355,511	Dryice Corp. of America	November 5, 1928
356,242	Linde's Eismachinen A.–G.	1928
357,269	Escher, Wyss and Cie	1928
357,643	Mid. Europ. Octr. Maatsch.	January 25, 1929
359,300	L'Acide Carb. Pur.	March 26, 1929
359,699	Solid Carbonic Co.	April 9, 1929
363,100	L'Acide Carb. Pur.	August 19, 1929
364,840	Stapp-Munchen	October 26, 1929
365,199	Stapp-Munchen	November 9, 1929

Brazil:

18,617	Mid. Europ. Octr. Maatsch	July 8, 1930

Great Britain:

2,450	Elworthy, E. G.	July 26, 1906
7,436	Elworthy, H. S.	February 15, 1895
10,378	Hall, L. B.	March 23, 1911
13,684	Tichborne, C. R. C.	August 3, 1892
27,576	Read, H. V. R.	1909
237,681	Slate, T. B.	May 23, 1924
294,584	Hessling, W.	July 26, 1927
294,614	Hessling, W.	July 27, 1927
298,792	Dryice Corp. of America	November 15, 1927
298,910	Hessling, W.	October 15, 1927
301,741	Ges. fur Linde's Eismachinen A.–G.	December 15, 1927
302,070	Dryice Corp. of America	January 17, 1928
302,359	Hessling, W.	December 15, 1927
304,958	DuBois, E.	April 3, 1928
312,231	Cole, H. W. and McLaren, M. W.	May 28, 1928
314,371	Mid. Europ. Octr. Maatsch.	June 26, 1928
322,807	Mortimer, J. E.	September 14, 1928
327,414	Solid Carbonic Co., Ltd.	December 31, 1928
329,772	Solid Carbonic Co., Ltd.	February 15, 1929
331,077	Dryice Equipment Corp.	June 13, 1929

Great Britain:

No.		
333,212	Peggs, K. C.	May 6, 1929
341,361	A.-G. für Kohlensäure-Industrie	April 27, 1929
343,012	Stapp, P.	November 7, 1929
345,229	Rudd, H. B.	November 17, 1928
347,050	Machinenfabrik Esslingen and Stoffels, J.	September 20, 1929
348,581	Fievet, H.	February 13, 1930
350,532	Jones, C. L. and Small, J. D.	March 28, 1929
353,014	Frankl, M.	April 16, 1929
355,602	Cribb, G. D. G.	November 18, 1930
355,923	Frankl, M.	August 19, 1929
358,820	Brotherhood, P., Dunkerley, H. M. and Carbon Dioxide Co. Ltd.	December 24, 1930
360,166	Priestley, W. C.	October 18, 1930
363,827	Small, J. D.	December 19, 1929
363,870	Grison, J.	January 28, 1931
364,322	Brotherhood, P., Dunkerley, H. M. and The Carbon Dioxide Co. Ltd.	December 23, 1930
367,492	Weber, G.	February 25, 1932
368,364	Rust, R. R. and Jones, C. L.	February 29, 1932
369,629	Comer, W. T.	March 23, 1932
378,490	Smith, W. L.	August 8, 1932
389,475	Foster, F. H. and Priestley, W. C.	March 13, 1933
394,039	Brier, H. and Brier, J. H.	June 22, 1933
404,833	Ges. fur Linde's Eismachinen A.-G.	January 25, 1934
408,458	Cribb, G. D. G. and Whitby, W. H.	April 12, 1934
408,459	Mid. Europ. Octr. Maatsch.	April 12, 1934
415,659	Maiuri Refrig. Patents Ltd. and Maiuri, G.	August 30, 1934

Canada:

285,166	Martin, J. W., Jr.	November 27, 1928
285,526	Josephson, W. S.	December 11, 1928

Cuba:

8,989	Cole, H. W. and McLaren, M. W.	October 23, 1929

Czecho-Slovakia:

4,857	Hessling, W.	July 25, 1928
4,890	Lejeune, F.	July 10, 1929

France:

642,057	Soc. Anon. des Ateliers	October 7, 1927
645,020	Dryice Corp. of America	November 29, 1927
649,395	Vieillard, J. H. J.	October 27, 1927
649,396	Vieillard, J. H. J.	October 28, 1927
649,483	Dryice Corp. of America	February 7, 1928
652,094	L'acide carb. pur (Soc. Anon.)	April 3, 1928
657,969	Hessling, W.	July 23, 1928
667,827	Mid. Europ. Octr. Maatsch.	January 1, 1929
668,298	Soc. Anon. des Ateliers	November 2, 1928
672,767	L'acide carb. pur.	April 6, 1929
672,825	The Solid Carbonic Co., Ltd.	April 8, 1929
673,129	Baumann, C.	April 16, 1929
677,429	La carbonique francaise	June 26, 1929
678,330	Lejeune, F.	July 12, 1929
705,190	I. G. Farbenind. A.-G.	November 6, 1930

No.		
France:		
739,816	Goosmann, J. C.	July 8, 1932
743,537	Hessling, W.	April 1, 1933
763,883	Carbonic Development Corp.	May 8, 1934
765,163	Office national ind. de l'azote	June 4, 1934
Germany:		
484,570	Hessling, W.	July 22, 1929
485,655	Hessling, W.	August 1, 1928
493,478	Hagstotz, W.	March 22, 1929
493,792	The Solid Carbonic Co., Ltd.	March 12, 1929
508,168	Machinenfabrik Esslingen	April 8, 1928
511,018	Machinenfabrik Esslingen	September 21, 1929
513,514	Fehrmann, K.	November 4, 1928
513,528	Ges. fur Linde's Eismachinen A.-G.	April 17, 1929
514,717	Mid. Europ. Octr. Maatsch.	September 4, 1928
535,647	Rudd, H. B.	November 16, 1929
537,764	Soc. la carbonique francaise	June 19, 1930
538,081	I. G. Farbenind. A.-G.	December 8, 1929
540,069	Grison, J. and Morton, C. R.	February 13, 1931
547,266	Dryice Corp. of America	November 18, 1927
550,474	Stapp, P.	September 13, 1928
564,757	Freundlich, F. A.	January 18, 1931
578.825	Stapp, P.	June 17, 1933
579,624	I. G. Farbenind. A.-G.	July 1, 1933
581,302	Dryice Corp. of America	July 27, 1933
581,727	Ges. fur Linde's Eismachinen A.-G.	August 1, 1933
599,367	Ges. fur Linde's Eismachinen A.-G.	July 3, 1934
Hungary:		
98,321	L'acide carb. pur.	September 4, 1928
98,928	Mid. Europ. Octr. Maatsch.	March 16, 1929
Italy:		
11,262	Pegna, E. G.	February 19, 1929
Japan:		
89,547	Okoti, M., Oyama, Y. and Inst. of Phys. and Chem. Research	December 13, 1930
90,628	Okoti, M. and Oyama, Y.	March 13, 1931
Switzerland:		
129,688	Hessling, W.	October 15, 1927
129,690	Hessling, W.	July 27, 1927
131,443	Escher Wyss and Cie.	January 18, 1928
136,481	Escher Wyss and Cie.	October 11, 1928
136,742	Escher Wyss and Cie.	October 29, 1928
137,132	Escher Wyss and Cie.	December 24, 1928
138,986	Baumann, C.	April 2, 1929
141,393	Escher Wyss and Cie.	October 19, 1929
143,815	Stapp, P.	November 7, 1929
154,917	Weber, G.	February 2, 1931

II. Applications of Solid Carbon Dioxide
(Methods and Apparatus)

United States:

No.		
1,592,993	Slate, T. B.	July 20, 1926
1,595,426	Slate, T. B.	August 10, 1926
1,634,089	Slate, T. B.	June 28, 1927
1,712,701	Hassensall, L. W.	May 14, 1929
1,735,082	Martin, J. W., Jr.	November 12, 1930
1,735,832	Martin, J. W., Jr.	November 12, 1930
1,736,706	Jones, A.	November 19, 1930
1,805,493	Martin, J. W., Jr.	May 19, 1931
1,825,073	Killeffer, D. H.	September 29, 1931
1,832,473	Payson, A. E. and Wetmore, M. P.	November 17, 1931
1,852,388	Wilcox, W. D.	April 5, 1932
1,855,313	Rudd, H. B.	April 26, 1932
1,870,684	Killeffer, D. H.	August 9, 1932
1,873,101	Banning, T. A., Jr.	August 23, 1932
1,873,364	Taylor, H. M.	August 23, 1932
1,874,091	Fahrney, E. H.	August 30, 1932
1,877,181	Killeffer, D. H.	September 13, 1932
1,877,187	Martin, J. W., Jr.	September 13, 1932
1,878,042	Wagner, J. S. et al	September 20, 1932
1,893,228	Copeman, L. G.	January 3, 1933
1,893,277	Eggleston, L. W.	January 3, 1933
1,893,483	Belt, J. S.	January 10, 1933
1,901,000	Robe, W. B.	March 14, 1933
1,924,059	Haskins, W.	August 22, 1933
1,933,256–7–8	Goosmann, J. C.	October 31, 1933
1,941,744	Heywood, F.	January 2, 1934
1,951,074	Warren, G. A. and Simpson, W. B., Jr.	March 13, 1934
1,951,758	Jones, C. L.	March 20, 1934
1,965,205	Smith, W. L.	July 3, 1934
1,975,177	Sherrick, S. T.	October 2, 1934
1,977,919	Reiss, L. P.	October 23, 1934

Austria:

136,291	Stark, L.	January 25, 1934

Great Britain:

301,764	Dehottay, H.	August 30, 1927

France:

661,487	Dryice Equipment Corp.	October 4, 1928
661,779	Dryice Equipment Corp.	October 3, 1928

Germany:

557,162	Wolfinger, A. and Surány, V.	April 15, 1930
558,072	Wolfinger, A. and Surány, V.	October 30, 1930
583,263	Alvarez, E. and Dauphin, A. L.,	August 31, 1933

III. Melting and Vaporizing of Solid Carbon Dioxide

No.		
United States:		
1,742,957	Stoffels, J.	January 7, 1930
1,760,953	Martin, J. W., Jr.	June 3, 1930
1,866,192	Comer, W. T.	July 5, 1932
1,928,396	Seck, F. C.	September 26, 1933
1,938,034	Lundy, T. F.	December 5, 1933
1,943,820	Goosmann, J. C.	January 16, 1934
1,951,758	Jones, C. L.	March 20, 1934
1,957,640	Grison, J.	May 8, 1934
1,972,771	Haid, W. S. and Terrell, P. A. H.	September 4, 1934
Great Britain:		
331,750	Machinenfabrik Esslingen and Stoffels, J.	September 3, 1929
366,239	Comer, W. T.	January 18, 1930
376,863	Lukàcs, E.	May 22, 1930
France:		
765,441	Mosonyi, J.	June 9, 1934
Germany:		
474,133	Machinenfabrik Esslingen	April 8, 1928
493,941	Hagstotz, W.	March 22, 1929
592,118	Stapp, P.	February 1, 1934
Switzerland:		
147,557	Hessling, W.	October 15, 1930

IV. Storage and Transportation

(Methods and Apparatus)

United States:		
1,786,161	Jones, C. L. and Small, J. D.	December 23, 1930
1,825,647	Martin, J. W., Jr.	September 29, 1931
1,885,769	Schlumbohm, P.	November 1, 1933
1,945,689	Hults, E. A.	February 6, 1934
1,980,727	Hults, E. A.	November 13, 1934
Great Britain:		
300,985	Martin, J. W., Jr.	November 22, 1927
388,212	Schlumbohm, P.	February 23, 1933
412,814	Dehottay, H.	July 5, 1934
Germany:		
561,815	Schlumbohm, P.	April 20, 1930
594,562	Geppert, H.	March 19, 1934
Switzerland:		
128,819	Hessling, W.	March 15, 1928
147,556	Hessling, W.	September 15, 1930

Tables of Physical Data Calculated to English Engineering Units

Saturated Liquid and Vapor

Table 71.—*Vapor Pressure of Carbon Dioxide in lbs. per sq. in.*
(g. = 980.665)
(By Meyers and Van Dusen)

°F.	0	1	2	3	4	5	6	7	8	9
−69.86	75.14	Triple point								
−60	94.75	92.60	90.49	88.42	86 39	84.38	82.42	80.48	78.59	76.72
−50	118.27	115.74	113.25	110.81	108.40	106.02	103.69	101.40	99.15	96.93
−40	145.87	142.91	140.00	137.14	134.31	131.53	128.80	126.11	123.45	120.84
−30	177.97	174.54	171.17	167.84	164.56	161.33	158.15	155.01	151.92	148.87
−20	215.02	211.08	207.19	203.36	199.57	195.85	192.17	188.55	184.97	181.45
−10	257.46	252.96	248.52	244.13	239.81	235.53	231.32	227.16	223.06	219.01
− 0	305.76	300.65	295.61	290.62	285.70	280.85	276.05	271.31	266.63	262.02
+ 0	305.8	310.9	316.2	321.5	326.8	332.2	337.7	343.3	348.9	354.6
10	360.4	366.2	372.1	378.1	384.1	390.2	396.4	402.6	409.0	415.4
20	421.8	428.4	435.0	441.7	448.4	455.3	462.2	469.2	476.3	483.4
30	490.6	497.9	505.3	512.8	520.3	528 0	535.7	543.5	551.3	559.3
40	567.3	575.5	583.7	592.0	600.4	608.9	617.5	626.1	634.9	643.7
50	652.7	661.7	670.8	680.0	689.4	698.8	708.3	717.9	727.6	737.5
60	747.4	757.4	767.5	777.7	788.1	798.6	809.1	819.8	830.6	841.5
70	852.5	863.6	874.9	886 2	897.7	909.3	921.1	933.0	945.0	957.1
80	969.3	981.7	994.2	1006.9	1019.7	1032.7	1045 7	1058.9		
87.98	1072.1	Critical point								

Table 72.—*Specific Volume of Carbon Dioxide Liquid in cu. ft. per lb.*
(Data of Plank and Kuprianoff)

°F.	0	1	2	3	4	5	6	7	8	9
−69.9	.01360	Triple point								
−60	.01384	.01381	.01378	.01376	.01373	.01371	.01369	.01366	.01363	.01361
−50	.01409	.01406	.01403	.01400	.01398	.01396	.01393	.01391	.01389	.01386
−40	.01437	.01433	.01430	.01427	.01425	.01422	.01419	.01416	.01414	.01411
−30	.01465	.01462	.01458	.01456	.01454	.01450	.01447	.01445	.01442	.01439
−20	.01498	.01494	.01491	.01488	.01485	.01481	.01478	.01475	.01472	.01468
−10	.01533	.01529	.01525	.01522	.01518	.01514	.01511	.01508	.01504	.01501
− 0	.01571	.01567	.01563	.01559	.01555	.01551	.01547	.01544	.01540	.01536
+ 0	.01571	.01575	.01579	.01583	.01587	.01592	.01597	.01601	.01605	.01609
+10	.01614	.01618	.01623	.01628	.01632	.01636	.01642	.01646	.01650	.01656
+20	.01662	.01667	.01672	.01678	.01684	.01689	.01695	.01701	.01707	.01713
+30	.01719	.01725	.01731	.01737	.01743	.01750	.01757	.01764	.01771	.01778
+40	.01786	.01794	.01801	.01809	.01817	.01825	.01834	.01842	.01852	.01860
+50	.01867	.01877	.01887	.01896	.01906	.01916	.01926	.01936	.01948	.01959
+60	.01970	.01982	.01997	.02009	.02012	.02035	.02049	.02064	.02079	.02093
+70	.02109	.02127	.02146	.02166	.02188	.02212	.02240	.02270	.02300	.02336
+80	.02370	.02414	.02458	.02504	.02556	.02619	.02686	.02794		
+87.8	.03453	Critical point								

TABLE 73.—*Specific Volume of Saturated Carbon Dioxide Vapor in cu. ft./lb.*

(Data of Plank and Kuprianoff)

°F.	0	1	2	3	4	5	6	7	8	9
−69.9	1.1570	Triple point								
−60	.9520	.9440	.9650	.9865	1.0100	1.0360	1.0590	1.0831	1.1095	1.1340
−50	.7500	.7670	.7840	.8000	.8180	.8350	.8520	.8690	.8875	.9055
−40	.6113	.6245	.6380	.6520	.6660	.6790	.6930	.7060	.7200	.7338
−30	.5025	.5127	.5210	.5315	.5420	.5530	.5650	.5760	.5880	.6000
−20	.4165	.4240	.4325	.4415	.4500	.4585	.4670	.4760	.4845	.4935
−10	.3465	.3530	.3590	.3666	.3725	.3795	.3865	.3940	.4015	.4090
− 0	.2905	.2958	.3012	.3065	.3118	.3173	.3228	.3285	.3345	.3405
+ 0	.2905	.2852	.2800	.2753	.2708	.2660	.2610	.2565	.2520	.2475
+10	.2435	.2395	.2350	.2310	.2274	.2232	.2195	.2158	.2120	.2082
+20	.2048	.2015	.1978	.1945	.1910	.1878	.1845	.1813	.1782	.1750
+30	.1720	.1690	.1663	.1635	.1605	.1578	.1550	.1522	.1495	.1468
+40	.1442	.1417	.1390	.1365	.1342	.1320	.1298	.1275	.1250	.1228
+50	.1204	.1185	.1163	.1142	.1122	.1111	.1080	.1060	.1038	.1013
+60	.0995	.0978	.0960	.0940	.0920	.0900	.0880	.0860	.0842	.0822
+70	.0800	.0780	.0760	.0740	.0720	.0700	.0680	.0667	.0640	.0620
+80	.0600	.0580	.0560	.0540	.0520	.0500	.0479	.0430		
+87.8	.0345	Critical point								

TABLE 74.—*Density of Liquid Carbon Dioxide in lbs./cu. ft.*

(Data of Plank and Kuprianoff)

°F.	0	1	2	3	4	5	6	7	8	9
−69.9	73.53	Triple point								
−60	72.27	72.40	72.53	72.65	72.78	72.91	73.04	73.17	73.30	73.42
−50	70.96	71.10	71.23	71.36	71.49	71.62	71.75	71.88	72.01	72.14
−40	69.61	69.75	69.88	70.02	70.15	70.28	70.42	70.55	70.68	70.82
−30	68.21	68.35	68.49	68.63	68.77	68.91	69.05	69.19	69.33	69.47
−20	66.76	66.91	67.06	67.20	67.35	67.49	67.64	67.79	67.93	68.07
−10	65.25	65.41	65.56	65.71	65.86	66.01	66 26	66.31	66.46	66.61
− 0	63.65	63.82	63.98	64.14	64.30	64.46	64.62	64.78	64.93	65.09
+ 0	63.65	63.48	63.31	63.15	62.98	62.81	62.64	62.47	62.30	62.13
+10	61.96	61.78	61.60	61.42	61.23	60.04	60 85	60.67	60.50	60.32
+20	60.13	59.93	59.74	59.54	59.35	59.17	58.98	58.78	58.58	58.37
+30	58.16	57.95	57.73	57.52	57.31	57.10	56.88	56.66	56.44	56.21
+40	55.98	55.75	55.52	55.29	55.06	54.83	54.60	54.35	54.09	53.83
+50	53.56	53.30	53.03	52.76	52.50	52.23	51.95	51.66	51.36	51.06
+60	50.80	50.50	50.20	49.90	49.60	49.26	48.90	48.53	48.11	47.75
+70	47.35	46.95	46.50	46.05	45.60	45.10	44.60	44.06	43.51	42.96
+80	42.36	41.75	41.05	40.30	39.50	38.50	37.23	35.20		
+87.8	28.96	Critical point								

TABLE 75.—*Density of Saturated Carbon Dioxide Vapor in lbs./cu. ft.*

(Data of Plank and Kuprianoff)

°F.	0	1	2	3	4	5	6	7	8	9
−69.9	.861	Triple point								
−60	1.085	1.062	1.039	1.016	.993	.970	.947	.924	.904	.885
−50	1.335	1.310	1.285	1.260	1.232	1.205	1.180	1.155	1.130	1.107
−40	1.636	1.605	1.574	1.542	1.510	1.480	1.450	1.420	1.390	1.361
−30	1.985	1.948	1.910	1.875	1.840	1.805	1.770	1.735	1.700	1.668
−20	2.395	2.350	2.310	2.270	2.230	2.182	2.142	2.101	2.061	2.023
−10	2.880	2.830	2.780	2.734	2.685	2.637	2.587	2.535	2.485	2.440
− 0	3.450	3.390	3.330	3.270	3.209	3.144	3.082	3.037	2.985	2.930
+ 0	3.450	3.510	3.570	3.630	3.694	3.758	3.820	3.890	3.965	4.040
+10	4.115	4.190	4.260	4.330	4.401	4.480	4.560	4.640	4.720	4.800
+20	4.890	4.978	5.060	5.144	5.230	5.320	5.415	5.510	5.600	5.700
+30	5.800	5.905	6.012	6.110	6.220	6.335	6.450	6.570	6.690	6.815
+40	6.935	7.054	7.180	7.310	7.440	7.570	7.710	7.850	8.000	8.150
+50	8.303	8.458	8.618	8.778	8.940	9.100	9.280	9.470	9.660	9.864
+60	10.07	10.28	10.48	10.70	10.92	11.14	11.36	11.60	11.87	12.14
+70	12.44	12.76	13.08	13.42	13.86	14.22	14.58	14.98	15.40	15.92
+80	16.44	16.98	17.58	18.20	18.92	19.78	20.88	23.40		
+87.8	28.96	Critical point								

TABLE 76.—*Enthalpy of Liquid Carbon Dioxide in B. t. u./lb.*

(Data of Plank and Kuprianoff)

°F.	0	1	2	3	4	5	6	7	8	9
−69.9	129.5	Triple point								
−60	134.1	133.6	133.1	132.7	132.3	131.8	131.3	130.9	130.4	129.9
−50	138.6	138.2	137.7	137.2	136.8	136.4	135.9	135.4	135.0	134.6
−40	143.2	142.8	142.3	141.8	141.4	140.9	140.5	140.0	139.6	139.1
−30	147.9	147.4	147.0	146 5	146.0	145 6	145.1	144.6	144.2	143.7
−20	152.4	152.0	151.5	151.1	150 6	150.2	149.7	149.3	148.8	148.3
−10	157.1	156.6	156 1	155 8	155.3	154.9	154.4	154.0	153.5	153.0
− 0	162.0	161.6	161.1	160.6	160.1	159.6	159.1	158.7	158.2	157.7
+ 0	162.0	162 5	163.0	163.5	164.0	164.5	165.0	165 5	166.1	166.6
+10	167.2	167.7	168.2	168.8	169.4	170.0	170.5	171.1	171.7	172.2
+20	172.8	173.4	174.0	174.5	175.0	175.7	176.3	176.9	177.5	178.2
+30	178.8	179.4	180.0	180.6	181.2	181.9	182.5	183.1	183.7	184.4
+40	185.0	185.6	186.3	187.0	187.6	188.2	188.9	189.6	190.3	191.0
+50	191.7	192.4	193.1	193.8	194.5	195.2	196.0	196.7	197.4	198.2
+60	198.9	199.7	200.4	201 2	202.0	202 8	203.6	204.4	205.2	206.1
+70	206.9	207.8	208.8	209.7	210.7	211.8	212.8	213.9	215.0	218.1
+80	217.2	218.5	219 8	221.2	222.8	224.6	226.6	230.8		
+87.8	240.3	Critical point								

TABLE 77.—*Enthalpy of Carbon Dioxide Vapor in B.t.u./lb.*

(Data of Plank and Kuprianoff)

°F.	0	1	2	3	4	5	6	7	8	9
−69.9	279.16	Triple point								
−60	279.90	279.83	279.75	279.68	279.62	279.55	279.48	279.40	279.37	279.20
−50	280.52	280.46	280.40	280.32	280.28	280.23	280.18	280.10	280.03	279.97
−40	281.11	281 05	280.98	280.83	280.88	280.82	280.78	280.72	280.65	280.60
−30	281.54	281 50	281.47	281.43	281.38	281.34	281.28	281.25	281.20	281.16
−20	281.87	281.84	281.81	281.78	281.75	281.71	281.67	281.64	281.61	281.57
−10	282.05	282.04	282.03	282 01	281.99	281.97	281.95	281.93	281.91	281.89
− 0	282.10	282.10	282.10	282.10	282.10	282.09	282.09	282.08	282.07	282.06
+ 0	282.10	282.09	282.08	282.08	282.07	282.06	282.05	282.04	282.02	282.00
+10	281.98	281.96	281.94	281.91	281.88	281.85	281.82	281.79	281.76	281.72
+20	281.68	281.64	281.59	281.54	281.47	281.40	281.33	281.27	281.19	281.10
+30	281.01	280.92	280 85	280.76	280.66	280.56	280.45	280.35	280.24	280.12
+40	279.97	279.81	279.67	279.53	279.37	279.20	279.02	278.83	278.65	278.46
+50	278.26	278 03	277.78	277.50	277.20	276.90	276.60	276 30	276.00	275.71
+60	275.36	275.00	274.65	274.28	273.90	273.47	273.04	272.57	272.07	271.54
+70	270.97	270.30	269.65	268.80	267.90	267.00	266.10	265.19	264.25	263.25
+80	262.18	261.00	259.80	258.60	257.15	255.50	253.71	250.00		
+87.8	240.30	Critical point								

TABLE 78.—*Heat of Vaporization of Carbon Dioxide in B. t. u./lb.*

(Data of Plank and Kuprianoff)

°F.	0	1	2	3	4	5	6	7	8	9
−69 9	149.6	Triple point								
−60	145.8	146.2	146.6	146.9	147.3	147.7	148.1	148.5	148.9	149.3
−50	141.9	142.3	142.6	143.0	143.4	143.8	144.2	144.6	145.0	145.4
−40	137.8	138.2	138.6	139.0	139.4	139.8	140.2	140.6	141.1	141.5
−30	133.7	134.1	134.5	135.0	135.4	135.8	136.2	136.6	137.0	137.4
−20	129.5	129.9	130.3	130.8	131.2	131.7	132.1	132.5	132.9	133.3
−10	124.9	125.4	125.8	126.3	126.8	127.2	127.7	128.2	128.6	129.0
− 0	120.0	120.5	121.0	121.5	122.0	122.5	123.0	123.5	124.0	124.5
+ 0	120.0	119.5	119.0	118.5	118.0	117.5	117.0	116.5	116.0	115.4
+10	114.9	114.3	113.7	113.1	112.5	112.0	111.4	110.8	110.2	109.6
+20	109.0	108.4	107.7	107.0	106.4	105.7	105.0	104.4	103.7	103.1
+30	102.4	101.7	101.0	100.3	99.60	98.90	98.15	97.40	96.60	95.82
+40	95.04	94.23	93.43	92.63	91.83	90.93	90.13	89.28	88.40	87.50
+50	86.56	85.61	84.65	83.68	82.70	81.70	80.70	79.68	78.60	77.53
+60	76.45	75.55	74.40	73.23	72.00	70.73	69.44	68.13	66.78	65.38
+70	63.90	62.25	60.55	58.80	57.00	55.20	53.30	51.35	49.40	47.40
+80	45.30	43.00	40.50	37.70	34.40	30.85	27.09	20.00		
+87.8	00.00	Critical point								

TABLE 79.—*Entropy of Saturated Liquid Carbon Dioxide*

(Data of Plank and Kuprianoff)

°F.	0	1	2	3	4	5	6	7	8	9
−69.9	.8885	Triple point								
−60	.8997	.8986	.8975	.8964	.8952	.8940	.8928	.8917	.8906	.8895
−50	.9109	.9098	.9087	.9076	.9065	.9054	.9043	.9032	.9020	.9009
−40	.9218	.9208	.9197	.9186	.9175	.9164	.9153	.9142	.9131	.9120
−30	.9324	.9314	.9303	.9293	.9283	.9272	.9261	.9250	.9240	.9229
−20	.9428	.9418	.9408	.9397	.9386	.9376	.9365	.9354	.9344	.9334
−10	.9532	.9521	.9511	.9501	.9490	.9480	.9470	.9459	.9449	.9439
− 0	.9637	.9626	.9615	.9605	.9594	.9584	.9574	.9564	.9553	.9542
+ 0	.9637	.9648	.9659	.9669	.9680	.9690	.9701	.9711	.9721	.9732
+10	.9743	.9754	.9765	.9776	.9787	.9798	.9809	.9820	.9831	.9842
+20	.9854	.9856	.9878	.9890	.9902	.9913	.9925	.9936	.9942	.9959
+30	.9971	.9982	.9996*	1.0007	1.0018	1.0030	1.0041	1.0053	1.0066	1.0078
+40	1.0090	1 0103	1.0116	1.0128	1.0140	1.0152	1.0165	1.0177	1.0190	1.0204
+50	1.0218	1.0231	1.0244	1.0257	1.0270	1.0284	1.0298	1.0312	1.0326	1.0340
+60	1.0354	1.0368	1.0382	1.0396	1.0410	1.0424	1.0439	1.0454	1.0468	1.0484
+70	1.0500	1.0517	1.0534	1.0551	1.0569	1.0588	1.0608	1.0628	1.0648	1.0667
+80	1.0687	1.0710	1.0732	1.0756	1.0782	1.0817	1.0854	1.0914		
+87.8	1.1098	Critical point								

*NOTE: The data of Plank and Kuprianoff are based on a value of 1.00000 Clausius at 32° F. a smooth curve, however, gives a value of .9996 Clausius at this temperature and this value is therefore used in this table.

TABLE 80.—*Entropy of Saturated Carbon Dioxide Vapor*

(Data of Plank and Kuprianoff)

°F.	0	1	2	3	4	5	6	7	8	9
−69 9	1.2724	Triple point.								
−60	1.2647	1.2655	1.2662	1.2670	1.2678	1.2685	1.2693	1.2700	1.2709	1.2717
−50	1 2572	1.2579	1.2586	1.2593	1.2601	1.2609	1.2616	1.2624	1.2631	1.2639
−40	1.2503	1.2509	1.2515	1.2522	1.2529	1 2536	1.2543	1.2550	1.2557	1.2565
−30	1.2437	1.2443	1 2450	1 2456	1.2463	1 2469	1.2476	1.2483	1.2489	1.2496
−20	1.2373	1.2379	1.2385	1.2392	1.2398	1.2405	1.2411	1.2417	1 2423	1.2430
−10	1.2309	1.2315	1.2322	1.2328	1.2335	1.2341	1.2348	1.2354	1.2360	1.2367
− 0	1.2248	1.2254	1.2260	1.2266	1.2272	1.2279	1.2285	1 2291	1.2297	1.2303
+ 0	1.2248	1 2242	1.2236	1.2230	1 2224	1 2218	1.2212	1.2206	1.2200	1.2194
+10	1.2188	1.2182	1.2176	1.2170	1.2163	1.2157	1.2151	1.2145	1.2139	1.2133
+20	1.2127	1.2121	1.2115	1.2109	1.2103	1.2097	1.2091	1.2085	1.2079	1.2073
+30	1.2067	1.2061	1 2055	1.2048	1.2041	1.2033	1.2025	1.2017	1.2009	1.2001
+40	1.1993	1.1985	1.1977	1.1971	1.1963	1.1956	1.1948	1.1940	1.1933	1.1925
+50	1.1917	1.1908	1.1899	1.1890	1.1882	1.1853	1.1863	1.1854	1.1945	1.1835
+60	1.1824	1.1814	1.1803	1.1792	1.1781	1.1770	1.1758	1.1746	1.1734	1.1718
+70	1.1703	1.1688	1.1673	1 1658	1.1641	1.1623	1.1604	1.1585	1.1565	1.1545
+80	1.1523	1.1500	1.1476	1.1452	1.1423	1.1390	1.1351	1.1280		
+87.8	1.1098	Critical point.								

SATURATED SOLID AND VAPOR

TABLE 81.—*Vapor Pressure of Solid Carbon Dioxide in lbs./in.² (absolute)*

(Data of Plank and Kuprianoff)

°F.	0	1	2	3	4	5	6	7	8	9
−69.9	75.08	Triple point.								
−70	74.90	72 10	69.40	66.75	64.25	61.75	59.44	57.20	55.00	52.80
−80	50.70	48 75	46.85	45.00	43.30	41.67	40.05	38.50	37.00	35.50
−90	34.05	32.60	31.20	29.90	28.72	27.63	26.54	25.45	24.40	23.35
−100	22 34	21.35	20.40	19.48	18 59	17.80	17.00	16.30	15.61	14.92
−110	14.22	13.60	13.00	12.34	11.76	11.20	10.67	10.18	9 70	9.27
−120	8.85	8.46	8.08	7.70	7.33	6.98	6.63	6.29	5.97	5.67
−130	5.39	5.11	4.85	4.61	4.38	4.16	3.95	3.75	3.55	3.36
−140	3.19	3.03	2.87	2.72	2.57	2.43	2.28	2.14	2.01	

TABLE 82.—*Specific Volume of Solid Carbon Dioxide in cu. ft./lb.*
(Data of Maass and Barnes)

°F.	0	1	2	3	4	5	6	7	8	9
− 69.9	0.01059	Triple point.								
− 70	0.01059	0.01058	0.01057	0.01056	0.01055	0.01054	0.01053	0.01052	0.01051	0.01050
− 80	.01049	.01048	.01047	.01046	.01045	.01044	.01043	.01042	.01041	.01040
− 90	.01040	.01039	.01038	.01037	.01036	.01036	.01035	.01034	.01033	.01032
−100	.01032	.01031	.01030	.01030	.01029	.01028	.01027	.01026	.01026	.01025
−110	.01024	.01024	.01023	.01022	.01022	.01021	.01020	.01020	.01019	.01018
−120	.01018	.01017	.01017	.01016	.01015	.01015	.01014	.01014	.01013	.01013
−130	.01012	.01012	.01011	.01011	.01010	.01009	.01009	.01008	.01008	.10007
−140	.01007	.01007	.01006	.01006	.01006	.01005	.01005	.01004	.01004	.01004

TABLE 83.—*Specific Volume of Saturated Carbon Dioxide Vapor over Solid in cu. ft./lb.*
(Data of Plank and Kuprianoff)

°F.	0	1	2	3	4	5	6	7	8	9
− 69.9	1.16	Triple point.								
− 70	1.17	1.21	1.25	1.30	1.35	1.40	1.46	1.51	1.56	1.63
− 80	1.70	1.76	1.83	1.91	1.99	2.07	2.15	2.24	2.33	2.42
− 90	2.52	2.63	2.74	2.85	2.97	3.09	3.22	3.36	3.50	3.65
−100	3.80	3.97	4.14	4.32	4.52	4.72	4.93	5.25	5.37	5.60
−110	5.85	6.10	6.37	6.65	6.95	7.27	7.60	7.97	8.34	8.73
−120	9.13	9.58	10.04	10.51	11.02	11.56	12.12	12.70	13.32	14.00
−130	14.74	15.48	16.20	16.98	17.80	18.70	19.70	20.78	21 96	23.11
−140	24.50	25.95	27.50	29.10	30.75	32.40	34.10	35.80	37.42	

TABLE 84.—*Density of Solid Carbon Dioxide in lb. cu./ft.*
(Data of Maass and Barnes)

°F.	0	1	2	3	4	5	6	7	8	9
− 69.9	94.42	Triple point.								
− 70	94.43	94.53	94.63	94.73	94.83	94.92	95.01	95 10	95.19	95.28
− 80	95.37	95.46	95.55	95.63	95.72	95.80	95.88	95.97	96.05	96.13
− 90	96.21	96.29	96.37	96.44	96.52	96.59	96.66	96.74	96.82	96.89
−100	96.96	97.03	97.10	97.17	97.24	97.31	97.38	97.44	97.51	97.57
−110	97.64	97.70	97.77	97.83	97.89	97.95	98.01	98.07	98.13	98.19
−120	98.25	98.31	98.36	98.41	98.47	98.52	98.57	98.62	98.67	98.72
−130	98.77	98.82	98.87	98.92	98.96	99.01	99.06	99.10	99.14	99.19
−140	99.23	99.27	99.32	99.36	99.41	99.45	99.49	99.54	99.58	99.62

TABLE 85.—*Density of Saturated Vapor over Solid Carbon Dioxide in lb./cu. ft.*

°F.	0	1	2	3	4	5	6	7	8	9
− 69.9	0.8640	Triple point.								
− 70	0.8600	0.8250	0.7920	0.7625	0.7360	0.7100	0.6848	0.6600	0.6350	0.6100
− 80	.5865	.5630	.5425	.5220	.5020	.4832	.4650	.4480	.4310	.4130
− 90	.3960	.3805	.3655	.3510	.3365	.3210	.3060	.2930	.2815	.2710
−100	.2605	.2505	.2410	.2316	.2225	.2130	.2045	.1960	.1875	.1795
−110	.1710	.1635	.1567	.1500	.1435	.1372	.1312	.1252	.1297	.1145
−120	.1093	.1044	.0995	.0950	.0905	.0862	.0822	.0782	.0745	.0710
−130	.0679	.0647	.0615	.0585	.0557	.0529	.0504	.0479	.0455	.0433
−140	.0410	.0390	.0372	.0354	.0337	.0320	.0303	.0285	.0267	.0250

TABLE 86.—*Enthalpy of Solid Carbon Dioxide in B. t. u./lb.*
(Data of Plank and Kuprianoff)

°F.	0	1	2	3	4	5	6	7	8	9
− 69.9	45.38	Triple point.								
− 70	45.22	44.82	44.40	43.97	43.54	43.11	42.68	42.22	41.77	41.32
− 80	40.87	40.42	39.98	39.54	39.11	38.68	38.28	37.88	37.48	37.08
− 90	36.69	36.32	35.96	35.61	35.26	34.91	34.57	34.23	33.89	33.55
−100	33.23	32.91	32.59	32.27	31.96	31.65	31.34	31.03	30.72	30.41
−110	30.11	29.82	29.53	29.24	28.95	28.66	28.37	28.08	27.79	27.51
−120	27.23	26.96	26.67	26.39	26.11	25.83	25.55	25.27	24.99	24.72
−130	24.46	24.18	23.91	23.64	23.37	23.10	22.82	22.55	22.28	22.01
−140	21.75	21.48	21.21	20.94	20.67	20.40	20.13	19.86	19.59	19.32

TABLE 87.—*Enthalpy of Saturated Carbon Dioxide Vapor in B. t. u./lb.*

(Data of Plank and Kuprianoff)

°F.	0	1	2	3	4	5	6	7	8	9
− 69.9	279.16	Triple point.								
− 70	279.16	279.15	279.15	279.14	279.13	279.12	279.11	279.10	279.07	279.04
− 80	279.00	278.96	278.92	278.87	278.82	278.77	278.71	278.65	278.59	278.52
− 90	278.45	278.38	278.30	278.22	278.14	278.06	277.98	277.89	277.80	277.71
−100	277.62	277.52	277.42	277.31	277.21	277.10	276.99	276.88	276.77	276.65
−110	276.53	276.41	276.29	276.16	276.04	275.91	275.78	275.65	275.53	275.40
−120	275.28	275.15	275.02	274.88	274.74	274.51	274.47	274.34	274.21	274.07
−130	273.93	273.79	273.65	273.61	273.37	273.23	273.08	272.93	272.78	272.63
−140	272.48	272.33	272.18	272.03	271.87	271.70	271.53	271.35	271.17	270.98

TABLE 88.—*Heat of Sublimation of Solid Carbon Dioxide in B. t. u./lb.*

(Data of Plank and Kuprianoff)

°F.	0	1	2	3	4	5	6	7	8	9
− 69.9	233.78	Triple point.								
− 70	233.82	234.26	234.70	235.14	235.58	236.02	236.43	236.86	237.28	237.70
− 80	238.12	238.52	238.91	239.30	239.69	240.08	240.45	240.80	241.16	241.48
− 90	241.79	242.08	242.36	242.63	242.88	243.14	243.40	243.66	243.90	244.14
−100	244.38	244.60	244.82	245.03	245.24	245.43	245.63	245.83	246.01	246.19
−110	246.38	246.57	246.74	246.92	247.08	247.25	247.41	247.57	247.73	247.88
−120	248.03	248.18	248.32	248.46	248.60	248.74	248.88	249.01	249.15	249.28
−130	249.42	249.55	249.68	249.81	249.93	250.05	250.17	250.29	250.42	250.54
−140	250.65	250.77	250.89	251.00	251.12	251.24	251.35	251.47	251.58	251.69

TABLE 89.—*Entropy of Solid Carbon Dioxide*

(Data of Plank and Kuprianoff)

°F.	0	1	2	3	4	5	6	7	8	9
− 69.9	0.6725	Triple point.								
− 70	0.6724	0.6713	0.6702	0.6690	0.6679	0.6667	0.6655	0.6643	0.6631	0.6619
− 80	0.6608	0.6596	0.6584	0.6573	0.6562	0.6551	0.6540	0.6530	0.6519	0.6509
− 90	0.6498	0.6488	0.6478	0.6469	0.6459	0.6450	0.6440	0.6431	0.6421	0.6412
−100	0.6403	0.6394	0.6385	0.6376	0.6367	0.6358	0.6350	0.6341	0.6332	0.6323
−110	0.6314	0.6307	0.6299	0.6290	0.6282	0.6274	0.6265	0.6257	0.6248	0.6240
−120	0.6232	0.6224	0.6216	0.6208	0.6199	0.6191	0.6183	0.6175	0.6167	0.6158
−130	0.6150	0.6141	0.6133	0.6124	0.6116	0.6108	0.6099	0.6091	0.6082	0.6074
−140	0.6065	0.6057	0.6048	0.6039	0.6031	0.6022	0.6013	0.6004	0.5996	0.5987

TABLE 90.—*Entropy of Saturated Carbon Dioxide Vapor*

(Data of Plank and Kuprianoff)

°F.	0	1	2	3	4	5	6	7	8	9
− 69.9	1.2724	Triple point.								
− 70	1.2726	1.2741	1.2757	1.2772	1.2788	1.2803	1.2819	1.2835	1.2851	1.2867
− 80	1.2883	1.2899	1.2914	1.2930	1.2945	1.2960	1.2976	1.2992	1.3008	1.3024
− 90	1.3040	1.3056	1.3071	1.3087	1.3103	1.3120	1.3136	1.3151	1.3167	1.3183
−100	1.3199	1.3215	1.3231	1.3248	1.3264	1.3280	1.3296	1.3313	1.3330	1.3346
−110	1.3363	1.3380	1.3398	1.3415	1.3431	1.3448	1.3467	1.3484	1.3501	1.3519
−120	1.3536	1.3554	1.3572	1.3590	1.3608	1.3627	1.3645	1.3663	1.3681	1.3700
−130	1.3718	1.3736	1.3755	1.3773	1.3792	1.3811	1.3831	1.3850	1.3870	1.3889
−140	1.3909	1.3929	1.3950	1.3970	1.3990	1.4010	1.4030	1.4050	1.4070	1.4090

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