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BIBLIOTEKA POLITECHNIKI ŚLĄSKIEJ

Carbon and Hydrogen

IT IS a privilege to present in this issue the first authoritative discussion in the American technical press on the hydrogenation of petroleum, a subject of immediate interest wherever one meets those engaged in the refining of petroleum or dependent upon its products. Regarded by its sponsors as supplementary to cracking in maintaining the supply of gasoline, the most pessimistic comment on the part of others is directed toward the present increase in cost of installation as compared with cracking processes.

To us the important point is that, whether cracked or hydrogenated or manipulated by other processes, whatever their name, crude oil should now be considered an abundant, conveniently transported source of carbon and hydrogen atoms, available to be recombined practically at will to produce compounds to meet the demand of the moment. Some day some pessimist will present a row of figures reaching astronomical proportions, and meaningless because of their magnitude, to emphasize how wasteful the world has been during the years when crude oil was grossly wasted before it was realized that to use it to greatest advantage it had to be first reduced to the atoms of carbon and hydrogen.

Modifying phrases differentiating between the cracking processes are going out of fashion. Cracking in the liquid phase, in the vapor phase, or in the gaseous phase is now regarded as just cracking, since it may be difficult to say just to what extent liquid or vapor or gas may be present. The results are far-reaching, however, when one remembers the hydrocarbon gases that are made available. In one system of cracking every 25 cubic feet of ethylene produced is accompanied by 16 cubic feet of propylene. What shall be done with these gases available in great quantity? Not only do they begin to affect city gas supply, but they beckon the chemist who would see in them raw materials for many processes. Just what will you do with ethylene at, say, two cents a pound, and may not the availability of propylene in advantageous quantities and at attractive prices revive considerations of synthetic rubber or rubberlike compounds by the isoprene route?

Isobutane, tertiary butane, butadiene—but why prolong the list? Once more we point out that it is carbon and hydrogen, and the question is, what would you make from them? That is what the future seems to offer. We are told that through hydrogenation the most astonishing things are possible, and possible commercially whenever the demand justifies. Of some importance now, its greatest importance would seem to be in the not very distant future. Irrespective of the characteristics of the crude oil, not only gasoline and kerosene to order, but lubricants of special qualifications seem possible.

All this means much to the chemical technologist. For some time to come the man at the wheel will remember most of all the possibility of continuing with engines operated by petroleum products for a longer time than would be possible if these new advances had not guaranteed the more complete and efficient use of crude oil—that natural resource which more than any other has shaped the world of our time sociologically, industrially, and even politically.

The New Directors

THE unanimity of the Council vote in recommending to the SOCIETY the changes in the Constitution and By-laws reported in our NEWS EDITION of September 20 indicates the certainty that they will be adopted by the SOCIETY. It is imperative that the membership vote with all promptness, if the SOCIETY is to derive the utmost benefit from the addition of four new Directors to our board.

The discussion at Cincinnati emphasized the growing business of the AMERICAN CHEMICAL SOCIETY, with a budget approaching $600,000 annually, and the need for increasing the Board of Directors, in order to distribute the burden over a larger number of pairs of shoulders and to facilitate such organization as the board might care to set up, that items of particular importance might have the special attention of committees created for the purpose.

The increase in the size of the board with these major objectives quite obviously is not a criticism of the service rendered by successive boards during the past, all of which have contributed to the present financial strength of the SOCIETY and have made possible such a financial record as was reported in detail in the NEWS EDITION of July 20. This record has spontaneously called forth the commendation of a number of business men, who find in the conduct of the SOCIETY'S affairs the reflection of a business policy which they approve.

In due course the nominating committee, appointed in accordance with the new constitutional provisions, will offer eight names, to which any group of twenty-five members in good standing may add additional names of men, all chosen with special regard to their business experience and ability. We have many such men in the AMERICAN CHEMICAL SOCIETY, who combine demonstrated success in financial affairs with the keenest interest in science and in those things which science strives to accomplish without regard to monetary returns. Of the group nominated only four can be elected. A wise membership, however, will not pass by the others placed in nomination for this election when filling future vacancies in the Board of Directors. If the constitutional changes accomplish nothing more than to focus thought upon the necessity of choosing men of such qualifications and the attention of the membership upon those of their number who are especially fitted to discharge the duties which are the Directors, the work which has been necessary to bring about this change in our plan of organization will yield handsome returns.

It has come to be recognized that, rather than a conflict between science and business, there is necessarily a close community of interest and a mutual interdependence. A man may be both a sound chemist and a successful financier. He may be either without the other, but among the many thousands constituting our membership there will be at all

times a sufficient number of those who possess the qualifications we want in our Board of Directors to assure the SOCIETY in perpetuity the soundest kind of business direction.

President McPherson's Address

THE presidential address at Cincinnati was much appreciated by a large audience and was commented upon as a constructive effort, carefully prepared and impressively presented. It was well received by the daily press, but one or two headline writers appear to have misconstrued one of the points made by President McPherson with regard to the popularization of our science. While it is true that a warning was raised against the overpopularization of chemistry, this pertained not to the non-technically trained but to the technical classroom. No one has a higher appreciation than President McPherson of what has been done to interest a public not technically trained in what science really means to it and its obligation to support science, both pure and applied. Evidence of this is to be found in his own writings, in his active interest in the Prize Essay Contest, and in many of his public utterances. When it comes to the teaching of chemistry, particularly to those who have chosen it as a career, no one is more concerned than our President in a proper emphasis upon fundamentals, and here it is that he fears the inclination on the part of some merely to present interesting facts rather than to inculcate the scientific habit of thought.

Surely there can be no real difference of opinion with this point of view. The student of chemistry finds in the writings and addresses prepared for the general public occasional facts of interest to him, but naturally his own thinking is along quite different lines and with an altogether different purpose. Everywhere we find stressed the necessity for a thorough grounding in fundamentals, if the student is at all serious about his science, whether it be chemistry, physics, mathematics, or any of the other sciences. There is a time and a place, so we are told, for all things, and chemistry must be presented always with proper regard for the ultimate goal. There was no ambiguity on these or other points in our President's address.

Dramatize Your Products

ONE of the most important events in American chemistry now visible on the horizon is the next Exposition of Chemical Industries, which will be held the week of May 4, 1931, in the Grand Central Palace, New York City. Already farsighted manufacturers are making their plans and much of the choice space is under contract. What are you, Mr. Chemical Manufacturer, planning to do to acquaint the public with your products and with your progress?

The old saying about keeping your light under a bushel still seems to apply to a number of business enterprises, which certainly would climb to healthier heights if their officers would but take the public into their confidence. A number of our greatest corporations have long since seen the wisdom of getting into the closest possible touch with their public, and particularly close to their stockholders. Some have made a great effort to secure especially their customers as stockholders in their corporations. As a result, for the first time in history there are a number which list among those directly concerned through investments approximately a quarter of a million individuals. Mr. X, a small investor in General Motors, let us say, is pretty sure to examine carefully the whole line before he considers buying a car of another make. For years the American Telephone and Telegraph Company has urged its subscribers to purchase at least enough stock to have the dividends meet their telephone bills. These examples could be multiplied.

These and similar corporations are at great pains to have their stockholders maintain an interest in the progress of the company. They make their stockholders familiar with the products and as a result they become boosters for the organization. This is contrary to the apparent policy of some of our greatest manufacturers of chemicals. It is all very well to issue financial statements and engage in high-sounding phrases concerning the stability of the corporation, but with this should go a careful dramatization of the products of the concern when such an opportunity as the Chemical Exposition is afforded. At a recent exposition one stockholder was greatly impressed with the exhibit of a company in which he had a few dollars. He said to an attendant, "I had no idea the company was so great. This is the first time I have ever seen photographs of the plants and the products of the company displayed. It is a great source of pride to own stock in the company." Surely to dramatize the products of that company, thus cementing closer relationship between it and its stockholders, was profitable. Carefully planned exhibits, informative as well as instructive, cannot fail to make a satisfactory impression upon prospective buyers of the securities, upon bankers, and upon the public, as well as upon the technical men for whom the exhibit is primarily held. The more people who become interested in the products of a company and the more knowledge that is spread with respect to the uses of these products in various lines of business and trade, the more benefit the exhibitor derives. What, then, may be said concerning those companies which fail to dramatize their products?

C. E. Griffin, professor of marketing and dean of the School of Business Administration of the University of Michigan, states in a booklet just issued to the motor-car trade:

> Effective marketing can exist only when the buyers have knowledge of the available supply and the sellers of the existing demand. Not only did the medieval fairs bring to the interested parties information concerning the supply and demand of staple goods, but they also served to introduce new products. Thus they performed the functions of the modern produce exchange as well as those now performed by advertising.
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> Even today the annual automobile shows are events of news value and the New York Show, even for people who do not attend, serves as a reminder of the progress being made in this tremendous industry as no amount of individual advertising could do. How much this focusing of attention once a year upon the industry is worth it is impossible to say, but in a broad view of the progress of the industry it seems to some to be worth a great deal. It is a means of making news of facts which, if offered by individual manufacturers, would be presentable only through the advertising columns.
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> In the case of automobile shows, particularly—and the same economic principle applies in the furniture, radio, electrical, and other industries—they produce widespread public acceptance at low unit cost.
>
> The application of the show principle to such unusual or unexpected technical fields, such as machine tools and productive equipment, has been demonstrated. The manufacturer desirous of keeping abreast of new methods of reducing costs finds the show a profitable marketing place and the designer and purveyor of even the most expensive machinery running into thousands of dollars has found the show an economical sales stimulant.

The 1931 exhibit is another possibility for industry which should be emphasized. We refer particularly to mergers and the consequent desirability of showing the public where well-known names and products are to be found in the new financial structures. It has been more common in other fields than chemistry to take new names for new combinations so that the securities of familiar brands are no longer listed. This was emphasized in the *Wall Street Journal* of August 5, where a reader pointed out that absorbing companies with new names made it impossible for the small investor to locate the present place of brands, stock in the ownership of which he wished to secure. A new grouping of old brands and the products of long-established chemical

companies in the exposition would convey a wealth of information to all concerned, among whom the public investor is not the least important.

That the dramatization of products is important is borne out by the enterprise of one of the floor brokers discussed in the *New York Times* of August 3. He surprised his fellow brokers by hanging on one of the trading posts neat samples of the products of the company in whose stock he is a specialist. It was a new idea and a fruitful one, though perhaps not capable of wholesale adoption on the stock exchange, for as the news item pointed out, how could American Locomotive or U. S. Steel set up a representative display without taking an extra building? The Chemical Exposition does, however, offer a place where for a whole week visitors may be educated in the products of the chemical industry. At the same time, in the hours set apart for their special benefit the technical experts of the industry, without interference on the part of crowds of the public, may further their information and pave the way for immediate substantial business.

Census Figures

SUFFICIENT data have been derived from the most recent census figures to make available certain sets of statistics of interest to industry. We learn, for example, that chemical plants are located to the number of 450 establishments in 156 counties in 33 states. Such information is helpful in indicating where those who would serve these industries may concentrate their sales efforts, and in time such statistics will be broken down to indicate the character of the establishment. As yet the tables do not distinguish between those which produce but a few thousand dollars' worth annually and those whose sales run into the millions.

Many deductions can be made from the figures which each decennial census makes available, but real difficulty lies in the old question of definition. For the figures indicated above only those plants engaged primarily in the production of acids and compounds are included. No chemist's definition of the chemical industry would coincide with the classification established and maintained by the Census Bureau, and consequently those who delve into statistics, while helped to a greater extent by the figures of the United States census than by the statistics compiled by any other country, must expect many disappointments and failure to get at the particularly significant figures which primarily interest them.

Technical Men Appreciated

SOME time ago we called attention to the change in the attitude of industry during the present recession in business as compared with former times in regard to technical men. It is true that there has been no such diminution in technical staffs as occurred during the previous business depression. On the other hand, plants that had been producing to their utmost capacity have taken advantage of existing conditions to carry on research and development for which there seemed to be no time a year or so ago. A few men have been made available because of mergers and in some cases because of poor business, with the result that other research staffs have been materially strengthened.

Now and then we find an industry which, very much against its preference, has been compelled, because of economic conditions, to reduce its technical staff. We have been impressed with the attitude of some of these concerns. They have parted with men who have been carefully selected and trained with the same reluctance as they would give up any treasure. They realize that in these men they have no small investment. It has cost time and effort to bring them to their present state of efficiency, and to lose them is not only to sacrifice all this but in many cases to lose men who have endeared themselves to the management because of what they have done and because of their personalities. It is gratifying, therefore, though not surprising, to find the personnel managers of some of these organizations doing their utmost to find proper places for these men. It is not customary to take such pains unless one has a sound appreciation of the men, of their accomplishments, and of their potentialities.

Growth of Power

THE increased use of power is a favorite way of comparing the industrial prosperity and the standard of civilization of the various countries. Power is fundamental in quantity production, which has been the delight of countries capable of absorbing a large amount of manufactured goods, and the despair of those in which underpaid hand labor is still the outstanding characteristic of industry.

The Bureau of Mines recently issued tables showing the relative rate of growth of coal, oil, and water power in the United States. Reduced to index numbers, taking the year 1918 as 100, we find the year 1889, which is the first for which water-power data are available, with an index of 20. The preliminary figure for 1929 is 121. This is by far the highest figure in our history, and if stated in trillions of British thermal units is 26,471 contrasted with 4316 in 1889.

A closer study of the figures which were compiled by F. G. Tryon discloses that since the war our consumption of coal has not materially advanced, and indeed was lower in 1929 than in 1920, 1923, or 1926. The total energy consumed, however, has notably increased as indicated. These increases, of course, are accounted for by the use of petroleum and petroleum products and natural gas, and in the steady development of our water-power resources.

The tables also give a direct measure of the total demand for energy and the sources which are preferred by an increasing number of large consumers. Few statistics are more interesting and more indicative of the state of our industry and the consuming capacity of our public than these from the Statistics Section, Coal Division, Bureau of Mines.

The Chemist's Blue Book

ALTHOUGH it appears in a golden colored cover, the new Directory of the AMERICAN CHEMICAL SOCIETY is the blue book of American chemists. This contains information not to be found elsewhere, and many members have already purchased copies, binding themselves not to use the Directory or allow it to be used for advertising purposes. The occupation of the individual is indicated, and there is the geographical summary. The list of corporation members is impressive, while the honorary membership embraces some of the most famous names in contemporary chemistry. The list of past Presidents and present officers, details of local sections, and dates and places of general meetings are of historic interest. A few men who gain their livelihood as chemists still fail to recognize their duty to their professional organization. Their names are not in this Directory.

There is an important use to which employers of chemists put this list, and those who do not have it available more frequently than is generally realized write the SOCIETY's officers to inquire whether one under consideration is a member of the AMERICAN CHEMICAL SOCIETY. These inquiries and this use of the Directory show an intelligent self-interest. Especially in these days of limited employment and readjustment, care should be taken to assist all such employers in securing the best the profession affords.

INDUSTRIAL HIGH-PRESSURE REACTIONS

Presented before a joint session of the Divisions of Industrial and Engineering Chemistry, Gas and Fuel Chemistry, and Petroleum Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930

Introduction

THE decision of the AMERICAN CHEMICAL SOCIETY to conduct a symposium on "Industrial High-Pressure Reactions" is timely. To my mind it gives recognition to one of the most important developments in American chemical industry since the war. The coöperation of three such large divisions of the SOCIETY as Industrial and Engineering, Petroleum, and Gas and Fuel is evidence of the wide interest and appeal of this subject.

The tremendous growth of industries based on high-pressure reactions is the most startling development of the decade. Synthetic ammonia is now one of our largest heavy-chemical industries. Synthetic-methanol production is mounting rapidly and oil hydrogenation promises to place the petroleum industry on a better economic basis and bring it into closer contact with more strictly chemical industries. Synthetic phenol and a host of similar miscellaneous developments promise much for the expansion and improvement of existing processes. The industrial chemist of today faces greater opportunity for exploration and accomplishment than ever before.

Not the least of the difficulties met in organizing a symposium such as this is a direct consequence of the novelty of the subject and the present rapid growth and development of processes based on high-pressure technic. The keen industrial competition existing and the comparatively limited number of laboratories from which to solicit contributions combine to enhance the difficulties. The fact that we have been able to secure such an impressive list of papers is a tribute to a developing spirit of coöperation in industrial, government, and university laboratories.

NORMAN W. KRASE, *Chairman*

Hydrogenation of Petroleum[1]

R. T. Haslam[2] and R. P. Russell[3]

STANDARD OIL DEVELOPMENT COMPANY AND HYDRO ENGINEERING & CHEMICAL COMPANY, ELIZABETH, N. J.

This paper deals with some of the recent developments in the hydrogenation of petroleum; and shows the adaptability of the process for converting fuel oil to gasoline and gas oil, increasing the paraffinic nature of kerosenes, burning oils, and lubricants; and discusses the reverse possibility of producing non-paraffinic gasoline. There is pointed out the flexibility of the process, particularly with respect to changes in the characteristics of the product, the handling of a wide variety of charging stock, the elimination of all forms of sulfur, and the conversion of all asphalts to distillate fuels.

THE conditions under which commercial hydrogenation has been practiced since the time of Sabatier have been restricted until the last few years to the use of (1) hydrogen at substantially normal pressure or 2 or 3 atmospheres above normal; (2) hydrogen of a high degree of purity particularly with respect to such catalyst poisons as sulfur, arsenic, and the like; (3) powerful but sensitive catalysts of the type of reduced nickel; and (4) temperatures safely below those at which thermal decomposition of the stock to be hydrogenated takes place. Coal and oil, both always containing sulfur, were not amenable to this type of hydrogenation, and it was therefore restricted to animal and vegetable fats and oils. By eliminating the catalyst and substituting hydrogen pressures one hundred fold greater than had previously been used, a high degree of liquefaction was obtained, but the oils thus produced contained relatively large percentages of oxygenated bodies of the cresolic type, making the oils hard to crack or refine. The able and resourceful research organization of the I. G. Farbenindustrie, through their experimentation, recognized the need of greater hydrogenation intensity than obtainable with hydrogen pressures then commercially permissible and developed a line of sulfur-resistant catalysts which materially speeded up hydrogenation and caused the elimination of all the oxygen from the hydrogenated product. In addition, their long experience in the field of synthetic ammonia enabled them to devise apparatus and methods for better carrying out this type of hydrogenation in a continuous manner.

About three years ago the Standard Oil Company (New Jersey), through its Development Company, joined with the I. G. in the further development and commercialization of this method of treatment, and erected special laboratories for high-pressure experimentation at the refinery of Jersey's subsidiary, the Standard Oil Company of Louisiana, at Baton Rouge, La. Previous efforts had been directed largely towards the conversion of coal to gasoline or the conversion of asphaltic crudes and residual fuel oils to distillate naphthas and gas oils. Although work along these lines was continued with particular emphasis on the simplification of the process, much of the effort of the Baton Rouge staff, in coöperation with the I. G., was to broaden the use of the process. It is now felt that something more than a process of adding hydrogen to coal and oil has been developed—namely, a flexible method of treating and refining by the use of hydrogen which should have wide application in the oil industry.

The work herein presented was carried out by the research staff of the Baton Rouge laboratory, and while some of the data are from half-barrel-per-day experimental units, prac-

[1] Received September 11, 1930.

[2] Vice president and general manager, Standard Oil Development Co.

[3] General manager, Hydro Engineering & Chemical Co.

tically all of the results given have also been demonstrated commercially in a 100-barrel-per-day pilot or demonstration plant erected about two years ago at Baton Rouge along the general lines of the larger plants of the I. G. Farbenindustrie in Germany.

It will be understood that disclosures to be made and the process and its applications as described are fully covered either by patents issued or by applications for patents.

Description of Process

In each of the major applications of hydrogenation discussed in this paper the equipment and even the arrangement of this equipment is essentially the same, the results obtained being controlled by suitable alteration of operating conditions. The charging stock together with sufficient hydrogen is pumped into a reaction vessel containing catalyst where at the desired temperature and at about 3000 pounds per square inch pressure the reaction is allowed to take place.

A panoramic view of the first large-scale plant in the United States, at the Bayway, N. J., refinery of the Standard Oil Company of New Jersey is shown in Figure 1.

Hydrogen may be produced by any of the usual processes. Since the hydrogen does not need to be sulfur-free, its production from coal or coke by the water-gas process is somewhat simpler than when the hydrogen is to be used for the production of ammonia. Hydrogen may also be produced by liquefaction and distillation of the easily condensable gases from by-product coke ovens, or electrolytically when the economies permit. For the oil industry, with its generous supply of refinery and natural gas, hydrogen may be made by the treatment of hydrocarbons with steam in accordance with the following reactions:

$$CH_4 + H_2O = CO + 3H_2 \quad (1)$$
$$CO + H_2O = CO_2 + H_2 \quad (2)$$

After scrubbing out the carbon dioxide the hydrogen is of sufficient purity. Catalysts are helpful and are generally used in carrying out each of the above reactions.

The oil and previously compressed hydrogen are mixed together and delivered through heat exchangers to a coil furnace and thence to a catalyst-containing reaction vessel. The degree of hydrogenation is carefully controlled depending on the results desired, control in general being maintained by alteration of catalyst or operating conditions.

From the reaction chamber the combined final products and gases pass through heat exchangers and coolers to a high-pressure separator, where the liquid product is separated from the unconsumed hydrogen and other gases. The liquid product is finally reduced to atmospheric pressure and sent to run-down pans.

Much of the sulfur in the feed stock appears as hydrogen sulfide in the unconsumed hydrogen leaving the high-pressure separator. This combined gas may then be scrubbed with oil under pressure to remove the hydrogen sulfide and "boosted" back to full operating pressure in a booster compressor which operates through a pressure interval equal to the pressure drop across the system. This unconsumed gas mixes with the feed oil and fresh hydrogen just before the exchanger inlet.

Since no coke is formed in the process, and since the catalysts employed are extremely rugged, the process is virtually continuous. Runs of as long as 8 months' duration have been made in Germany on full-scale units, and in the United States laboratory-scale and small commercial units have operated continuously for 3 months and more, the units being shut down only because the equipment was needed for other purposes.

Major Adaptations of Hydrogenation

There are five adaptations of hydrogenation which appear to be of most immediate importance in oil refining. These are:

(1) The conversion of heavy, high-sulfur, asphaltic crude oils and refinery residues into gasoline and distillates low in sulfur and free from asphalt, without concurrent formation of coke.

(2) The alteration of low-grade lubricating distillates, to obtain high yields of lubricating oils of premium quality as to temperature-viscosity relationship, Conradson carbon, flash, and gravity.

(3) The conversion of off-color, inferior-burning oil distillates or light gas oils into high-gravity, low-sulfur, water-white burning oils of excellent burning characteristics, with gasoline being the only other product except for a slight gas formation.

(4) The desulfurization and color- and gum-stabilization of high-sulfur, badly gumming cracked naphthas without marked alteration in distillation range and without major loss in antiknock value. (It is possible to operate so as actually to better the antiknock quality.)

(5) The conversion of paraffinic gas oils into low-sulfur, gum- and color-stable, good antiknock gasolines without the production of coke or heavy product.

Table I—Summary of Applications of Hydrogenation in Oil Refining

Process	Charging Stock	Primary Result	Approx. Volumetric Yield of: Gasoline	Burning oil	Gas oil	Lube oil	Total Volumetric Yield	Sulfur in Charge Removed in Process	Gas Formation
			%	%	%	%	%	%	% by wt.
1	High-sulfur, asphaltic heavy residue	Asphalt and sulfur elimination with simultaneous conversion entire charge into distillate oils	30	..	71	..	101	65 to 85	2 to 3
2	Low-grade lube distillate	Production premium lube, particularly as regards temperature-viscosity relationship, flash, carbon, and gravity	10	..	29	65	104	80 to 95	0.5 to 1.5
3	Low-grade burning oil distillate	Production of low-sulfur premium grade burning oil	30	73	..	..	103	80 to 95	0.5 to 2
4	Cracked naphtha	Desulfurization and gum stabilization without deterioration in yield and knock rating characteristic of acid treating	100	..	..	..	100	50 to 95	0.5
5	Paraffinic gas oil	Production of low-sulfur, low-gum, good antiknock gasoline	65 to 100	..	..	..	70 to 100	80 to 95	5 to 35

The processes described under (1), (2), and (3) may all give more than 100 per cent volumetric yield; i. e., from 100 barrels of a residual charging stock the process will give 101 or more barrels of gasoline and gas oil. Similarly, in treating 100 barrels of a low-grade lubricating distillate, 103 or more barrels of a mixture of gasoline and gas oil together with the improved lube oil will be obtained. In up-grading 100 barrels of a burning-oil distillate, 102 or more barrels of product (approximately 70 per cent burning oil and 30 per cent gasoline) will be obtained. The various processes mentioned are further summarized in Table I.

The salient features of these adaptations of hydrogenation are discussed in the following sections.

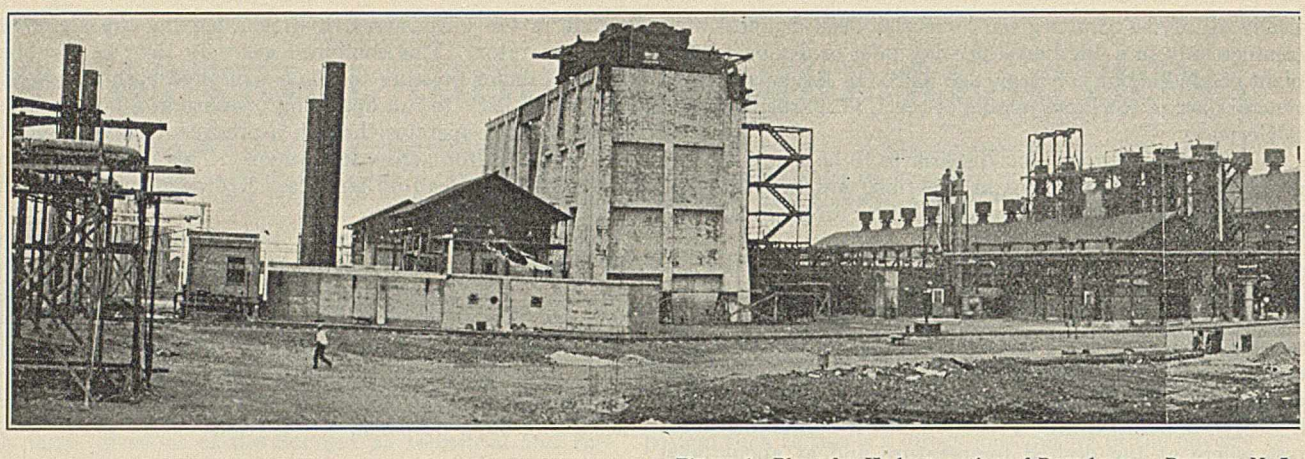


Figure 1—Plant for Hydrogenation of Petroleum. Bayway, N. J.,

Conversion of Refinery Residues into Gasoline and Gas Oil

The conversion of coal or heavy, asphaltic, high-sulfur products into high yields of gasoline is probably the most widely discussed adaptation of hydrogenation. By the present methods of cracking, part of the charge stock is upgraded into light, valuable product in the form of gasoline, while the remainder is degraded into gas, coke, and heavy fuel oil, all of lesser value than the feed stock. In contradistinction to the present processes for cracking, hydrogenation may upgrade, even up to 100 per cent of the charging stock, into lighter and lower-boiling-point products. This major difference from the other forms of increasing gasoline yield and the ability to utilize materials practically impossible to handle by other existing methods tended to make this application of hydrogenation appear spectacular.

For the hydrogenation of heavy asphaltic crudes or residues from these crude oils or from cracking processes, two types of operation may be used. The first of these takes place mainly in the liquid phase and serves to convert the heavy charging stock into 100 per cent or more by volume of product of a more highly paraffinic nature than the charge stock. The gasoline content may represent from 5 per cent to upwards of 35 per cent of the liquid product from this first stage in the operation, and the remainder is a distillate oil. If a higher yield of gasoline is desired, the heavier part of the product may be recycled in the same unit or the total product may be hydrogenated in the vapor phase in a separate unit and converted completely to gasoline.

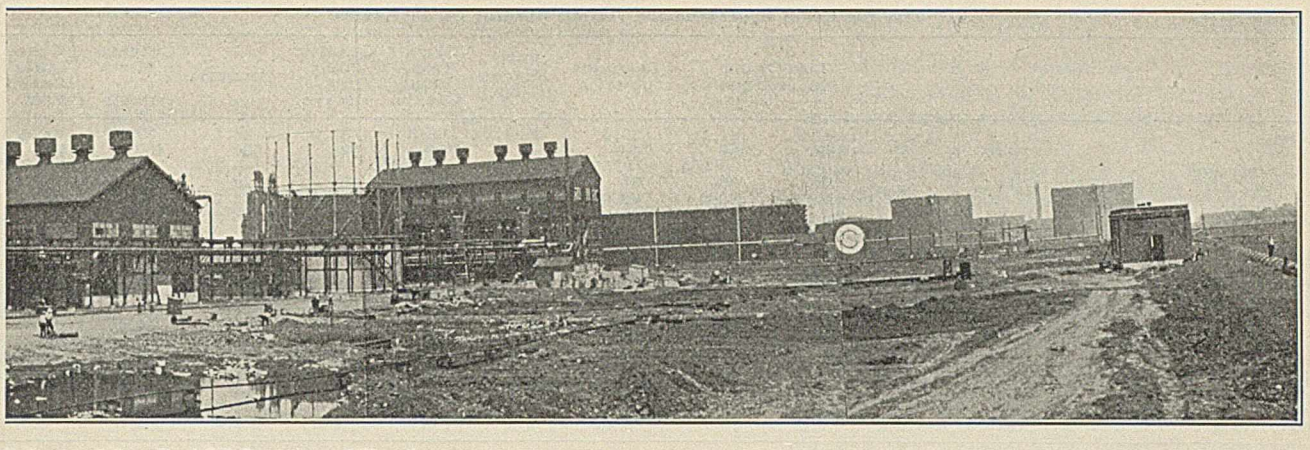
During liquid-phase hydrogenation the asphalt content may be completely converted and two-thirds to three-fourths of all the sulfur in the charging stock eliminated. This sulfur comes out as hydrogen sulfide and is scrubbed out of the recycle gases, as mentioned earlier. Even if the product charged is highly asphaltic and of high sulfur content, the gasoline produced is easily finished to give a low-sulfur, gum-stable product. The antiknock value of the gasoline by this application of hydrogenation is dependent somewhat on conditions, particularly the type of charging stock—crude residues from Smackover, Venezuela, Colombia, and similar crudes giving lower-knock-rating gasolines than residues from Midcontinent crude. The gas oil formed in the liquid-phase operation, in addition to having a relatively low sulfur content, cracks to give a gasoline which finishes to specification easily even though the gas oil was produced by hydrogenating a high-sulfur, high-asphalt crude or residue. The workability of this phase of the process has been demonstrated on fuel-oil residues from reduced Crane Upton, Panuco, Venezuela, Panhandle, Midcontinent, Talang Akar, Long Beach, Alamatos, Smackover, Reagan, and other crudes.

In general, it is believed that the early application of this phase of the hydrogenation process will be to run these heavy asphaltic products in the liquid phase to produce small yields of gasoline and the remainder gas oil, with a total volumetric yield of 101 to 104 per cent; the gas oil to be cracked to produce gasoline in existing cracking equipment or converted into good-knock-rating naphtha by hydrogenation as described in a later section of this article. If the gas oil is cracked in the present apparatus, as much of the cracking-plant tar as is needed for the production of steam and power in the refinery may be used as fuel and the remainder returned to the hydrogenation unit. In this way the greatest use of present refinery facilities and gasoline yield can be obtained with a minimum hydrogen consumption. Depending upon the stock and operating conditions, a yield of 80 to 90 per cent of gasoline may be obtained by this method.

Table II—Results of Hydrogenating Heavy Feed Stocks

	Topped Crane Upton Crude			Topped Nacona Crude		Cracking Plant Tar	
	Feed	Product		Feed	Product	Feed	Product
		Expt. 1	Expt. 2				
Product, per cent by volume		107.7[a]	100.5[a]		101.5[a]		98.9[a]
° A. P. I.	23.4	35.8	35.1	24.9	37.5	12.4	23.5
I. B. P., ° F.	350	138	....	344	130	340	153
Per cent at 212° F.	...	4.0	....	...	4.0	...	3.0
Per cent at 284° F.	...	8.5	....	...	10.0	...	6.5
Per cent at 374° F.	...	18.0	24.5	...	21.0	...	12.5
Per cent at 400° F.	...	22.0	30.0	1.0	25.0	0.5	14.0
Per cent at 460° F.	6.5	33.5	41.0	1.5	36.5	...	20.5
Per cent at 650° F.	40.5	77.5	79.0	34.0	76.0	34.5	67.0
Per cent at 700° F.	66.0	87.5	86.5	82.0	85.5	49.0	82.0
Per cent sulfur	1.25	0.198	0.530	0.760	0.108	0.702	0.246
Per cent gasoline[a]		22.0	30.0		25.0		14.0
° A. P. I. gasoline		57.3	57.6		60.8		56.4
Per cent sulfur in gasoline		0.034	0.056		0.049		0.019

[a] Does not include a small yield of absorption naphtha produced concurrently.



Refinery of Standard Oil Company of New Jersey

If none of the cracking plant tar were burned as fuel, the combined yield of gasoline would be approximately 100 per cent.

Some typical examples of the liquid-phase operation are given in Table II, in which a comparison is shown of the inspections of three heavy feed stocks before and after hydrogenation. All the asphalt present in the charge was converted into more paraffinic type products, about two-thirds of the sulfur eliminated and the entire product was a yellow distillate oil. As another example, it was found, in hydrogenating a 7.2° A. P. I. cracking coil tar, that the sulfur was reduced from 2.77 per cent in the charge stock to 0.49 per cent in the total overhead, and this product contained 22.1 per cent of gasoline of 0.071 per cent sulfur without further treatment.

Improvement of Low-Quality Lubricating Distillates

With the improvement in the internal-combustion engine and particularly with the rapid expansion in air transportation, there has developed an insistent demand for better motor lubricants. The modern motor lubricating oil, to give good service, should have (1) a flat temperature-viscosity relationship, (2) a high flash point, (3) a low Conradson carbon content (to give minimum carbon deposition in the motor), and (4) should flow sufficiently freely at low temperatures to permit adequate lubrication under extreme conditions. With present refining methods it has not been possible to meet all of these requirements in a single oil, even from the best crude oils available.

To meet this situation a considerable amount of work has been done to determine whether, by the use of the hydrogenation process, all of the above characteristics could be combined in a single oil. In general, hydrogenated paraffinic lubricating oils with a flat temperature-viscosity relationship are characterized by unusually high flash points and low Conradson carbon content. The high quality of these hydrogenated lubricating oils predictable from the laboratory inspection has been substantiated in actual engine tests. In view of the possibility of producing essentially the same premium quality lubricating oils from a wide variety of inferior lubricating distillates, it would seem that hydrogenation will have an important influence in this field of refining in the future.

It has been found that by hydrogenation it is possible to make marked improvement in a number of inferior lubricating distillates. Under the best conditions for this type of hydrogenation there are produced from 100 barrels of lubricating distillate 103 to 104 barrels of hydrogenated product containing from 60 to 85 barrels of lube oil, somewhat lower in viscosity but much more paraffinic than the charge, together with about 10 barrels of gasoline and from 10 to 30 barrels of gas oil. From 80 to 90 per cent of the sulfur in the feed stock is eliminated during hydrogenation.

Figures 2 to 5[4] show the products obtained using various charging stocks.

[4] The term "viscosity index" used in these charts was devised by Dean and Davis, *Chem. Met. Eng.*, **36**, 618 (1929), and indicates the viscosity-temperature characteristics of the lubricating oil. Thus, paraffinic oils such as Pennsylvania have a viscosity index of 100, and Coastal oils a viscosity index of from 0 to 20.

Figure 2

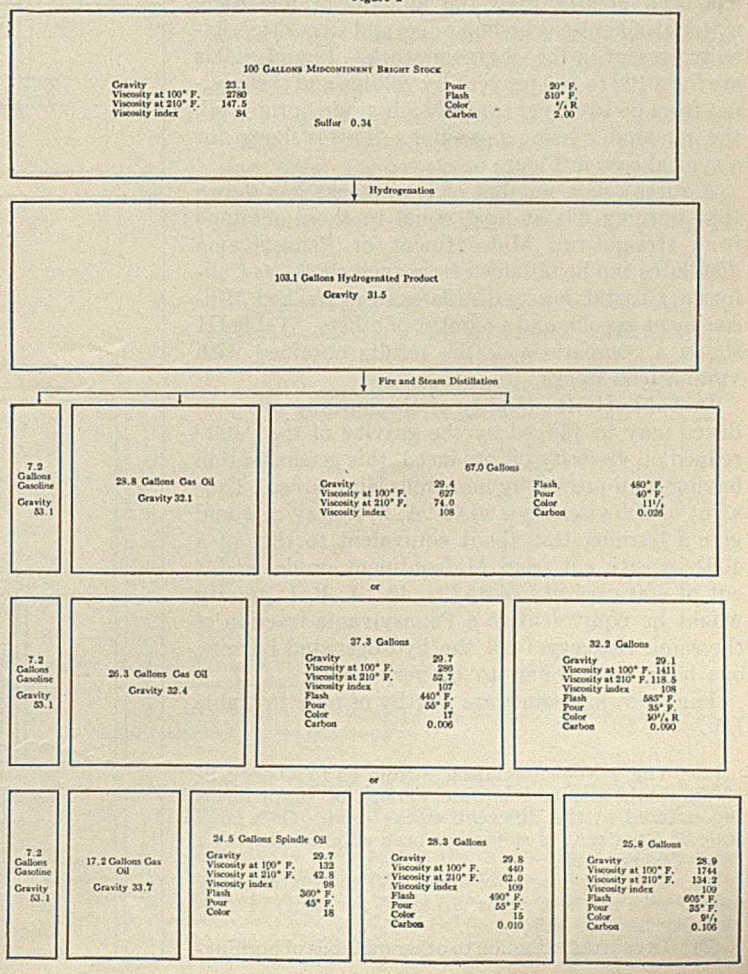


Table III—Results of Hydrogenating Various Burning Oil Distillates

	Low-Grade Mid-continent		Alamatos (Calif.)	Long Beach (Calif.)	West Texas Light Gas Oil	Cracked Plant Distillate	Colombia	Cracked Mid-continent	West Texas Diesel Fuel
Gravity, °A. P. I.	40.2	41.1	36.4	36.8	35.3	39.0	36.1	39.7	30.5
Viscosity[a]	485	480	750	750	705	335	600	400	595
Sulfur, per cent	0.221	0.285	0.550	0.240	0.761	0.157	0.202	0.334	0.487
Per cent "400" viscosity oil[b] in original	58	90	38	40	30	100	30	100	40
° A. P. I. of "400" viscosity oil	41.2	40.0	40.0	39.9	39.1	39.0	38.9	39.7	35.1
Viscosity of "400" viscosity oil	400	450	380	400	410	335	400	400	400
RESULTS OF HYDROGENATION									
Volumetric recovery[c]	106	100	106	99	102	100	101	103	105
°A. P. I. of total product	48.9	52.1	46.0	45.6	54.2	45.8	51.6	47.2	51.0
Per cent sulfur of total product	0.006	0.011	0.022	0.025	0.026	0.024	0.029	0.014	0.019
Per cent "400" viscosity oil in total product	83	75	65	60	58	85	73	80	65
A. P. I. of "400" viscosity fraction	46.0	46.7	43.0	43.3	45.5	43.8	44.1	44.4	44.0
Viscosity[a] of "400" viscosity fraction	415	380	410	400	375	335	355	360	360
Sulfur, per cent	0.007	0.012	0.013	0.012	0.018	0.022	0.013	0.025	0.015
Flash, ° F. (Abel)	107	100	122	120	109	128	104	106	115
Color (Saybolt)	22	25	17	25	25	25	18	25	...
Per cent sulfur elimination	97	96	96	90	97	85	86	96	96
Improvement in A. P. I. of "400"-viscosity fraction	4.8	6.7	3.0	3.4	6.4	4.8	5.2	4.7	8.9

[a] Saybolt Thermo. refined oil viscosity at 60° F.
[b] The term "400" viscosity oil is used to denote the fraction of about 400 viscosity and above 100° F. Abel flash. As will be noted, the true viscosity of most of the cuts actually made was slightly above or slightly below 400.
[c] Not including a small yield of recovery naphtha produced concurrently.

Production of High-Grade Kerosenes

High-sulfur, low-gravity off-color kerosene distillates and poor-quality light gas oils may be hydrogenated to produce high yields of water-white distillates and burning oils of high quality. In general these products meet specifications as to sulfur, color, and smoke tendency with no other treatment than reduction to flash and viscosity.

In this adaptation of hydrogenation it has been found desirable to start with a stock somewhat more viscous than the desired finished oil, with the result that in many cases the actual yield of finished high-grade burning oil has been greater than the amount of low-grade material of kerosene boiling range and viscosity originally present in the charging stock. Liquid yields are from 100 to 105 per cent by volume and the product from 65 to 85 per cent of high-grade burning oil, the remainder being a gasoline. This is shown for a typical case in Figure 6.

A survey of a number of feed stocks has shown that burning oils at least equal to those obtained from straight-run Midcontinent or Pennsylvania distillates can be obtained from such stocks as California, Coastal, heavy distillates from cracked Midcontinent gas oils, and a number of others. Table III shows a comparison of the results obtained with various feed stocks.

In Table III the quality of the burning oils produced may be judged by the gravity of the "400" refined oil viscosity oil produced, this generalization having been proved by numerous lamp tests. Thus a cut of 400 viscosity and 42° A. P. I. gravity would give a burning test about equivalent to that of a 400-viscosity cut from Midcontinent crude, and a cut of 400 viscosity of 45° to 46° A. P. I. gravity would be equivalent to a Pennsylvania fraction of the same viscosity. All the hydrogenated burning oils have been found to be very stable.

The following points are worthy of note in Table III:

(1) The sulfur elimination is from 85 to 90 per cent of the total, despite the wide variety of sulfur forms encountered in the different stocks used. On a large scale 98.5 per cent of sulfur has been eliminated from a West Texas gas oil.

(2) Charging stocks of from 450 to 600 viscosity usually give the best yields (75 to 85 per cent) of 400-viscosity finished refined oil.

(3) In contradistinction to other methods of burning-oil improvement now available, none of the charge is degraded. The entire hydrogenated product consists of burning oil and gasoline, both of which are more valuable than the charging stock. In other words, hydrogenation actually reconstructs the undesirable constituents present in the feed rather than separating them out by some such method as solvent extraction.

(4) All the stocks, although differing widely in initial chemical characteristics, after hydrogenation equal the very highest A. P. I. gravity natural burning oils in physical characteristics. Analysis indicates that by hydrogenation (*a*) olefins are almost completely eliminated, (*b*) the greater portion of the aromatics are converted into naphthenes and paraffins, and (*c*) there is very little apparent effect on the naphthenes, probably since new naphthenes are formed from aromatics in the charge, thus

Figure 3

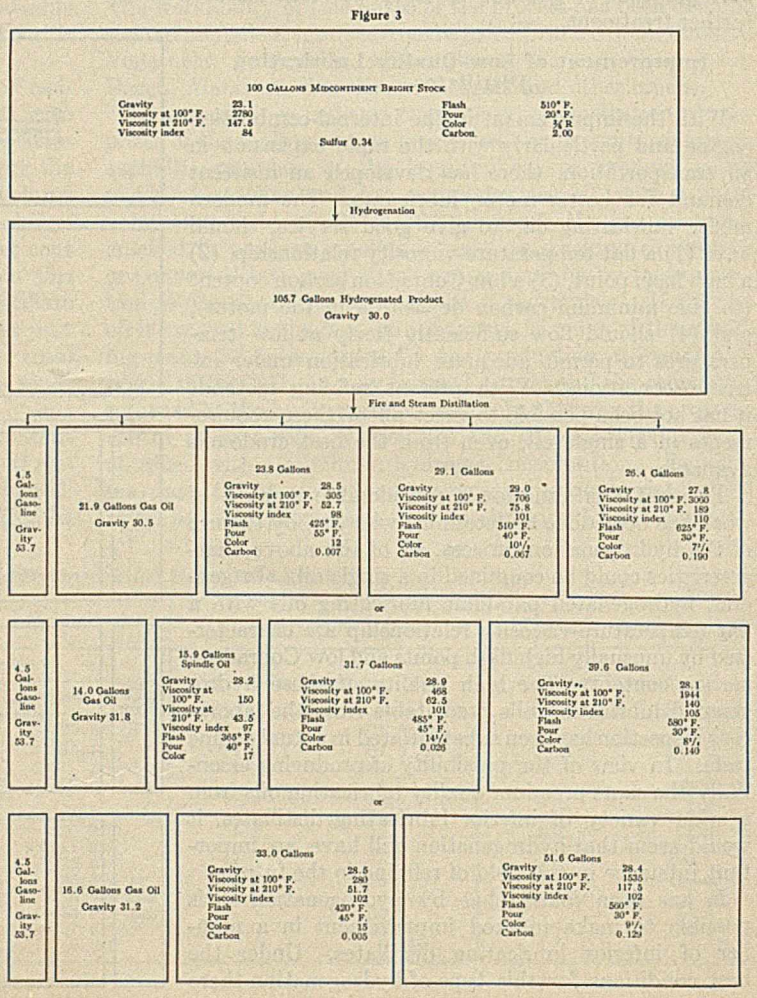
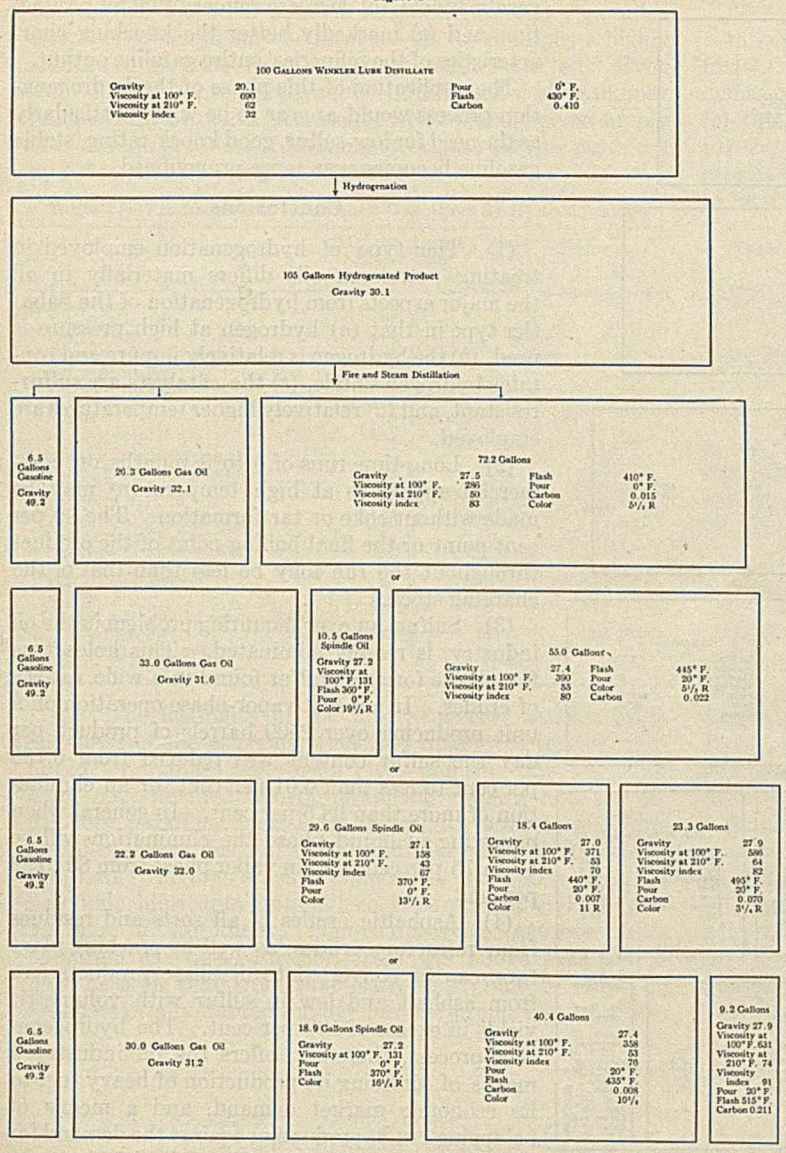


Figure 4



offsetting the improvement brought about as the original naphthenes are changed into more paraffinic compounds.

Treatment of Naphthas for Elimination of Sulfur and Gumming Tendency

In view of the remarkable facility with which catalytic hydrogenation eliminates sulfur, this process has been used for the treatment of natural or cracked naphthas. By a mild hydrogenation a high-sulfur, high-gum, and unstable gasoline may be rendered stable, with about 50 per cent of the sulfur eliminated under such conditions of operation that the antiknock value is lowered only to about the same extent as would result from a slight chemical treatment. This phase of the process would be carried out in such a way that no appreciable change would be made in the boiling range of the naphtha. The process may also be so operated as almost entirely to eliminate sulfur from a high-sulfur, cracked naphtha, with a small increase and in some cases an actual material decrease in knocking tendency. Depending upon conditions of operation, this treatment eliminates from 65 to 98 per cent of the sulfur in the feed stock and gives a gum- and color-stable naphtha which, after a light wash with caustic soda, passes corrosion and doctor tests. Tables IV and V show the character of the stock charged and the finished product. Improvement in color, gum, and sulfur is readily apparent.

Production of Stable Low-Knock Gasolines

The production of stable low-knock gasolines by hydrogenation, although carried out in the same equipment as those modifications described earlier, differ from them considerably in both aims and results. For example, in converting a fuel oil into gasoline and gas oil, or in upgrading a lubricating oil or refined-oil distillate, hydrogen is added to materials naturally deficient in this respect. In other words, hydrogenation has served to saturate the hydrocarbon molecule and to render it more paraffinic. By suitably changing the operating conditions but still utilizing the same equipment, the process may be reversed to yield stable, but non-paraffinic products. Thus, in one run on the hydrogenation pilot plant at Baton Rouge, using a Midcontinent gas oil as charging stock, the first product made was a paraffinic burning oil of high gravity; without stopping operation, and merely by changing the conditions, the same charging stock yielded over 85 per cent of a stable, low-sulfur gasoline having the same knocking tendency as 72.6 per cent of isoöctane in *n*-heptane.

It will be recalled that in those adaptations of hydrogenation described earlier the volumetric yield is 100 per cent or more. This is not the case in producing gasoline from gas oil, unless the knocking tendency is immaterial, the yield of gasoline being less than 100 per cent if antiknock quality is desired. In making antiknock gasoline by hydrogenation, however, no tar or coke is formed and only two products are obtained—gasoline and gas. Any material not converted into gasoline in the first pass through the system is recycled.

The gasolines produced thus far have been practically sulfur-free, pass doctor and corrosion after lye-washing, and are quite gum-stable; in a few cases some treating has been necessary, but this has been very small in amount.

Table IV—Finishing of Cracked Smackover Naphtha by Hydrogenation

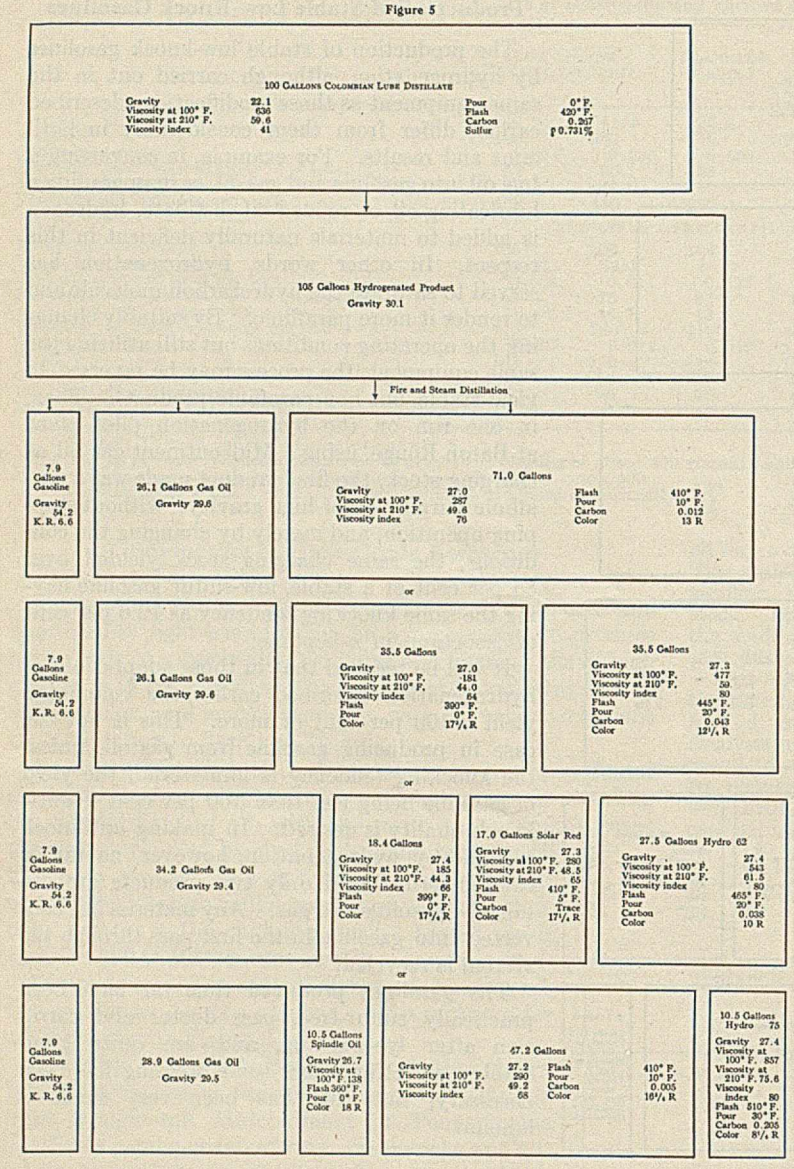
	Charge Cracked Smackover Naphtha	Hydrogenated Product (100% Yield)
Total Product:		
Gravity, ° A. P. I.	46.4	51.9
Sulfur, per cent	0.395	0.019
Doctor	Does not pass	Passes
Color	Straw	+25 Saybolt
I.B.P., ° F.	124	134[a]
Per cent at 212° F.	14.5	12.0
Per cent at 302° F.	40.5	45.0
Per cent at 374° F.	64.0	73.5
Per cent at 400° F.	71.5	82.0
F.B.P., ° F.	540	502
Gasoline:		
Gravity, ° A. P. I.	53.9	55.3
Sulfur, per cent	0.188	0.006
Porcelain dish gum, mg.	12	1
Copper dish gum, mg.	21	4

[a] Change in initial boiling point is due to incomplete recovery of the low-boiling fractions from the recycle gases.

Some results obtained by this operation using light gas oils[5] are given in Table VI, which shows the properties of

[5] This adaptation of hydrogenation has thus far been applied mainly on gas oils having final boiling points of 650° F. or under, although some stocks with 40 per cent or more boiling above this temperature have been found susceptible to this type of treatment. An investigation is now in progress to determine quantitatively the influence of end point and boiling range on the results obtained.

Figure 5



both the feed stock and product. It will be noted that better knock ratings are obtained with more favorable stocks; i. e., with less paraffinic charging stocks it is possible to obtain higher yields of gasoline of given knock rating, or much better knock ratings for a given yield.

Table V—Finishing of Cracked Midcontinent Naphtha by Hydrogenation

	Feed Cracked Naphtha	Acid-Treated[a]	Hydrogenation	
			Expt. 1	Expt. 2
400° F. F.B.P. gasoline, based on feed, per cent	71.5	64.2	65.4	65.7
Gravity, °A. P. I.	53.9	53.1	56.1	44.3
Sulfur, per cent	0.39	0.15	0.15	0.02
Porcelain dish gum, mg.	12	8	3	3
Accelerated gum, mg.	51	37	3	4
Antiknock value as per cent iso-octane in *n*-heptane	65.3	62.2	63.8	78.0

[a] 7 pounds 98 per cent acid per barrel.

Table VII shows quite strikingly this influence of character of charging stock on knocking tendency of the gasoline produced.

The potential value of these highly antiknock gasolines as blending agents is readily apparent, and many interesting combinations with cracking have been developed by experimentation—e. g., hydrogenation of cycle gas oils, to (*a*) increase gasoline yield, (*b*) decrease refinery fuel oil production, and (*c*) markedly better the knocking characteristics of the refineries' entire gasoline output.

The application of this phase of the hydrogenation process would appear to be wide, particularly as the need for low-sulfur, good knock-rating, stable gasoline becomes even more pronounced.

Conclusions

(1) The type of hydrogenation employed in treating petroleum oils differs materially in all the major aspects from hydrogenation of the Sabatier type in that (*a*) hydrogen at high pressure is used, (*b*) the hydrogen is relatively impure and contains hydrogen sulfide, (*c*) the catalysts are sulfur-resistant, and (*d*) relatively higher temperatures are employed.

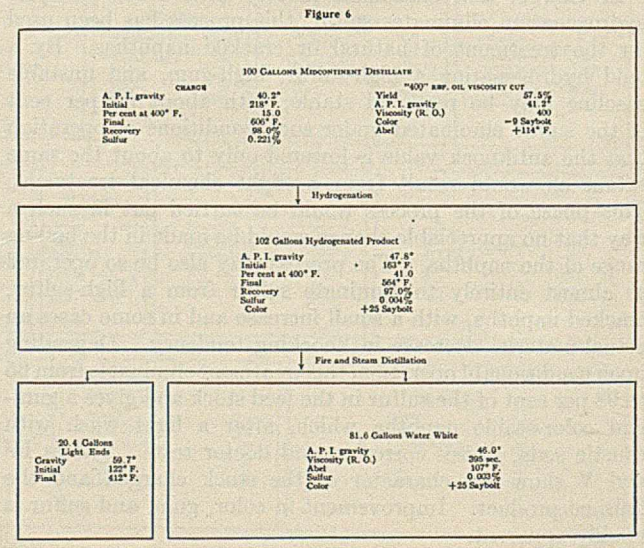
(2) Long-time runs of 6 to 8 months on commercial apparatus at high temperature may be made without coke or tar formation. The 90 per cent point or the final boiling point of the product throughout the run may be less than that of the charging stock.

(3) Sulfur, an ever mounting problem in the oil industry, is readily eliminated. This holds true for all the forms of sulfur found in a wide variety of crudes. In a recent vapor-phase operation on a unit producing over 2500 barrels of product per day the sulfur content was reduced from 0.708 per cent to less than 0.01 per cent, or an elimination of more than 98.5 per cent. In general when operating in liquid phase the elimination will be 60 to 75 per cent and in vapor phase from 80 to 99 per cent.

(4) Asphaltic crudes of all sorts and residues from refractory crudes, as well as cracking plant tars, can be converted to distillate products free from asphalt and low in sulfur with volumetric yields in excess of 100 per cent. The hydrogenation process, therefore, offers the oil industry a means of confining its production of heavy fuel to its economic market demand, and a means of balancing crude production against the demand for refined white products, gasoline, Diesel fuels, burning oils, and the like, independent of the natural, heavy fuel content of the crude.

(5) From mixed-base crudes highly paraffinic products such as gas oils, burning oils, and lubricants may be pro-

Figure 6



duced. On the other hand, from paraffinic crudes so-called aromatic products may be formed—as, for example, a highly antiknock gasoline from a very paraffinic gas oil. Even from the same gas oil paraffinic burning oil and antiknock gasoline may be made. Consequently, from any given supply of crude the products of the quality desired may be produced by refineries employing hydrogenation.

Table VI—Production of Antiknock Gasolines by Hydrogenation

	Midcontinent Light Gas Oil	West Texas Cycle Gas Oil	
Feed Stock:			
° A. P. I.	37.4	30.3	
I.B.P., ° F.	474	400	
Per cent at 460° F.	2.5	56.0	
Per cent at 550° F.	89.0	..	
Per cent at 650° F.	..	..	
F.B.P. ° F.	618	612	
Sulfur	0.153	0.192	
Aniline point	161	102	
Hydrogenated Product:			
Yield, per cent by volume	89.9	94.5	88.0
° A. P. I.	55.4	39.8	42.3
I.B.P., ° F.	95	110	109
Per cent at 212° F.	35.0	13.5	12.0
Per cent at 284° F.	54.0	25.0	32.5
Per cent at 356° F.	72.5	..	..
Per cent at 374° F.	79.0	50.5	70.5
Per cent at 400° F.	87.0	70.5	90 (392° F.)
F.B.P., ° F.	428	436	412
Knock rating as per cent isoöctane in *n*-heptane	72.6	82.2	85.0
Dissolved gum, per cent	17.7	9.0	..
Sulfur, per cent	0.013	0.005	0.006

(6) The flexibility of the process is very marked as to character of the charging stock and quality of product produced. Examples have been given showing how the same plant may be used (*a*) for producing gasoline and gas oil, (*b*) very paraffinic high A. P. I. gravity burning oils from mixed-base gas oils, (*c*) color- and gum-stabilizing and desulfurizing highly cracked naphthas, (*d*) production of paraffinic lubricants from mixed base stocks, and (*e*) production of antiknock, high-compression gasoline from paraffinic gas oils. Further, from the above examples it may be seen that from practically any grade of crude oil products of any desired quality may be produced.

(7) The hydrogenation process uses compressed hydrogen, a rather costly material. Offsetting this are the following factors: (*a*) the ability to balance crude run to white product demand, (*b*) the premium quality of products produced, (*c*) the low value charging stocks that may be used, and (*d*) the extreme utility of the process, due to its flexibility, especially where types of crudes to be refined and markets to be supplied vary from time to time.

Table VII—Influence of Character of Feed Stock on Knocking Tendency of Hydrogenated Gasolines

Gasoline yield, per cent	89.9	91.4	88.0	89.0
Aniline point of charge stock	161	139	102	79
General characteristics of charge	Highly paraffinic	Medium paraffinic	Medium aromatic	Highly aromatic
Knock rating, as per cent iso-octane in *n*-heptane	72.6	75.3	85.0	86.2

(8) Because of the oversupply of crude oil, hydrogenation in its present state of development may be considered as supplementary to present refining methods. It probably will supplant them as the supply of crude oil and demand for light products approach a balance.

Acknowledgment

The authors wish to take this opportunity of acknowledging their indebtedness to many of their associates, but particularly to the entire staff of the high-pressure research laboratory at Baton Rouge, especially W. C. Asbury, M. W. Boyer, P. J. Byrne, Jr., G. H. B. Davis, W. V. Hanks, and J. M. Jennings; and to E. M. Clark, president, and F. A. Howard, vice president, of the Standard Oil Development Company.

Since the original research and development of high-pressure hydrogenation of coal and oil has been one of the most, if not the most, costly process developments ever undertaken, the authors wish to express their respect for and admiration of the two corporations most directly responsible, the I. G. Farbenindustrie, A.-G., and the Standard Oil Company (New Jersey), and their respective presidents, Carl Bosch and W. C. Teagle.

Reactions That Occur on a Methanol Catalyst[1]

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It has been shown that carbon dioxide and hydrogen react upon a zinc oxide–chromium oxide catalyst at 304° C. to form methanol, carbon monoxide, and water. Likewise carbon monoxide and water react to form carbon dioxide and hydrogen and equilibrium can be closely approached in the water-gas reaction. Of the reactions that may occur through the action of this catalyst at 304° C. upon hydrogen–carbon dioxide-water mixtures, it has not been found possible to determine which reaction comes nearest to equilibrium. As most known methanol catalysts produce carbon dioxide or water or both along with methanol, it is possible that the formation of methanol from carbon monoxide and hydrogen may not be direct, especially as a steady state is approached.

THE thermodynamic properties of methanol have been the subject of considerable investigation. The results obtained by a number of investigators (*4*, *5*, *7*) on equilibrium in the reaction

$$CO + 2H_2 = CH_3OH\ (g) \qquad (1)$$

agree as to order of magnitude. But these results differ considerably from those calculated from low-temperature heat-capacity measurements on methanol by use of the third law of thermodynamics (*3*). No satisfactory explanation of this discrepancy has yet been furnished although a number of suggestions have been made (*1*, *4*, *8*).

Certain phases of the earlier work (*7*) led us to investigate an aspect of the problem which has not received attention aside from the mention made by Smith and Branting (*7*, footnote 15) in their preliminary experiments. If, as an equilibrium condition is approached in one reaction, other reactions are taking place at rates comparable with that of the reaction in question, equilibrium may not be

[1] Received August 29, 1930. Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

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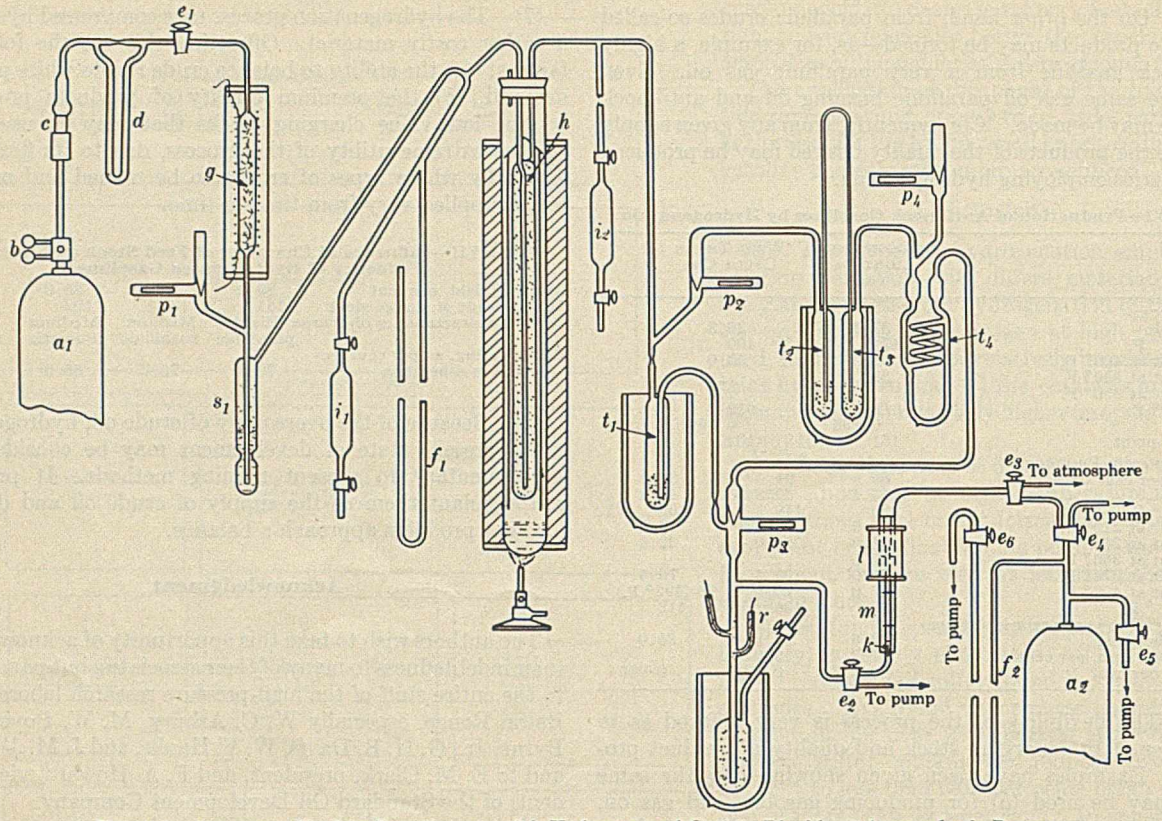

Figure 1—Apparatus Used in Experiments with Hydrogen and Carbon Dioxide at Atmospheric Pressure

readily reached. The object of the work described herein was to determine whether such a condition existed in the case of measurements thus far made of the methanol equilibrium.

It is known that, depending upon the experimental conditions, dimethyl ether, higher alcohols, methane, carbon dioxide, or water may accompany the formation of methanol from carbon monoxide and hydrogen. However, these products usually occur in amounts minor to that of the methanol. The natural assumption is, therefore, that the approach to equilibrium in the methanol reaction would not be appreciably affected by these reactions. But this need not be the case, particularly if the mechanism of the reaction by which methanol is produced is not simply that indicated by Equation 1.

EXPERIMENTAL WORK

The catalysts used in the following work were prepared by adding chromic acid solution to purified zinc oxide. The atomic proportions were about 4 Zn to 1 Cr. All of the following work was done at 304° C. on 600 cc. of catalyst.

At first several experiments were made essentially as described by Smith and Branting, but with some improvements. The total volume of gas passed over the catalyst was measured by exhausting the off-gas through an electrically operated pressure regulator into an evacuated cylinder whose volume was carefully determined and to which was attached a thermometer and a manometer for determining the amount of gas within the cylinder; also, the colorimetric method of determining the methanol was carefully investigated. By checking against known solutions of pure methanol it was found, as stated by Smith and Branting, that accurate results could be obtained only when the unknown solution was very close in concentration to the known solution with which it was compared. Some of the data reported in the preliminary experiments of Smith and Branting may be in error on this score. Lacy, Dunning, and Storch (*4*) suggested that a small amount of organic product might have passed into the apparatus and vitiated the methanol determination. But the entering gas was purified by remaining in a liquid-air trap for from 30 to 60 minutes and, in the present work, the catalyst, while hot, was thoroughly evacuated with a mercury diffusion pump.

Experiments with this improved apparatus gave results in which the variations were more than seemed to be accounted for by the limits of error of the method, and the apparent nearness of approach to equilibrium did not correspond to what would be expected from the rates of gas flow used in different experiments.

Reaction upon $ZnO-Cr_2O_3$ Catalyst

As the reaction of carbon dioxide and hydrogen to form methanol and water was known to take place on a catalyst very similar to the one we were using, we were led to investigate this reaction upon our catalyst. A mixture of carbon dioxide and hydrogen was made from commercial carbon dioxide and electrolytic hydrogen. After passing over hot platinized asbestos, the mixture analyzed 24 per cent CO_2, 74 per cent H_2, and 2 per cent N_2. This gas mixture was passed over the catalyst at about the space velocity used in previous equilibrium experiments with carbon monoxide–hydrogen mixtures. After passage over the catalyst the methanol was removed by passage through two efficient water wash coils at 0° C. The gas then passed through the pressure regulator and into the calibrated cylinder. The first wash coil recovered 0.00095 gram of methanol. No detectable amount of methanol was found in the second wash coil. The off-gas analyzed 14.1 per cent CO_2, 69 per cent H_2, and 12.3 per cent CO. From these data, the total pressure and the total amount of gas collected in the calibrated cylinder, the constant $CH_3OH/CO(H_2)^2$ was calculated to be 3.68×10^{-4}. This value is comparable

with those obtained using carbon monoxide–hydrogen mixtures, in spite of the fact that in this case reactions other than those that produce methanol have taken place to a large extent.

This result suggested that the water-gas reaction might be occurring on the catalyst. Accordingly, pure carbon monoxide saturated with the vapor from water at 76.5° C. was passed over the catalyst. The off-gas analyzed 33 per cent CO_2, 33 per cent CO, and 31 per cent H_2. Experiments at 300° C. and at 50 and 200 atmospheres with gas mixtures containing 60 per cent CO and 40 per cent H_2O showed that the water-gas reaction still took place at a rate comparable with that at which methanol is formed from carbon monoxide and hydrogen, although large concentrations of water vapor in the gas at temperatures as low as 300° C. caused a rather rapid deterioration in the activity of the catalyst—probably accompanying hydration of the chromium oxide. Considerable methanol was obtained from the carbon monoxide–water mixture upon some catalysts tried.

Further Study of Reactions and Determination of Equilibrium

It was thought of interest to study in greater detail the reaction between hydrogen and carbon dioxide using the original catalyst and determining the partial pressure of water in the equilibrium mixtures. The apparatus shown in Figure 1 was used. The storage cylinder, *a*, contained the hydrogen–carbon dioxide mixture and was connected to the apparatus through the copper-to-glass seal, *c*. The gas from the cylinder passed through a high grade reducing valve, *b*, by means of which the rate of gas flow, as indicated by the flowmeter, *d*, was controlled. A tube, *g*, containing platinized asbestos, removed oxygen from the gas, and a magnetically operated device, *p*, introduced water to the saturator, s_1, kept at a constant temperature of 20° C. The tubing between s_1, i_1, f_1, and *h* was 1.5 mm. in internal diameter and was heated by resistance wire to prevent condensation of water vapor from the saturator. The catalyst, *h*, was surrounded by a thin metal "umbrella" and heated by the vapor of boiling benzophenone. After thorough evacuation of the heated catalyst with a mercury diffusion pump, the gas was introduced to the apparatus and the saturator, s_1, was filled with water by operating the slug, p_1. The gas was passed through the apparatus for several days in order to bring the catalyst into equilibrium with the H_2–CO_2–H_2O mixture. During this period the gas passed through the trap, t_1, through the electrically operated pressure regulator, *r*, and to the atmosphere. Then t_1 was sealed off and the glass tips at p_2 and p_3 were broken by the slugs. The gas now passed through the traps t_2 and t_3, cooled in acetone–carbon dioxide snow, and a weighed amount of water was introduced to the wash coil, t_4, by operating the slug, p_4. Methanol and water were condensed in the traps t_2 and t_3, and the last traces of methanol were removed by the water in t_4 kept at 0° C. However, as no methanol or water was found in the second trap, it was later eliminated. The off-gas then passed through the magnetically operated valve, *l*, into the cylinder, a_2, the volume of which was known and in which the gas pressure could be measured. Condensation of water was prevented by electrically heating the tubing from *h* to i_2. The water passing out in the gas was determined by sealing off and weighing the trap, t_2, after displacing the gas with dry air. The water in t_4 was added to t_2 after it was again cooled in acetone–carbon dioxide snow. The methanol was determined in the uniform solution.

The data obtained in four experiments are recorded in Table I. The gas used in these experiments originally analyzed 24 per cent CO_2, 74 per cent H_2, and 2 per cent N_2 after passage over the platinized asbestos. This gas was saturated with the vapor from water held at 20° C.

Table I—"Equilibrium" in System H_2-CO_2-CO-H_2O-CH_3OH at 304° C.

Expt.	Gas Flow Rate	CH_3OH	H_2O	Composition of Off-Gas			Total Pressure	Volume Off-Gas at S. T. P.
				CO_2	H_2	CO		
	Liters per hour	*Gram*	*Grams*	%	%	%	*Mm. Hg.*	*Liters*
1	0.6	0.0008	1.95	20.0	66.0	13.2	800	41.0
2	0.8	0.0006	1.87	27.2	64.6	5.1	817	34.9
3	0.33	0.00024	1.97	25.6	67.3	5.2	813	30.5
4	0.93	0.00030	1.03	25.5	66.1	4.8	817	30.9

The data in Table II are calculated from those given in Table I. They show equilibrium constants and corresponding values of the free-energy change for four possible reactions. The values of ΔF_{CH_3OH} are calculated from the corresponding ΔF and Eastman's (*2*) values for the free energies of carbon monoxide, carbon dioxide, and water.

It was hoped in this series of experiments to determine which of these possible reactions came nearest to equilibrium at the different rates of gas flow. This purpose was probably defeated by uncontrollable changes in activity of the catalyst. However, examination of the data recorded in Table II, together with the facts presented above, shows the inconsistency of picking out any one reaction involving methanol (for example, the hydrogen–carbon monoxide reaction) as the one in which the methanol is nearest to equilibrium. The writers believe that the data presented here indicate that side reactions may under certain conditions introduce some error into measurements of the methanol equilibrium.

Table II—"Equilibrium" in Four Possible Reactions at 304° C.

Run	$2H_2 + CO = CH_3OH$			$3CO + 2H_2O = CH_3OH + 2CO_2$			$CO_2 + 3H_2 = CH_3OH + H_2O$			$CO + H_2O = H_2 + CO_2$	
	K	ΔF	$\Delta F^0_{CH_3OH}$	K	ΔF	$\Delta F^0_{CH_3OH}$	K	ΔF	$\Delta F^0_{CH_3OH}$	K	ΔF
1	3.8×10^{-4}	+9037	−28,886	6.8×10^{-1}	+437	−29,447	8.9×10^{-6}	+13,345	−28,597	42	−4300
2	6.7×10^{-4}	+8390	−29,533	17.0×10^{-1}	−595	−30,480	13.0×10^{-6}	+12,897	−29,045	50	−4498
3	2.4×10^{-4}	+9300	−28,623	4.2×10^{-1}	+995	−28,890	5.7×10^{-6}	+13,857	−28,085	41	−4264
4	3.67×10^{-4}	+9078	−28,845	24.8×10^{-1}	−1043	−30,928	4.5×10^{-6}	+14,128	−27,814	80	−5029

Note—Recently Walther A. Roth of Germany has given, in a personal communication, a brief account of results he has obtained in a redetermination of the heat of combustion of methanol. He finds the heat of combustion of liquid methanol to be 173,300 calories per gram-molecule at constant pressure and (presumably) 18° C. He considers the earlier data by Richards and Davis (*6*) to be in error due to the presence of water in their sample of methanol. Using the specific-heat data given by Kelley (*3*), the free energy of CO given by Eastman (*2*) and this new value of the heat of combustion of methanol, the equation for the free-energy change in Reaction 1 is

$$\Delta F = -18{,}050 + 45.00\,T \log_{10} T - 0.01586T^2 - 69.4T$$

The equilibrium constant calculated from this equation for 304° C. is 7.4×10^{-4}. This is in very satisfactory agreement with the value 5.6×10^{-4} experimentally determined by Smith and Branting (*1*). This equation combined with the value for the free energy of carbon monoxide as given by Eastman (*2*) gives −29,590 calories for the free-energy of $CH_3OH(g)$ at 304° C., which may be compared with the data in Table II.

Eastman's data (*2*) give the equilibrium constant for the water-gas reaction as 34 at 304° C. It is interesting to note how closely equilibrium is apparently reached in this reaction.

Lack of time prevented further investigation of these reactions and use of other catalysts. However, most methanol catalysts of which we have knowledge produce carbon dioxide or water or both with methanol. An investigation similar to the present one at high pressures with accurate determination of water and carbon dioxide partial pressures at equilibrium would be of interest. It is possible that the mechanism of formation of methanol from hydrogen and carbon monoxide may not be so simple as indicated by Equation 1, especially as a steady state is approached.

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The Methanol Equilibrium[1,2]

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In spite of all the published work on this subject there are still some striking discrepancies to be cleared up. Previous workers have attacked the problem from three angles: (1) calculation of the equilibrium constant, K_p, via the third law of thermodynamics making use of absolute entropies or by means of the Nernst approximation; (2) indirect measurement of K_p by experimental study of equilibrium for reactions whose combination yields the methanol synthesis reaction; and (3) direct determination of K_p for the methanol reaction at atmospheric and higher pressures.

The experimental investigations agree only as to order of magnitude, the disagreement being as much as several hundred per cent. Only a small part of this discrepancy can be accounted for by the effect of pressure on K_p. This is treated in detail in the paper and values of K_{p_0} (equilibrium constant at low pressures, where gases are substantially ideal) are calculated with the aid of van der Waals' equation. The equilibrium constants calculated via the third law are anywhere from 12 to 1500 times the experimental ones. It is believed that a large part of this difference is due to inaccuracies in the thermal data, though this has been disputed by others.

Some new experimental data obtained by the direct method at 170 atmospheres and temperatures ranging from 260° to 310° C. are presented. These data must be regarded as preliminary, but it is believed that they represent an improvement over the previous data obtained at pressures higher than atmospheric. The constants agree fairly well, at the lower temperatures, with those obtained in the one published investigation by the direct method at 1 atmosphere and are considerably higher than those obtained in two investigations at higher pressures.

The results of previous investigations are critically compared with these new data and various sources of error in the experimental determination of K_p's and their interpolation and extrapolation by means of thermal data are discussed. The influence of side reactions on the experimental measurements is particularly stressed. The new data still leave an enormous gap between experimental and calculated results.

In spite of the many recent papers on this subject, there still exists considerable uncertainty as to the exact position of the equilibrium in the reaction:

$$CO + 2H_2 \rightleftharpoons CH_3OH \qquad (1)$$

Results of the various experimental investigations are quite conflicting. Equilibrium constants calculated from thermal data are scarcely of the same order of magnitude as those obtained experimentally. The need for more work is obvious, especially in view of the fact that this reaction is of great importance both industrially and scientifically. It is particularly important to establish the reasons for the great difference between calculated and experimental results, because many such calculations are now being made and we can have but little confidence in them when we fail to get even order-of-magnitude agreement in a test case where the data are probably better than the average.

It is the purpose of this paper to review the work on this subject and to present some new experimental results, of a preliminary nature, obtained at a pressure of 170 atmospheres.

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[2] Taken in part from a dissertation presented by Mr. von Wettberg to the Graduate School of Yale University in partial fulfilment of the requirements for the degree of doctor of philosophy, June, 1930.

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Previous Work

There have been three main avenues of attack on this problem:

(1) Calculation by means of the Nernst approximation formula or by the third law of thermodynamics.

(2) Indirect measurement involving the reactions

$$2H_2 + HCOOCH_3 \rightleftharpoons 2CH_3OH \qquad (2)$$
$$CH_3OH + CO \rightleftharpoons HCOOCH_3 \qquad (3)$$

or the reactions

$$H_2 + CO \rightleftharpoons HCOH \qquad (4)$$
$$HCOH + H_2 \rightleftharpoons CH_3OH \qquad (5)$$

(3) Direct measurements on Reaction 1.

Matignon (*16*), Audibert and Raineau (*1*), and Brown and Galloway (*3*) have calculated K_p for Reaction 1 by means of the Nernst approximation formula. Kelley (*11*), Smith (*18*), Francis (*8*), and Dodge (*6*) have attempted to calculate $\Delta F°$ and, hence, K_p for Reaction 1 with the aid of absolute entropies and the third law of thermodynamics. Ghosh and Chakravarty (*9*), Christiansen (*5*), and Lacy, Dunning, and Storch (*13*) used the indirect method, the first mentioned pair of investigators making use of Reactions 4 and 5 and the others of Reactions 2 and 3.

Direct equilibrium measurements on Reaction 1 have been published by Smith and Branting (*19*), Newitt, Byrne, and

Strong (*17*), and Lacy, Dunning, and Storch (*13*). Audibert and Raineau (*1*), Lewis and Frolich (*14*), and Brown and Galloway (*3*) have measured the percentage of carbon monoxide converted to methanol by Reaction 1 at low space velocities in connection with catalyst investigations. Although these measurements were not made primarily for the purpose of determining the equilibrium, nevertheless they should give results approximating equilibrium conditions, and are properly classed with the direct equilibrium measurements. Fieldner and Brown (*7*) have summarized the work of these last three pairs of investigators.

In Table I there are presented some typical results by various investigators. Results calculated via the Nernst approximation formula are not included, as this formula has little scientific foundation and the results could not be expected to be more than order of magnitude. The most outstanding discrepancy is that between the calculated results and those obtained from experimental measurements. Even the calculated results do not agree very well among themselves. The reasons why accurate results can hardly be expected from the third-law calculations have been discussed in a recent paper (*6*) by one of the authors. Smith and Hirst (*20*) have, however, taken exception to the conclusions reached in this paper. They also pointed out a numerical error, which is hereby acknowledged but which does not seem to the authors to invalidate the general conclusions reached. The experimental measurements with one exception agree as to order of magnitude, but the problem can hardly be regarded as solved when differences of several hundred per cent in the experimental values of K_p still exist. Curiously enough, the one exception consists of results that agree as to order of magnitude with the third-law calculations, but a critical study of the paper convinced the present writers that these results cannot be given much weight.

It is recognized that part of the differences shown in Table I are due to the fact that the results are not all for the same pressure, and K_p is known to be a function of pressure. The calculated results, being based on standard free-energy changes, give directly K_p for a standard state of pressure which, in Lewis' (*15*) system of thermodynamics is practically 1 atmosphere. It should also be noted that K_p is a function of the composition of the equilibrium mixture at a given pressure and temperature. It is believed that neither of these effects is sufficient to account even for the discrepancies between the various experimental K_p's. This point will be taken up later. Finally, it should be noted that some of the differences exhibited in Table I are due to the use by the various investigators of different thermal data to interpolate and extrapolate their experimental results.

Apparatus and Experimental Procedure

Equilibrium was approached from both sides, using a dynamic method whose general features may best be explained with reference to Figure 1. Carbon monoxide was generated by the dehydration of formic acid over phosphoric acid and mixed in approximately the stoichiometric proportions with commercial electrolytic hydrogen that had been deoxidized over a copper catalyst. The mixture was scrubbed with caustic soda solution and then compressed to the four cylinders shown, two being used to maintain a constant pressure supply of gas to the reactor and the other two used as auxiliary storage. From the storage system the gas passed through the purifying tower, *F*, containing activated silica gel. Beyond this tower the system up to the catalyst was essentially non-ferrous in order to eliminate the possibility of trouble from iron carbonyl. After this final purification the gas passed to the saturator, *J*, where it bubbled through methanol. The saturator, shown in greater detail in Figure 2, was constructed from bronze hexagon stock and provided with suitable head for gas and liquid connections. It was surrounded by a motor-stirred oil bath which was electrically heated by means of an immersion heater and a nichrome ribbon winding on the outside of the container. The oil bath was well insulated thermally and its temperature automatically controlled by a bimetallic thermostat. The maximum possible methanol pressure that can be produced is, of course, the critical pressure of 78.7 atmospheres. The mol per cent of methanol in the saturated gas is approximately double that calculated from the vapor pressure, assuming ideal gases. The saturator was calibrated at several temperatures by passing the storage gas mixture through it at 170 atmospheres, expanding the gas to 1 atmosphere, and condensing the methanol at the temperature of solid carbon dioxide. A calibration curve was constructed from which the mol per cent of methanol in the gas at any temperature could be read. From the saturator the gas passed through an electrically heated tube to the catalyst reactor, *L*. The reactor, shown in greater detail in Figure 3, was constructed from a

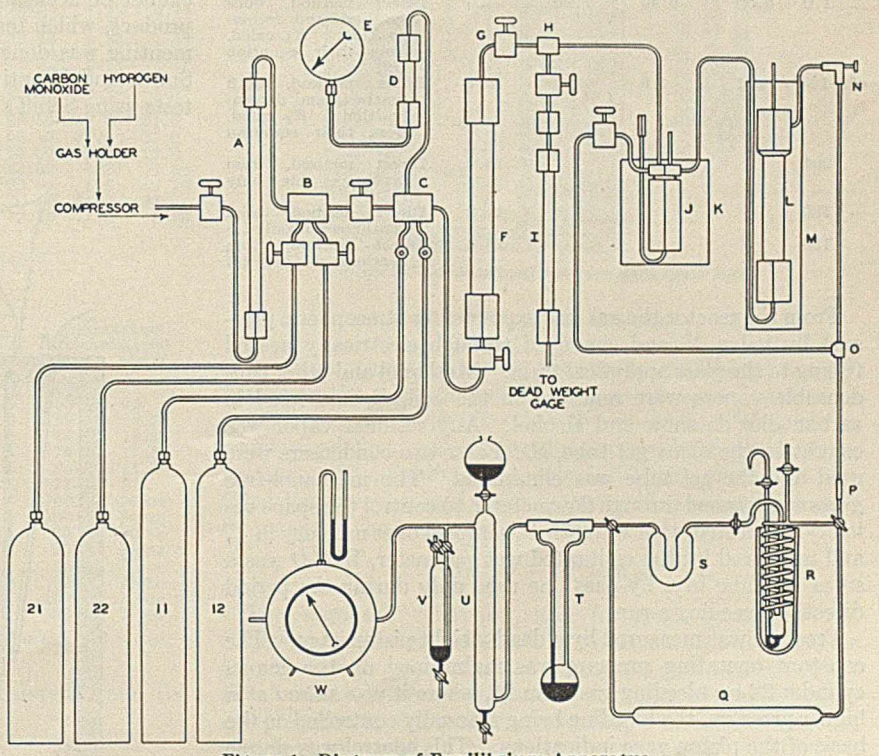

Figure 1—Diagram of Equilibrium Apparatus

chrome-vanadium steel tube, *A*, fitted with copper liner, *D*. Head *B*, carrying thermocouple well, *F*, and gas exit connection was welded to the alloy steel tube. The bottom of the reactor was closed by the nipple, *E*, held by nut *C* against a confined copper gasket. The gas inlet and outlet connections were made by means of 60-degree cones on the ends of the copper-lined steel tubing. (U. S. Dept. Agriculture, *Circ.* **61.**) The thermocouple well was held in place by a cone-type compression union.

For temperature control the reactor was immersed in a

lead-antimony bath contained in the steel pipe, H, which was wound with nichrome ribbon for heating and thermally insulated with 85 per cent magnesia. The ribbon was insulated from the metal by four thicknesses of asbestos paper. Suitable means were provided for holding the reactor in the bath against the buoyant force of the lead. Considerable trouble was experienced from lead working into the joints and loosening the heads and tubing connections. The loosening did not seem to occur as long as the lead was kept molten, but only when it was allowed to solidify and then remelted. The difficulty was largely overcome by coating all joints with a liberal application of a mixture of talc and Meprolene oil to keep out the lead and also by maintaining the lead molten for long periods.

Table I—Values of K_p Obtained by Previous Investigators

Pressure *Atm.*	$K_p \times 10^3$ at 250° C.	$K_p \times 10^4$ at 300° C.	$K_p \times 10^5$ at 350° C.	$K_p \times 10^6$ at 400° C.	Method of Investigator
...	74	81	140	280	Calcd. by third law (*11*)
...	1300	800	1200	2500	Calcd. by third law (*18*)
...	1300	1400	2200	4500	Calcd. by third law (*8*)
1.0	320	430			Indirect method using Reactions 4 and 5; K_p calcd. from their equations (*9*)
1.0	4.7	6.0			Indirect method using Reactions 2 and 3; K_p calcd. from his equation (*5*)
1.0	3.1	4.5			Indirect method using Reactions 2 and 3; K_p calcd. from his equation (*13*)
50	1.25	1.90			Direct method, both synthesis and decomposition (*13*)
1.0	5.90	6.40	7.90	20	Direct method, both synthesis and decomposition; K_p calcd. from their equation (*19*)
70–100	2.1	1.6	2.0	3.1	Direct method, both synthesis and decomposition; K_p calcd. from their equation (*17*)
204				18.0	Direct method, from synthesis side only (*14*)
150				19.2	Direct method, from synthesis side only (*1*)
180				19.8	Direct method, from synthesis side only (*3*)

From the reactor the gas was expanded to atmospheric pressure by valve N, and conveyed through electrically heated tubing to the glass analytical train. Methanol and other condensable vapors were removed in the coil, R, immersed in carbon dioxide snow and alcohol. Any residual vapor was caught in the silica gel tube, S. Later two condensers were used and the gel tube was eliminated. The methanol-free gases were passed through flowmeter T to control the space velocity, saturated with water in U, sampled over mercury in V, and measured by the calibrated wet gas meter, W. Q was a silica gel tube in a by-pass line used only during the period directly preceding a run.

Pressure was measured by a dead-weight piston gage. The constant operating pressure was maintained on the gas in cylinder 22 by bleeding gas from 21, where it was stored at a higher pressure, the bleeding being manually controlled on the basis of the piston gage indications. This control was simple and variations easily held to less than 0.5 atmosphere. Temperatures in the lead bath and in the catalyst bed were measured by chromel-X-copel couples and Leeds and Northrup portable indicating potentiometers. Variations of 1.0° C. were about the smallest that could be detected with certainty. The temperature of the lead bath was readily controlled manually, so that its temperature variation was no more than the limit of temperature variation that could be detected. The thermocouple well, F (Figure 3), could be varied in position and was placed so that it projected only a short distance into the catalyst bed near the gas exit end. Temperatures measured by this couple were consistently higher than the temperature measured in the bath. The differences between the two varied between different runs, but was very constant during any given run. In the majority of runs the difference was less than 3° C., but in some cases was greater, the extreme difference being 12° C. Owing to the exothermal character of the reaction, conduction along thermocouple well, and relatively low rate of heat transfer from a fluid moving at such a low velocity, it is not easy to obtain a reliable temperature measurement. If any error existed, the temperatures are believed to be low rather than high.

The reactor was filled with about 60 cc. of 8- to 14-mesh catalyst granules. In runs 8 to 12, inclusive, a zinc-chromium catalyst was used, and in the remainder of the runs a zinc-copper catalyst was used. Each run was preceded by a warming-up period long enough so that the gas in the catalyst space was completely changed at least once. During this period all instruments were read to give an indication of the attainment of constant conditions, but no measurements recorded as final data. The condenser, R, was by-passed and the gas sent through Q during this time. At the conclusion of the run the liquid condensate was blown from the condenser into a previously chilled receiver and tightly stoppered. The condenser was then rinsed out with small portions of water. When the gel tube, S, was used, its adsorbed liquid was removed by steaming.

Various methods were tried for the determination of the methanol in the condensate. Estimation by gravity or refractive index is open to the objection that these methods cannot be accurate unless water is the only condensable by-product, which may be far from true. Considerable experimenting was done on the colorimetric method developed by Smith and Branting (*19*) from the well-known formaldehyde tests using Schiff's reagent. In spite of their statement to the

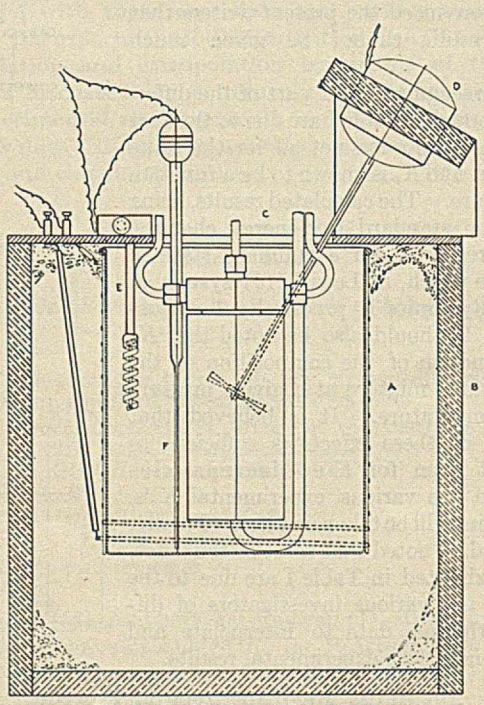

Figure 2—Methanol Saturator

contrary, the present writers have proved beyond a doubt that dimethyl ether does interfere in this test. Since dimethyl ether was shown to be present in many of the runs, this method was abandoned. Rectification was finally adopted as the most satisfactory method of determining methanol. The condensate (from 14 to 40 cc. were available from a run) was distilled through a Hempel column and, by using at the

start a reflux condenser with cooling medium at about −25° C., dimethyl ether and methanol could both be determined with reasonable accuracy.

The storage gas was substantially a 2-to-1 hydrogen–carbon monoxide gas containing a small percentage of inerts. Its exact composition varied somewhat and no attempt was made to determine it for each run. The gases leaving the catalyst were, however, sampled continuously during the run and carefully analyzed using a modified Orsat apparatus equipped with mercury-filled, compensated buret.

Data and Calculations

Twenty-seven runs were made, but data for only fourteen of them are presented in this paper. The results calculated from the data taken in these runs are shown in Table II. It should be emphasized that these data are preliminary and are presented largely to bring out more clearly than has been done in the past some of the serious obstacles in the way of determining accurately the equilibrium in a reaction of this type. Certain of the data are believed to be more reliable than previously published data obtained in the study of this reaction under pressure. Table III gives the analyses of off-gas and methanol content of the condensate.

Table II—Summary of Equilibrium Data

Run	Temp.	Off-Gas[a]	Space Velocity[b]	MeOH in Entering Gas	H_2 Off-Gases	CO Off-Gases	MeOH Off-Gases	$K_p \times 10^4$	$K_{p_0} \times 10^4$
	° C.	Liters		Mol %	Mol %	Mol %	Mol %		
8	329	60.0	1040	None	57.90	12.68	16.95	1.40	0.71
9A	300	36.2	1208	None	55.20	14.45	22.35	1.80	0.85
$9B_1$	302	19.5	309	None	53.40	8.32	22.10	3.20	1.45
$9B_2$	301.5	24.2	301	None	55.10	8.05	21.20	3.00	1.43
10	309	41.1	1110	None	60.90	13.50	21.30	1.50	0.73
12	302	28.5	273	30.5	44.90	9.47	23.70	4.30	1.94
15	258.5	6.39	547	47.5	17.80	6.07	71.70	129.0	48.3
16	259	6.36	221	0	21.90	5.70	66.50	84.0	31.0
17	274	9.78	224	40.0	26.90	7.30	56.10	37.0	15.0
18	273	5.41	114	40.0	28.70	7.80	53.00	29.0	11.8
19	307	17.1	259	25.5	46.60	8.65	23.30	4.30	1.96
20	307	14.35	248	40.5	43.30	9.04	25.00	4.6	2.10
22	258	7.97	500	47.0	18.90	8.14	70.40	84.0	31.4
23	298	27.0	575	16.5	34.40	11.20	42.40	11.0	5.20

[a] Dry and at standard conditions.
[b] Liters of total off-gas per hour per liter of catalyst.

Table III—Analytical Data

Run	Gas Analyses: CO_2	Ill.	O_2	CO	CH_4	H_2	N_2	Analysis of Condensate[a]: MeOH	Me_2O
	%	%	%	%	%	%	%	% by wt.	
8	6.0	0.1	0.4	16.2	0.6	74.1	2.6	83	12
9A	2.6	0.1	0.5	19.3	0.4	73.8	3.3	89	8.2
$9B_1$	6.0	0.1	0.6	11.8	0.5	75.7	5.3	74.5	18.2
$9B_2$	6.4	0.1	0.7	11.2	0.4	76.7	4.5	76	17.5
10	3.9	0.1	0.5	18.0	0.4	73.9	3.2	85	11.7
12	13.3	0.6	0.2	14.2	2.0	67.4	2.3	71	21
15	2.6	0.2	1.2	21.4	1.9	70.8	1.9	100	None
16	3.4	0.3	0.5	17.1	2.7	65.4	10.6	103	None
17	8.3	0.3	0.6	17.6	3.8	64.9	4.5	95	None
18	10.8	0.5	0.7	14.7	4.9	64.7	3.7	95	None
19	11.4	0.3	0.8	12.1	6.6	65.4	3.4	84	None
20	14.3	0.2	0.4	13.1	7.3	62.8	1.9	86	None
22	2.1	0.2	0.7	27.4	1.7	63.2	4.7	100	None
23	6.3	0.9	0.8	21.0	2.9	64.5	3.6	93	None

[a] Assuming it to consist only of methanol, methyl ether, and water.

The equilibrium constant, K_p, was calculated from the following expression:

$$K_p = \frac{Px_{MeOH}}{(Px_{H_2})^2 \times (Px_{CO})} \qquad (6)$$

P = total gas pressure
x = mol fraction in equilibrium mixture

In getting the mol fractions of the three gases at equilibrium the total number of mols of gas present are needed. Certain assumptions were made in arriving at this figure for each run. An amount of water vapor equivalent to the methyl ether was assumed to be present in the runs with zinc-chromium catalysts. In the later runs, although there was no ether, there appeared to be small amounts of water and higher alcohols, which were estimated from the total weight of condensate and the distillation curves. The effect of these assumptions is to make only a small correction. The question as to the side from which equilibrium was approached in a given run is not always easy to decide. In case of a run like No. 20, where the mol per cent of methanol in the entering gases is much greater than in the off-gases, there appears to be no doubt that the equilibrium was approached from the decomposition side. In cases like run 19 one cannot be certain. Runs 12 and 20 are the only ones in which equilibrium was certainly approached from the decomposition side.

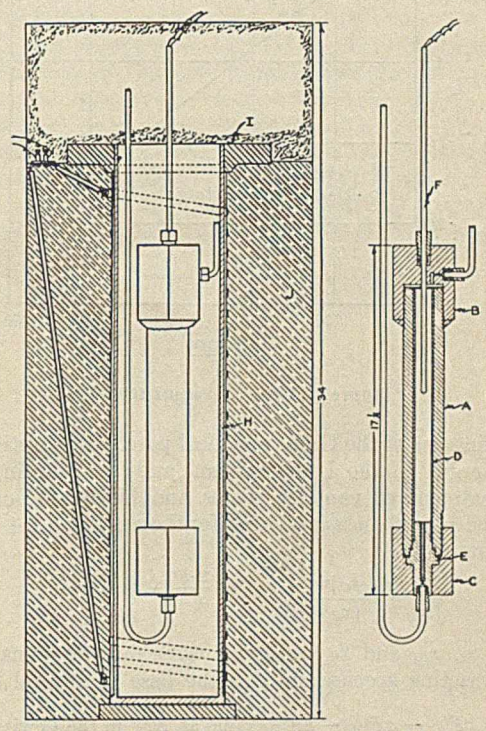

Figure 3—Equilibrium Reactor and Lead Bath

Discussion of Results

In attempting to compare the results of different investigators on the methanol equilibrium, one is immediately confronted with the difficulty that the equilibrium constant as ordinarily defined and as it is defined above is a function of the pressure. The values of K_p calculated with the aid of the third law are obtained from "standard" free-energy values by means of the well-known relation

$$\Delta F^\circ = -RT \ln K_p$$

The standard reference state for gases usually chosen, following Lewis and Randall (*15*), is one for which the fugacity is unity and the properties are those for a gas at infinite dilution. This is a purely hypothetical standard, but for all practical purposes is equivalent to choosing 1 atmosphere as the standard pressure. Thus, we have values of K_p for the methanol reaction at various pressures from 1 to 200 atmospheres and, to be comparable, they should be reduced to a common pressure. Furthermore, they are not strictly comparable unless the composition is the same at a given temperature and pressure. This latter effect will be neglected for the present.

Detailed treatment of equilibria for the general case—that is, without the assumption of ideal solutions—was given many years ago by van der Waals, based on the work of Gibbs, and is summarized in the text by van der Waals and Kohnstamm (*21*). Another treatment, the same in principle but

differing in detail, is that of Lewis (*15*), involving the use of the special functions fugacity and activity. Still more recent treatments have been published by Gillespie (*10*), Keyes (*12*), and Beattie (*2*), the latter giving the most completely developed and comprehensive treatment yet published for the particular case of chemical equilibrium in non-ideal systems.

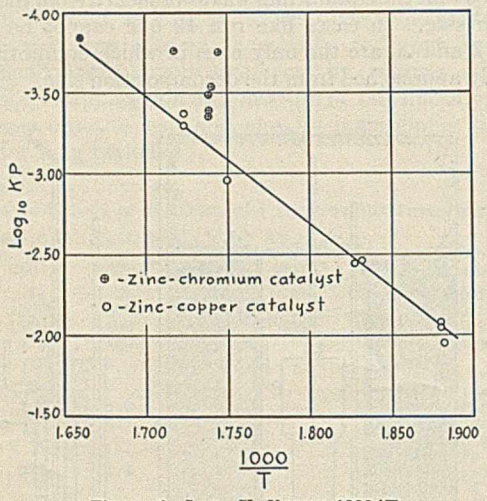

Figure 4—$\text{Log}_{10} K_p$ Versus $1000/T$

Making use of the Gibbs chemical potentials (partial molal free energies in the Lewis system) and following in general the treatment of van der Waals and his pupils, one may write the general mass-action law for the reaction $aA + bB \rightleftharpoons cC$ as follows:

$$\frac{[x_C e^{\phi_C}]^c}{[x_A e^{\phi_A}]^a [x_B e^{\phi_B}]^b} = e^{-\frac{\Sigma\nu F'}{RT} - \Sigma\nu \ln p'} \qquad (7)$$

where x_A, x_B, and x_C are equilibrium mol fractions of the three reacting species and e is the base of natural logs.

$\Sigma\nu F' = cF'_C - aF'_A - bF'_B$ (same as $\Delta F°$ in the Lewis system)

F'_A, etc., are the thermodynamic potentials or free energies of components A, etc., at the temperature in question and at some initial, arbitrary, standard pressure, p'.

R is the gas constant.

$$\phi_A = \pi - x_B\left(\frac{\partial\pi}{\partial x_B}\right) - x_C\left(\frac{\partial\pi}{\partial x_C}\right)$$

$$\phi_B = \pi + (1 - x_B)\left(\frac{\partial\pi}{\partial x_B}\right) - x_C\left(\frac{\partial\pi}{\partial x_C}\right)$$

$$\phi_C = \pi + (1 - x_C)\left(\frac{\partial\pi}{\partial x_C}\right) - x_B\left(\frac{\partial\pi}{\partial x_B}\right)$$

$$\text{and } \pi = \frac{\int v dp}{RT}$$

Choosing 1 atmosphere for the standard pressure, p', the expression on the right-hand side of Equation 7 reduces to $e^{-\frac{\Sigma\nu F'}{RT}}$. This is an equilibrium constant which is a function of temperature, but independent of the pressure or composition, and will be represented by K_{p_0}. Comparing this constant with K_p as expressed by Equation 6, it is clear that K_p must depend on both pressure and composition. It can readily be shown that $x_A e^{\phi_A}$ is identical with Lewis' $\bar{f}_A$, the "partial fugacity" of component A in the solution, and similarly for the expressions involving B and C. The application of Equation 7 to obtain numerical values of K_{p_0} requires a knowledge of the compressibilities of the gaseous solutions of the three components over the pressure and temperature range to be covered, or, better still, an equation of state for mixtures of these components, valid over the desired range. Such data are not available for the system under consideration. Beattie (*2*) has given the complete solution in terms of his own equation of state, but the constants of his equation of state for methanol are not known, and his method of getting the constants of the equation for the mixtures from those of the pure components is not well established.

Assuming the equilibrium mixture to be a solution of ideal gases, Equation 7 at once reduces to the familiar mass-action law for ideal gases, since for this case $\pi = \ln p$ and $\left(\frac{\partial\pi}{\partial x}\right) = 0$. Since, under the experimental conditions chosen, methanol is in the neighborhood of its critical state, the deviations from ideal behavior must be very large. Probably the best assumption that can be made at present is that each gas in the mixture behaves as if it were alone at the given temperature and at the total pressure of the mixture. This is the same as using for each gas its own equation of state, which would be valid if it were the only gas present. Such an assumption cannot possibly be true. Nevertheless, it may be a much closer approximation to the truth than the assumption of ideal gases. Mathematically, this is equivalent to assuming that π is not a function of x or that $\left(\frac{\partial\pi}{\partial x}\right) = 0$. Making this assumption, Equation 7 reduces to:

$$\frac{[x_C e^{\pi_C}]^c}{[x_A e^{\pi_A}]^a [x_B e^{\pi_B}]^b} = K_{p_0} \qquad (8)$$

This assumption is the same as that involved in the fugacity rule of Lewis and Randall (*15*, p. 226), which has been used by various investigators (*3*, *19*, *10*), to aid in interpreting high-pressure equilibrium data. This simple interpretation of the rule has not been published before to the writers' knowledge. Thus, if, as given above, $\bar{f}_A = x_A e^{\phi_A}$, then $\bar{f}_A = x_A e^{\pi_A}$, when $\left(\frac{\partial\pi}{\partial x}\right) = 0$, but e^{π_A} or $e^{\frac{\int v dp}{RT}} = f_A$ by definition of fugacity where f_A is the fugacity of pure component A at the given temperature and total pressure.

The validity of this rule has been the subject of a number of investigations and, as one would expect, it is far from exact. It would lead us too far afield to enter into any discussion of this point.

K_{p_0} may now be calculated directly from K_p by means of the relation

$$K_{p_0} = K_p \frac{\left(\frac{e^{\pi_C}}{p}\right)^c}{\left(\frac{e^{\pi_A}}{p}\right)^a \left(\frac{e^{\pi_B}}{p}\right)^b} \qquad (9)$$

In the absence of an equation of state for mixtures of carbon monoxide, hydrogen, and methanol, the writers have attempted to treat their data by means of Equation 9. Accurate equations of state are available for carbon monoxide and hydrogen, but not for methanol. Van der Waals' equation has been used for all three gases, the constants a and b being evaluated from the best published values of critical pressure and temperature.

Note—It should be noted that $\int v dp$ cannot be directly obtained from van der Waals' equation. It is necessary to change to v as the independent variable. This is liable to lead one into error because the lower-limit of the integral has already been substituted. It can easily be shown that if dp is changed to dv and the integral then evaluated, as an indefinite integral, the expression e^{π} should be multiplied by RT. In other words, for this case $f = RTe^{\pi}$.

A few calculations on hydrogen using the Beattie-Bridgman equation of state gave results but slightly different from those using the much simpler equation. Since methanol is the most important component and, since Equation 9 is only a rough approximation anyway, it did not appear worth

while to use any more complex equations of state for hydrogen and carbon monoxide.

Values of K_{p_0} calculated in this way are given in the last column of Table II. From this table it will be seen that the effect of pressure on the equilibrium constant at the pressure of these experiments is very considerable. In Figures 4 and 5 the data are shown in the form of graphs of $\log_{10} K_p$ and $\log_{10} K_{p_0}$, respectively, as a function of $1000/T$. The best straight line has been put through the points, omitting from consideration points from runs earlier than No. 15, excepting No. 8. It will be noted that all these earlier runs were made with a zinc-chromium catalyst, and they are believed to be less reliable than the later runs, owing to the greater amount of side reactions. Considered by themselves, without reference to the later experiments with a zinc-copper catalyst, these points are fairly consistent. Thus, 9A and 10 were at considerably higher space velocities and it is probable that equilibrium was not attained. The two synthesis runs, $9B_1$ and $9B_2$, check well and give somewhat lower values of K_p than the decomposition run 12, as would be expected. Furthermore, the average of these three runs agrees fairly well with the result obtained by Lacy, Dunning, and Storch at 300° C. It appeared to the present writers, however, that side reactions would tend to give too low K_p values and that therefore the higher values obtained with the zinc-copper catalyst were closer to the truth. Logically, run 8 should also be omitted, but since it falls nicely into line with the later runs using a zinc-copper catalyst, it has been retained. The equations of the two straight lines, determined by the method of averages, are:

$$\log_{10} K_p = \frac{7974}{T} - 17.045$$

$$\log_{10} K_{p_0} = \frac{7358}{T} - 16.312$$

From the K_{p_0} values standard ΔF's have also been calculated and from them the integration constant, I, of the standard free-energy equation using the same thermal data used by Smith and Branting (*19*). The results are given in Table IV.

Table IV—Calculation of Integration Constant of Free-Energy Equation

Run	ΔF^0	I
8	11400	−52.4
15	5620	−54.7
16	6100	−54.0
17	7070	−53.8
18	7310	−53.2
19	9840	−52.6
20	9750	−52.8
22	6100	−54.0
23	8590	−54.1
	Av.	−53.50

Using the average value of I, we get for the final K_{p_0} equation,

$$\log_{10} K_{p_0} = \frac{4570}{T} - 9.010 \log_{10} T + 0.00312\, T + 11.70$$

In Table V are compared values of K_{p_0} calculated from this equation with those obtained by other investigators. The data of Lacy, Dunning, and Storch were extrapolated beyond 300° C. by using the K_{p_0} values calculated from their best K_p values at 250° and 300° C. to give an average I, just as in the treatment of the data of the present writers. The data of Newitt, Byrne, and Strong (*17*) were extrapolated by calculating K_p from their equation at 10-degree intervals from 280° to 320° C. (about their experimental range), converting these to K_{p_0} assuming an average pressure of 80 atmospheres and then getting an I value for each K_{p_0} just as previously done for the writers' own data.

Table V—Calculated Values of K_{p_0} Obtained from K_p Given by Various Investigators

Investigator	Pressure *Atm.*	$K_{p_0} \times 10^3$ at 250° C.	$K_{p_0} \times 10^4$ at 300° C.	$K_{p_0} \times 10^5$ at 350° C.	$K_{p_0} \times 10^6$ at 400° C.
Authors	170	3.7	4.6	6.3	13.8
(*13*)	50	1.3	1.35	2.0	3.8
(*19*)	1.0	5.9	6.4	7.9	20
(*17*)	70–100	1.15	1.2	1.8	3.5
(*14*)	204				9.4
(*1*)	150				12.1
(*3*)	180				11.2

It will be noted that the present writers' results are intermediate between those of Smith and Branting obtained at 1 atmosphere and those of the two pairs of investigators who worked at higher pressures, being, however, much closer to the former. The writers' value for 400° C. is in pretty good agreement with those of the three investigators who have reported experimental data for this temperature only.

The writers believe that the results of Newitt, Byrne, and Strong and of Lacy, Dunning, and Storch are too low in spite of their excellent agreement. In the first place, the present writers have repeatedly obtained yields of methanol at temperatures from 350° to 400° C. and at fairly high space

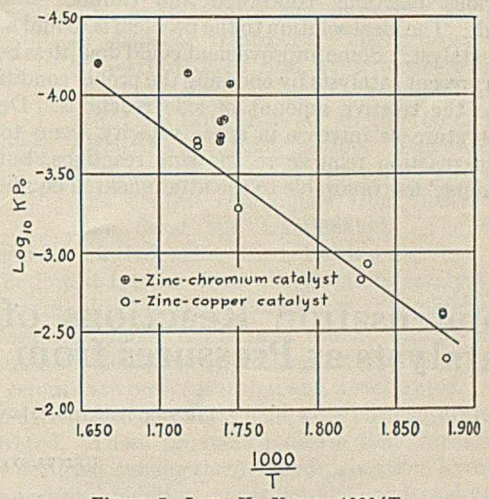

Figure 5—$\log_{10} K_{p_0}$ Versus $1000/T$

velocities (from 5000 to 30,000), which yields are greater than those corresponding to the equilibrium obtained by these investigators. In the second place, they did not take any account of side reactions, but assumed that the exit gas had the same composition as the inlet gas. In the experiments of the present writers this was far from true, as a glance at Table III will show. With a catalyst containing chromium the writers' results show that considerable amounts of dimethyl ether are formed at low space velocities. This is in agreement with the results obtained by Brown and Galloway (*4*). Newitt, Byrne, and Strong used a zinc chromate catalyst, but do not mention ether formation, nor did they report any systematic analyses of their off-gases. Lacy, Dunning, and Storch did not analyze their off-gases and so were obliged to assume them to have the same composition as the inlet gas. The present writers' experience indicates that this might easily give a K_p which is much too low. Although no evidences of any ether formation were observed with their zinc-copper catalyst, yet there were appreciable amounts of carbon dioxide and methane formed. Because of the very great shrinkage in gas volume due to the high conversion to methanol obtained at temperatures of 300° C. and lower, even a small amount of side reactions will greatly affect the percentage of hydrogen and carbon monoxide at equilibrium and, therefore, the equilibrium constant. Thus, if for run 17 one calculates the equilibrium constant on the assumption that the off-gases are hydrogen and carbon monoxide in the

stoichiometric ratio, the result obtained is only one-half the value based on the actual gas analysis. It should also be noted that the purity of the condensate produced is not a safe criterion of the absence of side reactions, as is shown by the data in Table III.

If dimethyl ether was formed in the experiments of Smith and Branting—and one would certainly expect it to be since they used a chromate catalyst and since the dehydration of methanol occurs without volume change—their results would probably be high, because the tests of the present writers show that dimethyl ether would be determined as methanol by the analytical method of Smith and Branting. Allowing for this fact would bring their results into quite close agreement with those of the present writers.

It is difficult to estimate the effect of side reactions on the establishment of equilibrium. It is obvious, however, that a true equilibrium cannot be established with respect to the methanol reaction when side reactions are proceeding simultaneously at a considerable distance from equilibrium. The question as to how closely one comes to the methanol equilibrium in spite of side reactions involves the relative rates of the various reactions concerned and cannot be readily answered. The ideal solution to the problem is to find a highly specific catalyst. Some improvement could doubtless be made with the present catalysts by choosing the proper conditions to minimize the relative amount of side reactions. Decrease in temperature or increase in space velocity seems to favor the main reaction relative to the side reactions, but both are, of course, less favorable to the attainment of equilibrium.

Although the writers' equilibrium constants may still be somewhat low owing to the influence of side reactions, they believe that further and more accurate experimental work will not alter them greatly. The results further strengthen the belief that the experimentally determined equilibrium constants are of the right order of magnitude and that those calculated by means of the third law and the best available heat data are incorrect.

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Condensation Reactions of Acetaldehyde over Certain Oxide Catalysts at Pressures from 1 to 500 Atmospheres of Hydrogen[1]

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Apparatus is described for carrying out reactions of organic liquids under pressure in the vapor state in an atmosphere of hydrogen. The experimental work is reported in two parts—one dealing with the effect of pressure, temperature, rate of flow, composition of catalyst, water content, etc., on the ratio and rate of formation of hydrogen and ethylene; and the other with the effect of these variables on the character of the liquid products.

The liquid products are in all cases complicated mixtures which were partially fractionated and then reduced over nickel catalysts. A list of compounds and yields are given ranging from ethyl alcohol and acetaldehyde through esters of acetic, butyric, and caproic acids and alcohols higher than octyl. Equations suggesting probable mechanisms are given for these products.

WHEN ethanol is passed over dehydrogenating catalysts such as zinc oxide at temperatures of 300° to 400° C. it is dehydrogenated to acetaldehyde. If this reaction takes place under a sufficient pressure of hydrogen practically no acetaldehyde but substances of higher molecular weight are to be found in the reaction products. The results obtained in a beginning of an experimental study of these reactions are the basis for the present paper.

Apparatus

The essential parts of the apparatus used in carrying out the reactions under pressure were a pump, a vaporizer, a catalyst chamber, a condenser, a receiver, a hydraulic gage, and the necessary valves, tubing, and connections. The pump had two cylinders, each having an internal volume of 150 ml., one of which at any given time was delivering and the other receiving liquid. The liquid could be delivered at rates from 60 to 600 ml. per hour against pressures up to 1000 atmospheres. The vaporizer was a chrome-vanadium steel bomb similar in construction to the catalyst chamber but having an internal volume of only 50 ml. It was filled with $^1/_4$-inch (6.4-mm.) steel balls. The catalyst chamber was essentially the same as that supplied by the American Instrument Company as their standard catalyst chamber for ammonia synthesis on a laboratory scale but modified in that external heating was used and the catalyst holder had a capacity for about 75 ml. of catalyst. The condenser was a 3-foot (91.4-cm.) length of $^1/_4 \times {}^1/_{16}$ inch (6.4 × 1.6 mm.) steel tubing in a jacket through which water was circulated. The receiver was similar in design to the catalyst chamber except that it had an internal volume of 200 ml. and was of somewhat lighter construction. It was provided with an outlet at both top and bottom so that either gas or liquid could be withdrawn from the system. The catalyst was in the form of pellets and was prepared by the ignition of zinc

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oxolate or basic zinc ammonium chromate or the corresponding manganese or copper chromate as described by Lazier.

Operation

The catalyst being in place, hydrogen or nitrogen was introduced into the system to give the desired pressure. The vaporizer was then heated to about 265° C. and the catalyst chamber to the desired temperature. The pump was then started and the liquid forced at the desired rate into the vaporizer. Gas or liquid was removed from the receiver as was necessary or desired. The gases so removed from the receiver were passed through ice-cold condensers and washing towers and, when desired, measured and analyzed.

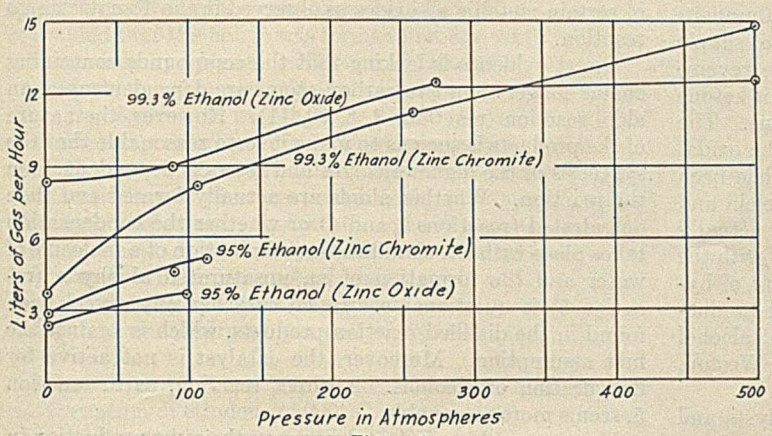


Figure 1

Experimental Work

The experimental work to be reported in this paper may be divided into two parts—the one having to do with the effect of various pressures, temperatures, rates of pumpage, kind and amounts of catalyst, and water content upon the ratio and rates of the formation of hydrogen and ethylene, and the other, with the effect of these same variables upon the character of the liquid products of the reaction.

The relationship of the pressure to the rate of dehydrogenation of ethanol is shown in Figure 1. A comparison of the rate of dehydrogenation of 95 per cent alcohol and of 99 and 100 per cent ethanol is also shown in Figure 1.

The variation in ratio of hydrogen to ethylene at various pressures is shown in Figure 2.

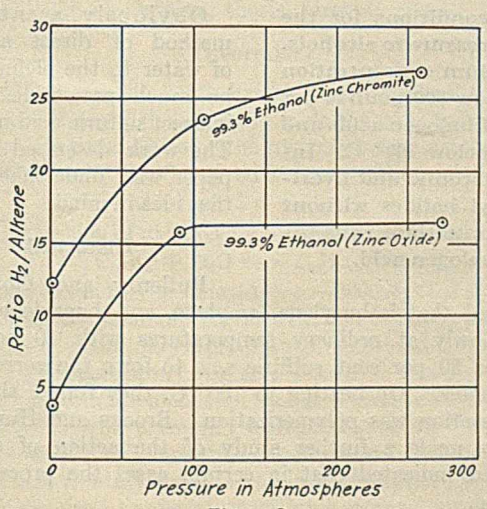


Figure 2

When 60 ml. per hour of ethanol were passed over 10 ml. of zinc chromite catalyst under a pressure of 500 atmospheres, the liquid product was found to contain 5.3 per cent of ethyl acetate, 1.9 per cent *n*-butanol, traces of acetaldehyde, and 1 per cent of material boiling above 125° C. This constitutes so low a yield of condensation products that it was deemed advisable to replace a part of the ethanol with acetaldehyde. Under these conditions there is some dehydrogenation, but a far greater amount of condensation products is obtained in a given length of time than if it were dependent upon acetaldehyde produced by dehydrogenation. The proportion of non-volatile products was considerably increased if the temperature was lowered much below 36° C., but there was no apparent advantage in operating at temperatures up to 400° C. The further discussion of the liquid products obtained in the condensation will be based upon the product obtained as the result of the passage of 270 ml. per hour of a mixture of 1 part ethanol and 2 parts acetaldehyde over 30 ml. of zinc chromite catalyst held at a temperature of 360° ± 5° C.

The product obtained under high pressure from the reactions of ethanol and acetaldehyde over a zinc chromite catalyst is an exceedingly complicated mixture. It was not found possible to resolve it into its components through fractionation, so it became necessary first to subject it to chemical treatment. The process ultimately adopted involved, first, a fractionation into 4 parts, one boiling up to 85° C., a second from 85° to 170° C., a third from 50° to 160° C. (2 mm.), and a fourth, a tarlike residue. The three distilled fractions were reduced over nickel and saponified. The neutral compounds from this process were then dried and fractionated. The acids were obtained from their salts, dried, and fractionated.

The lowest fraction from the chromite catalyst contained aldehydes, alcohols, esters, and water. The higher fractions contained alcohols, esters, and ethers, but no appreciable amounts of aldehydes or ketones or glycols. The alcohols and esters were both saturated and unsaturated. The esters were derivatives of acids which were both saturated and unsaturated. These products indicate that various reactions have occurred, among them dehydrogenation, hydrogenation, dehydration, oxidation, and aldol-like condensation.

The fractionation of 4730 grams of material showed that 62.2 per cent of the material distilled below 85° C., 16 per cent from 85° to 170° C., 11 per cent from 50° to 160° C. (2 mm.), and 8 to 9 per cent residue. The weights of the products may be summarized as follows:

	Grams		*Grams*
Acetaldehyde	570	*n*-Butyl alcohol	480
Ethyl alcohol	1870	*n*-Hexyl alcohol	25
Ethyl acetate	390	*x*-Hexyl alcohol	20
Ethyl butyrate	20	*x*-Octyl alcohols	15
Ethyl caproate	170	Higher alcohols	190
Ethyl esters and lactones of higher acids	160	Ethers	70
		Tar	420
Total		4400 grams	

It should be emphasized that these products were not, in general, actually present in the reaction product from the chromite catalyst but as unsaturated derivatives.

Discussion of Reactions Involved

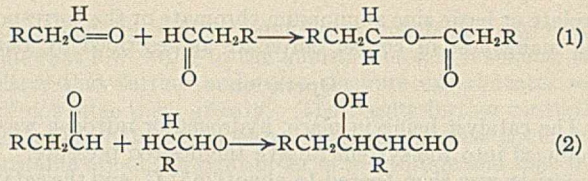
Reactions through which the simpler compounds might be formed are listed below.

$$CH_3CH_2OH = CH_3CHO + H_2 \quad (1)$$
$$CH_3CHO + CH_3CHO = CH_3CO_2C_2H_5 \quad (2)$$
$$CH_3CHO + CH_3CHO = CH_3CHOHCH_2CHO \quad (3)$$
$$CH_3CHOHCH_2CHO = CH_3CH{=}CHCHO + H_2O \quad (4)$$
$$CH_3CHO + CH_3CHO = CH_3CH{=}CHCHO + H_2O \quad (5)$$
$$CH_3CH{=}CHCHO + CH_3CH_2OH = CH_3CH_2CH_2CHO + CH_3CHO \quad (6)$$
$$CH_3CH_2CH_2CHO + H_2 = CH_3CH_2CH_2OH \quad (7)$$
$$CH_3CH{=}CHCHO + H_2 = CH_3CH{=}CHCH_2OH \quad (8)$$

$$CH_3CH{=}CHCHOH = CH_3CH_2CH_2CHO \quad (9)$$
$$CH_3CH_2CH_2CHO + CH_3CHO = CH_3CH_2CH_2CH{=}CHCHO \quad (10)$$
$$CH_3CHO + CH_3CH_2CH_2CHO = CH_3CH{=}C(C_2H_3)CHO \quad (11)$$
$$2\ CH_3CH{=}CHCHO = CH_3CH{=}CHCO_2CH_2CH{=}CHCH_3 \quad (12)$$
$$2\ CH_3CH_2CH_2CHO = C_3H_7CO_2C_4H_9 \quad (13)$$
$$C_3H_7CO_2C_4H_9 + C_2H_5OH = C_3H_7CO_2C_2H_5 + C_4H_9OH \quad (14)$$
$$2\ C_4H_{11}OH = C_4H_{11}OC_4H_{11} + H_2O \quad (15)$$
$$2\ C_5H_{11}CHO = C_5H_{11}CO_2C_6H_{13} \quad (16)$$

These reactions are divisible into two types—those with no increase and those with an increase in the number of carbon atoms per molecule. The first type of reactions over oxide catalysts has been extensively studied and there is abundant experimental evidence for their occurrence. The simple splitting out of hydrogen from an alcohol and the reverse reaction of the addition of hydrogen to an aldehyde or ketone (reactions 1, 7, 8) are too well known to need comment. The reduction of an alkene linkage by an alcohol with the oxidation of the alcohol to an aldehyde (reaction 6) has been observed by Weston and Adkins in the case of acrolein and cinnamic aldehyde. Crotonic aldehyde has been actually reduced over a chromite catalyst to crotonyl alcohol with the formation of almost no butanol. The rearrangement of hydrogen from a carbinol to an alkene linkage with the production of a saturated aldehyde from an unsaturated alcohol (reaction 9) has also been observed by Constable, Weston, and Adkins.

The type of reactions occurring over oxide catalysts and involving an increase in the number of carbon atoms per molecule has not been studied, but it appears more than probable that the synthesis of substances of higher molecular weight from ethanol or acetaldehyde is dependent upon two reactions both involving the addition to each other of two molecules containing carbonyl groups—i .e.,



The autoxidation reduction of an alcohol with the formation of hydrocarbon and an aldehyde has been observed by Bischoff, Folkers, and Adkins, so that a similar autoxidation reduction of an aldehyde to the ester (reactions 2, 12, 13) seems a reasonable assumption, especially in view of the ease of the conversion of aldehydes to esters in the presence of of certain metallic alkoxides as observed in the Tischtsckenko reaction.

Direct evidence is lacking that the compounds containing chains longer than two carbon atoms are dependent upon an aldol reaction (reactions 3, 5, 10, 11). However, the nature of the products is such as to make it seem reasonable that the synthesis of the higher alcohols and esters is dependent upon the reaction. Whether aldols are actually formed and then dehydrated (reactions 3 and 4) or whether the condensation takes place with the simultaneous elimination of a molecule of water and the formation of an unsaturated aldehyde (reaction 5) is questionable. In no case has any glycol been found in the distilled reaction products, which is against the first assumption. Moreover, the catalyst is not active for dehydration of alcohols. A direct reaction, as in reaction 5, seems more reasonable.

Manganese chromite catalysts gave the same production in approximately the same proportions as did the zinc chromite catalysts. Copper chromite left almost no aldehyde in the reaction product, and produced two and a half times as much of the esters of ethyl and butyl alcohols. There was very little tar or high-boiling material.

Catalytic Hydration of Olefins[1]

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A study has been made of the conditions for the catalytic hydration of olefins under pressure to alcohols. It has been found that the equilibrium concentration of alcohols is small at pressures below 800 pounds per square inch, using dilute solutions of halogen acids and salts as catalysts at temperatures below 200° C. Increasing the concentration of hydrobromic and hydriodic acids favors formation of alkyl halides without apparently increasing the alcohol formation, thus indicating the catalytic action of the halogen acid.

During the past decade there has been an increasing demand for lower aliphatic alcohols as solvents and antiknock motor fuels. A very large potential source of such alcohols exists in the unsaturated hydrocarbons in cracking still gases, but a commercially economical process for hydrating the olefins must be developed before still gases can be used. Consequently much research has been done towards the development of such a process. However, the only process which has thus far attained industrial proportions is an indirect one in which the olefin is allowed to react with relatively concentrated sulfuric acid to form the alkyl sulfuric acid, which is then hydrolyzed and the alcohol separated by distillation. This method has the disadvantages of requiring a reconcentration of the acid and of giving some polymerized products.

Obviously, a catalytic method of direct addition of water to the olefin would be much preferable to the indirect sulfuric acid method. The work described in this paper was undertaken with that idea in mind.

Historical

Butlerow and Goriainow (*4*) found that isobutylene, amylene, and heptylene would react slowly at ordinary temperatures with 10 per cent nitric or 50 per cent sulfuric acid to form the corresponding alcohols. On heating to 100° C. they found that the main reaction was polymerization. Brooks and Humphrey (*3*) have made a further study of the action of sulfuric acid and indicated that in certain cases the process was catalytic.

Miklaschewsky (*15*) found that isobutylene and some of the amylenes and hexylenes could be hydrated by 5 to 10 per cent aqueous solutions of formic, acetic, or oxalic acid without any appreciable polymerization.

[1] Received August 27, 1930. Published by permission of the Director of the Engineering Experiment Station of the University of Illinois.

Solonina (*19*) reported the production of propylene glycol by refluxing allyl alcohol with 10 per cent by weight of hydrochloric acid. Michael and Brunel (*14*) found that when isobutylene reacts with hydriodic acid the iodide is formed almost entirely at concentrations greater than 60 per cent HI, but that as the concentration decreases below this value the proportion of alcohol formed increases rapidly. With trimethylethylene and hydrobromic acid they found that with acid stronger than 9.66 normal the bromide was formed almost exclusively, and below 5.54 normal only the alcohol was formed. Intermediate concentrations gave a mixture of the halide and the alcohol. From the fact that the rate of formation of the alcohol is of the same order of magnitude as the rate of hydrolysis of the corresponding halide, they concluded that the halide was formed first and was subsequently hydrolyzed. Klever and Glaser (*12*) arrived at the same conclusion. They reported that the hydration of ethylene at 100° C. and atmospheric pressure is very slow even in contact with dilute (6 to 9 per cent) mineral acids. Higher temperatures and pressures increase the reaction velocity considerably. At 200° C. and 100 atmospheres without catalyst only 0.0008 mol of ethylene was hydrated per mol of water, while with 1.93 per cent hydrochloric acid more than 1 mol of ethylene was hydrated per mol of hydrochloric acid.

Johannsen and Gross (*11*) claim a process for the hydration of ethylene at 200° C. and 20 atmospheres using a 4.3 per cent hydrochloric acid solution. Smith and Bridges (*17*) claim the process of hydrating ethylene to ethyl alcohol at 200-300° C. and high pressures in presence of aqueous solutions or suspensions of salts having an affinity for ethylene, such as silver nitrate, cuprous chloride, or mercuric chloride. The I. G. Farbenindustrie (*10*) and Carpmeal (*5*) claim processes for production of secondary and tertiary alcohols by reaction of the olefins with a dilute acid in the presence of a salt of copper, bismuth, or silver at elevated temperatures and pressures.

Slade (*16*) claims a process for making ethyl alcohol, and McKee and Burke (*13*) a process for making higher alcohols, by vapor-phase hydration using a mixture of steam and the olefin at temperatures of 350° to 500° C. and pressures of 25 to 200 atmospheres in the presence of dehydrating oxide catalysts, such as alumina, thoria, zirconia, etc.

Theoretical

The data on specific heats, heats of combustion, and equilibria are as yet insufficient for a reliable thermodynamic calculation of the possibilities of the hydration reaction. Francis and Kleinschmidt (*6, 7*) arrived at an equation

$$\Delta F = -5320 + 815\,n + 17.2\,T - 0.5\,nt$$

for the formation of alcohols by hydration of olefins:

$$C_nH_{2n} + H_2O \longrightarrow C_nH_{2n+1}OH$$

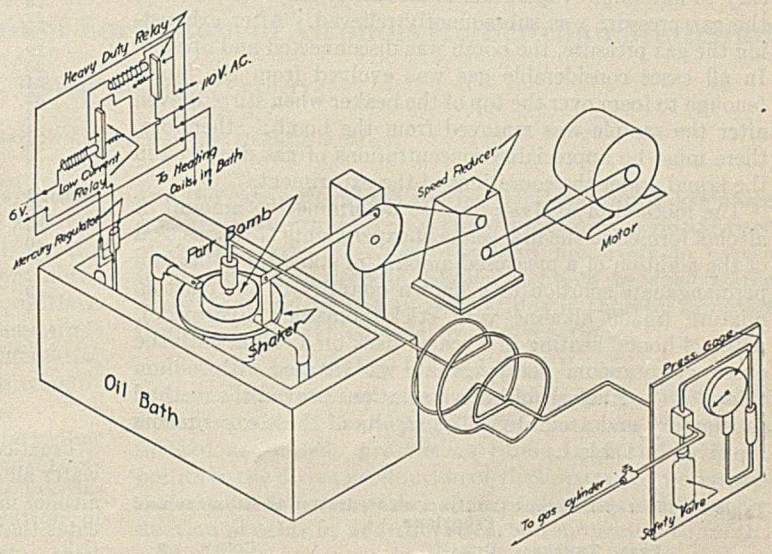
For ethyl alcohol this becomes $\Delta F = -3690 + 16.2\,T$, and indicates that the tendency for the reaction to take place would be very small at ordinary temperatures and would decrease with increasing temperature. Higher pressures should increase the tendency to form the alcohol. The best conditions for hydration should then be: extremely high pressures, the lowest temperature at which the reaction can be made to take place, and contact with a catalyst which will bring the system to equilibrium at the given temperature within a reasonable time.

Any substance, such as silver nitrate or cuprous chloride, which can increase the solubility of the olefin in the aqueous phase might also affect favorably both the speed and the extent of the hydration.

It has been found that dry hydrochloric acid is a very effective dehydrating agent. There is also the possibility that, in presence of large concentrations of water, hydrochloric acid would catalyze the hydration reaction. Such was found to be the case in the catalytic hydration of allyl alcohol to propylene glycol (*9*). It was therefore decided to test the catalytic effect of hydrochloric acid and a few salts on the hydration of ethylene and propylene.

Apparatus

The accompanying diagram shows the apparatus employed. Essentially it consists of a reaction chamber which is gently



Apparatus for Hydration

shaken in an oil bath, the temperature of which is thermostatically controlled.

The reaction chamber, which has a safe working limit of 1000 pounds per square inch, is an ordinary Parr oxygen bomb from which the self-seating valve has been removed. To prevent excessive corrosion the bomb is lined with a tall lipless Pyrex beaker. During the first series of experiments the rubber gasket of the Parr bomb was replaced by asbestos cord covered by fresh mixture of litharge and glycerol; later a lead gasket was used. The bomb is connected to the control panel, which carries a pressure gage, safety valve, and a lead to the hydrocarbon supply tank, by means of a special coupling and standard $^1/_4$ by $^1/_{15}$ inch copper-lined high-pressure tubing. Putting three turns, each about 1 foot in diameter, in the pressure tubing as shown and clamping the tubing to a stationary object at the right angle bend just back of the control panel allows the reaction chamber to be shaken without causing the tube connections to become loosened. All tubing joints were of the standard pressure joint type—namely, that of an accurately cut cone fitting into a similarly shaped slot of slightly smaller angle and held in place by a threaded collar. The shaking device consists of a standard 3-inch pipe flange, into which the bomb fits, mounted on an axle so that it can be rocked by the eccentric.

Experimental Procedure

In conducting a run the aqueous solution employed was first placed in the bomb, which was then assembled and connected to the system. In the experiments with ethylene the gas was then admitted until about 500 pounds pressure was reached, after which the heating coil and shaker were started. Final pressure adjustments were made after the bath reached

the operating temperature. However, since the vapor pressure of propylene at room temperature is only 180 pounds per square inch, it was necessary in the experiments with this gas first to cool the reaction chamber with ice and leave it connected to the supply tank until the desired quantity of propylene was liquefied. The valve of the supply tank was then closed. Subsequent heating in the oil bath produced the working pressures of 600 and 800 pounds in the reaction vessel. After the time period of the run had elapsed the shaker and heater were turned off. The reaction vessel was then removed from the oil bath without disconnecting from the system and cooled in a vessel of ice water until no further pressure drop was observed. This cooling was necessary to minimize evaporation of alcohol or alkyl halide when the gas pressure was subsequently relieved. After exhausting the gas pressure, the bomb was disconnected and opened. In all cases considerable gas was evolved from the liquid (enough to foam over the top of the beaker when stirred) even after the sample was removed from the bomb; therefore, there must be appreciable concentrations of gas dissolved in the liquid under the conditions of the experiment.

The method of analysis used to determine the amount of alcohol formed in the first series of experiments (*18*) consisted of the addition of a measured amount of standard potassium permanganate solution to a known quantity of the reaction mixture (made alkaline with stick potassium hydroxide). After 24 hours' heating in a sealed flask on a steam bath the excess of potassium permanganate was titrated with sodium thiosulfate. Analysis of known solutions proved the method satisfactory and accurate. The results of these experiments are given in Table I.

Table I—Effect of Different Catalysts on Hydration of Ethylene and Propylene

Expt.	Pressure	Temperature	Duration	Catalyst	Concn. of Alcohol
	Lbs./sq. in.	*° C.*	*Hours*		*Wt. %*
			HYDRATION OF ETHYLENE		
1	600	135	21	5% HCl	0.09
2	600	135	2	5% HCl	0.13
3	600	135	1	5% HCl	0.11
4	600	200	1	5% HCl	0.06
5	600	150	1	$HgCl_2$ + 5% HCl	0.03
6	600	150	1	$AgNO_3$	0.14
7	600	100	1	5% HCl	0.06
8	600	125	1	5% HCl	0.10
9	600	150	1	None	0.007
10	800	150	21	5% HCl	0.10
11	800	150	2	5% HCl	0.15
12	800	150	1	5% HCl	0.132
13	800	200	1	5% HCl	0.088
14	800	150	1	$HgCl_2$	0.045
15	800	150	1	$AgNO_3$	0.202
16	800	100	1	5% HCl	0.087
17	800	125	1	5% HCl	0.14
18	800	150	1	None	0.008
			HYDRATION OF PROPYLENE		
19	600	135	1	5% HCl	0.44
20	600	135	1	$AgNO_3$	0.22
21	800	135	1	5% HCl	0.63
22	800	135	1	$AgNO_3$	0.316
23	800	135	1	$AgNO_3$	0.29

The experiments with ethylene in Table II were carried out similarly, except that the method of analysis was modified somewhat. The reaction product from the bomb was cooled and carefully neutralized with concentrated caustic. It was then distilled until more than half the volume of the original liquid had been collected as distillate. This distillate, which would contain substantially all the alcohol formed and no inorganic material, was then subjected to the liquid combustion method of analysis described by Franz and Lutze (*8*).

The alcohol was oxidized by ammonium persulfate and the carbon dioxide formed was carried over by a stream of purified air through a drying tower containing anhydrone to an ascarite bulb in which the carbon dioxide was absorbed and weighed. The method was tested with known solutions of alcohol and acetic acid. It is much more rapid than the potassium permanganate method.

In view of the results reported by Michael and Brunel (*14*) it seemed desirable to investigate the effect of higher concentrations of the halogen acids.

Table II—Effect of Different Concentrations of Acid upon Hydration of Ethylene

Pressure	800 lbs. per sq. in.
Temperature	150° C.
Time of experiment	3 hours
Charge of aqueous solution	150 cc.

Experiment	Catalyst	Concn. of Alcohol	Yield of Alkyl Halide
		Wt. %	*Grams*
25	None	0.00647	..
26	None	0.00016	..
27	5% HCl[a]	0.034	..
28	5% HCl	0.038	..
29	10% HCl	0.0867	..
30	15% HCl	0.083	..
31	20% HCl	0.052	..
32	25% HCl	0.063	..
33	25% HI	0.122	0.5
34	45% HI	0.141	24.0[b]
35	35% HI	.....	10.0
36	170 grams 45% HI 18 grams concd. HCl	0.073	30.0
37	10% HCl + $AlCl_3$ (satd.)	0.0479	..
38	10% HCl + Cu_2Cl_2 (satd.)	0.0452	..
39	10% HCl + 1% $BiCl_3$	0.0335	..
40	10% HCl + 1% $HgCl_2$	0.061	..
41	20% HNO_3 + 1% $AgNO_3$	0.0043	..
42	40% HBr	0.0833	4.5
43	20% HBr	0.0842	..
44	11% HBr	0.0378	..

[a] All percentages by weight.
[b] Boils 71.8–72.2°.

Discussion

Practically no hydration takes place in the presence of water alone. The formation of the detectable quantities of alcohol in the presence of halogen acids and some salts indicates that those acids and salts do actually function as catalysts. Apparently the equilibrium is reached rapidly and there is no noticeable increase in alcohol after the first 2 hours. The equilibrium concentration of alcohol is very small as predicted by theoretical considerations. If the true equilibrium has been reached in these experiments, it appears that much higher activities of the olefin in the water phase must be realized in order to obtain commercially profitable concentrations of alcohol from ethylene or propylene.

Increasing the concentration of hydrobromic or hydroiodic acid favors the formation of the alkyl halide without apparently increasing the alcohol formation. With the concentrated acid large proportions of the alkyl halide are formed. Since the halides are so easily obtained in large quantities and since they may be rather easily hydrolyzed photochemically (*2*) or catalytically (*1*) an indirect process may be developed involving the steps: formation of alkyl halide, hydrolysis of halide, and reconcentration of acid.

Note—Badische Anilin und Sodafabrik (*1*) claims almost 100 per cent yield of ethyl alcohol, when a mixture of 1 part by weight of ethyl chloride and 10 parts of water vapor is passed at 250° C. over a catalyst composed of activated charcoal with 5 per cent zinc sulfate (or copper sulfate, cadmium sulfate, or zinc chloride).

Further study of the equilibria between olefins and halogen acids will be carried on.

Acknowledgment

The authors wish to acknowledge the able assistance of the following students at the University of Illinois—John Griswold, T. J. Walsh, E. R. Gilliland, and F. J. Smith.

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Catalysts for the Formation of Alcohols from Carbon Monoxide and Hydrogen[1]

VI—Investigation of the Mechanism of Formation of Alcohols Higher than Methanol

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In continuing the study of the high-pressure synthesis of alcohols from mixtures of carbon monoxide and hydrogen, experiments have been made to investigate the mechanism of formation of alcohols higher than methanol. By studying the behavior, under the conditions of high-pressure synthesis, of the individual compounds which might conceivably be formed as intermediates, it has been possible to arrive at rather definite conclusions concerning the mechanism of the reactions.

With methanol as an intermediate product the higher alcohols are chiefly formed by successive condensations of lower ones. The over-all rate of this stepwise process is apparently controlled by the initial condensation of methanol to ethyl alcohol,

$$2CH_3OH = C_2H_5OH + H_2O$$

and the ease with which further condensation takes place explains why ethyl alcohol constitutes only a minor part of the product. The use of carbon monoxide in excess favors the formation of higher alcohols because water vapor liberated by the condensations is thereby removed from the catalyst surface by the reaction

$$H_2O + CO = CO_2 + H_2$$

This reaction also accounts for the large production of carbon dioxide in the higher alcohol synthesis. The acids formed are chiefly present as esters, and the evidence points to the direct production of these esters by polymerization of aldehydes, rather than to the intermediate production of acids by addition of carbon monoxide to methanol.

FOR several years this laboratory has been conducting extensive research on catalysts for the decomposition and synthesis of methanol (*9*, *13*, *14*, *16*, *20*) and for the synthesis of higher alcohols (*15*).

The present investigation is a continuation of this work with particular emphasis on the mechanism of the reactions leading to the formation of higher alcohols from carbon monoxide and hydrogen.

Theoretical Considerations

There are no direct experimental data available in the literature relating to the mechanism of the formation of higher alcohols from carbon monoxide and hydrogen. It is generally agreed, however, that the compounds of high molecular weight do not result by direct reaction of carbon monoxide and hydrogen in one step. While the stepwise nature of the process is emphasized by Mittasch (*21*), the only hypothesis so far advanced is that of Fischer (*10*), suggesting that the higher alcohols may be formed from methanol by successive reactions represented by the following equations:

$$CH_3OH + CO = CH_3COOH \quad (1)$$
$$CH_3COOH + H_2 = CH_3CHO + H_2O \quad (2)$$
$$CH_3CHO + H_2 = C_2H_5OH \quad (3)$$

By a repetition of this process the ethyl alcohol thus formed is in turn supposed to react with another molecule of carbon monoxide to produce propionic acid, which is then reduced to normal propyl alcohol, etc. To account for the presence of iso-alcohols, Fischer suggests that the acetic acid produced by Reaction 1 may form acetone, which is subsequently reduced to isopropyl alcohol:

$$2CH_3COOH = (CH_3)_2CO + CO_2 + H_2O \quad (4)$$
$$(CH_3)_2CO + H_2 = (CH_3)_2CHOH \quad (5)$$

The isopropyl alcohol may then react with carbon monoxide and hydrogen as before, producing higher iso-alcohols. Incidentally, the synthesis of higher alcohols from a mixture of methanol and carbon monoxide has been claimed in the patent literature (*5*, *31*).

In addition to the above mechanism, many other reactions may be formulated to express the formation of higher alcohols from carbon monoxide and hydrogen. Omitting reactions of third order and higher, however, it would seem that the simplest mechanism is one involving the condensation of two alcohol molecules with the formation of one molecule of a higher alcohol. This may be illustrated by the elimination of water from two molecules of methanol to form one of ethyl alcohol:

$$2CH_3OH = C_2H_5OH + H_2O \quad (6)$$

Likewise it is conceivable that ethyl alcohol may form butyl alcohol, methyl and ethyl alcohol may form propyl alcohol, etc. In this manner, starting with methyl alcohol, a whole series of normal or branched alcohols might be synthesized.

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Guerbet (*17*) and later Terentiev (*29*) prepared small quantities of higher alcohols by a somewhat similar reaction at atmospheric pressure and in the liquid phase from the sodium and barium alcoholates of lower alcohols. The reaction involved was primarily one of condensation and dehydration. Neither investigator was able, however, to produce higher alcohols from methanol. Moreover, it should be pointed out that the metal alcoholates are chemical reagents and not catalysts.

Fischer (*10*) repeated Guerbet's experiments employing sodium methylate and methanol under pressure in a steel autoclave. Although the methanol was largely decomposed into gaseous products in the presence of an iron-alkali catalyst at 400° C., a considerable amount of dimethyl ether was

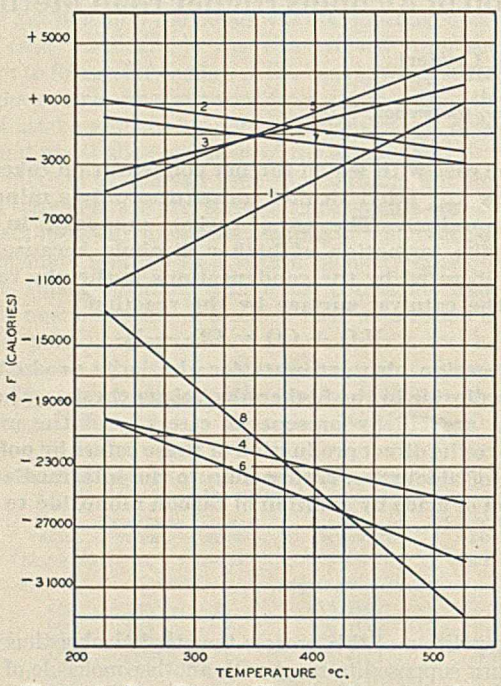

Figure 1—Free-Energy Changes Accompanying Reactions 1 to 8

obtained at 240° C. Furthermore, Brown and Galloway (*6*) have shown that, in the synthesis of methanol from carbon monoxide and hydrogen over a zinc oxide–chromium oxide catalyst above 300° C., considerable quantities of dimethyl ether are formed. This suggests that the over-all dehydration of methanol as represented by Reaction 6 may actually occur in two stages—(1) the dehydration to dimethyl ether and (2) the rearrangement of the ether to ethyl alcohol, as the two are isomers.

$$2CH_3OH = (CH_3)_2O + H_2O \quad (7)$$
$$(CH_3)_2O = C_2H_5OH \quad (8)$$

However, in spite of this evidence in favor of dimethyl ether formation, there may be some question as to the existence of ethers as intermediates in the production of still higher alcohols. Sabatier (*25*) has observed that the dehydration to ethers of alcohols above ethanol is difficult at high temperatures and ordinary pressure, the tendency being for further dehydration to unsaturated hydrocarbons. Although this complete dehydration to olefins would be counteracted by pressure, the thermodynamic data available are not sufficiently accurate to warrant any conclusions as to what might be expected at higher pressures.

Thermodynamic Considerations

The changes in free energy accompanying the reactions discussed above have been calculated as functions of temperature and the results plotted in Figure 1. The free-energy values for the formation of the alcohols were obtained by using the equation of Smith and Branting (*28*) for methanol and those of Francis (*11*) for the higher alcohols. For acetaldehyde the data of Rideal (*24*) were used in conjunction with the following thermal values:

Molal heat of vaporization = 6000 calories
Heat of combustion = 281,900 calories per mol

The value for acetic acid was obtained from the data of Parks (*22*) together with the following thermal values:

Molal heat of vaporization = 5000 calories
Vapor pressure at 25° C. = 15.2 mm.
Specific heat at constant pressure = 0.35 calorie per gram

For acetone the values of Kelly (*19*) for the heat of formation, free energy of formation, and specific heat were used, together with the following values:

Molal heat of vaporization = 8000 calories
Vapor pressure at 25° C. = 240 mm.

From a consideration of the curves in Figure 1 it will be seen that, with the exception of Reactions 3 and 5 representing hydrogenation of an aldehyde and a ketone, all the above reactions proceed with a decrease in free energy up to about 400° C. The reduction of acetaldehyde and acetone is accompanied by a decrease in volume, so that high pressures offset the unfavorable free-energy changes. Calculations show that at 400° C., with a partial pressure of 30 atmospheres for acetone or acetaldehyde, and 170 atmospheres of hydrogen approximately 95 per cent of the acetone and 92 per cent of the aldehyde will be reduced to the corresponding alcohols at equilibrium.

The formation of higher alcohols by dehydration is especially favorable. At the conditions obtaining in high-pressure operation these reactions proceed almost to completion at equilibrium.

Plan of Present Work

It is characteristic of high-pressure syntheses with carbon monoxide and hydrogen in the presence of a higher alcohol catalyst that many products are formed simultaneously (*12*), making it hopeless to study the individual reactions. However, by attacking the problem from various angles it should be possible, by a process of elimination, to reduce the number of variables which must be considered. With this in mind, the following plan of work was adopted as being the most logical method of establishing the controlling mechanism of the formation of higher alcohols from carbon monoxide and hydrogen:

(1) Establish the existence or non-existence of methanol as the primary product.
(2) Study the behavior of a mixture of methanol vapor with carbon monoxide, and with hydrogen over suitable catalysts.
(3) Investigate the behavior of other alcohols—e. g. ethanol, or mixtures of alcohols such as methanol and ethanol—over the same catalysts.
(4) Study the possibility of reduction by hydrogen of acetic acid, acetaldehyde, and acetone to alcohols.
(5) Investigate the behavior of ethers over metallic oxide catalysts.

In carrying out the experimental work, attention was paid to the conditions most favorable for the formation of higher alcohols as emphasized in the patent literature (*4*) and verified by the experiments of Frolich and Lewis (*15*). This comprised: (1) the use of a methanol catalyst to which an alkali or alkaline earth was added; (2) the employment of higher temperatures, a higher carbon monoxide content

in the entering gases, and a lower rate of gas flow than is used in the synthesis of methanol; and (3) the adequate purification of entering gases from iron carbonyl and the prevention of contact between the gas and iron.

Apparatus

Figure 2 illustrates the assembly of equipment. The reactor was similar to that used in a previous investigation (*14*) and consisted essentially of a copper-lined chrome-vanadium steel tube. The copper tube containing the catalyst was silver-soldered to a steel plug at the top of the reactor. This plug also served to hold the copper capillary tubes by means of which the gas entered and left the reactor. An important modification in design was the insertion of a copper-ideal thermocouple through this steel plug directly into the catalyst mass. The lower face of the plug was completely covered with silver solder. By means of this arrangement the entering gases were preheated by passage downward around the catalyst tube and were removed from the reactor without being in contact with iron at any point. The measurement of the actual catalyst temperature was found to be highly essential, since fluctuations in the gas velocity caused marked temperature variations, owing to the exothermic nature of the reactions involved. The reactor was heated by placing it in an electrically heated iron tube, an aluminum sleeve around the reactor serving as a heat conductor.

The gas was admitted to the system from the main high-pressure supply through the valve *S*. *A* and *D* served as auxiliary storage. The purification train consisted of copper-lined tubes, *E* and *F*. *E* contained, in succession, calcium chloride, soda lime, and activated charcoal. *F* contained reduced copper kept at 300° C. by means of an external resistance winding. This system of purification permitted the gas to enter the reactor free from iron carbonyl and other catalyst poisons. The temperature of the catalyst bed and copper purification tube was measured by means of a potentiometer, *L*. After leaving the reactor the gases passed in turn through a preliminary water cooler, *M*, an ice-cooled product collector, *N*, both operated under full pressure, thence through the pressure release valve, *T*, to the wet meter, *O*, and the exit line, *P*. The rate of flow of gases through the system was controlled by the valve *T*.

The introduction of a mixture of gas and liquid into the reactor gave considerable difficulty. The method of saturating a gas by bubbling it through a given liquid kept at a definite temperature, as described in several patents (*5*, *10*), was tried, but did not work satisfactorily. The main difficulty with such an arrangement was the tendency for the liquid to siphon back through the entrance tube for even very small pressure differences across the saturator tube. Such small pressure variations were usually encountered at some time during the progress of a run, and consequently it was difficult to make a satisfactory material balance. Another disadvantage of this method was the narrow range of saturation possible.

The final method employed, and one which proved entirely satisfactory, consisted in dropping the liquid from an overhead reservoir into the gas stream. The reservoir was kept at the full pressure of the system by means of by-pass tubing and the liquid allowed to flow through a valve into a suitably constructed gage glass by means of which the drop rate could be measured. After passing through the gage glass the liquid entered the gas stream through a tee. This set-up permitted the independent regulation of either gas or liquid velocity and was found to be very reliable.

Preparation of Catalyst

Of the seventeen catalysts investigated the most active in the formation of higher alcohols from carbon monoxide and hydrogen consisted of a mixture of the basic carbonates of zinc and manganese together with potassium chromate. Eight different mixtures of these materials were made up to observe the effect of a change in the proportion of one constituent on the nature of the liquid product obtained from carbon monoxide and hydrogen. The most notable effect was a 60 per cent increase in butanol content produced by a variation in the proportion of zinc. The catalyst finally chosen consisted of the above mixture in the molal proportions—Zn 1.0 : Mn 1.1 : Cr 1.03. It was prepared as follows:

The basic carbonates of zinc and manganese were precipitated from the solution of their nitrates, using a solution of sodium carbonate. The washed precipitate was made into a thin paste with water and a solution of potassium chromate added while stirring. The mass was dried first over a steam bath and then at 110° C., dehydrated at 220° C. in a stream of nitrogen, and reduced in a stream of methanol vapor and hydrogen.

Analysis of Products

Gases—The exit gases were analyzed by means of a modified Burrell apparatus using potassium hydroxide solution for the absorption of carbon dioxide, fuming sulfuric acid for unsaturated hydrocarbons, pyrogallol for oxygen, copper oxide (at 300° C.) for carbon monoxide and hydrogen, and a combustion pipet for saturated hydrocarbons.

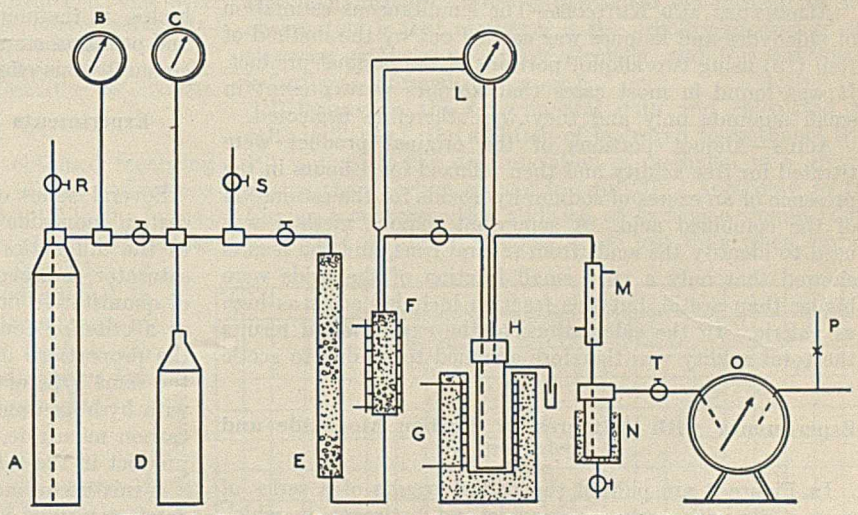

Figure 2—Diagram of Apparatus for Synthesis of Higher Alcohols

Liquids—The chief method of identification of the liquid components consisted in the determination of their boiling points and refractive indices. The distillation of the liquid product was carried out in the micro-fractionating column described by Cooper and Fasce (*8*). As might be expected, owing to the complex nature of the product, azeotropic mixtures were formed in the distillation. In these cases, and with the products lying between the individual fractions, the approximate composition was calculated from the refractive index of the mixture of the two substances.

Additional tests were made as follows:

ALCOHOLS—Since the ordinary method of identification of the alcohols, that of conversion into the 3,5-dinitrobenzoic acid derivative, could not be used owing to the unavoidable presence of small amounts of other alcohols in the individual fractions, the method of converting the alcohols into the corresponding halides and redistilling was tried. Fractions having the same boiling range were collected from a large number of runs and converted into the alkyl halides by treatment with phosphorus pentachloride. By this means the boiling points of the constituents were spread farther apart, and as a result refractionation gave satisfactory checks for methyl, ethyl, *n*-propyl, and isopropyl chlorides. The chlorides boiling above propyl chloride decomposed under these conditions.

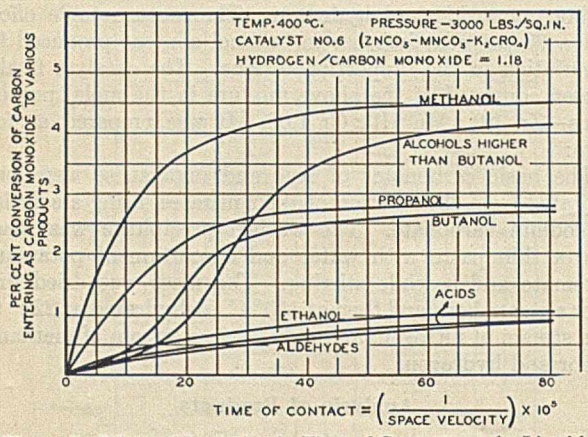

Figure 3—Effect of Variation in Time of Contact on the Liquid Product Obtained from Carbon Monoxide and Hydrogen

ALDEHYDES AND KETONES—The simultaneous estimation of aldehydes and ketones was carried out by the method of Reif (*23*) using two aliquot portions of the original product. It was found in most cases that ketones were present in small amounts only and they were therefore neglected.

ACIDS—Aliquot portions of the original product were titrated for free acidity and then refluxed for 4 hours in the presence of an excess of sodium hydroxide for the estimation of the combined acid. A somewhat tedious method was used to identify the acids from several runs, and the results showed that only a very small fraction of the acids were higher than acetic, but this fraction included acids as high as valeric. In the calculations of the experimental results the total acidity was therefore assumed to be due to acetic acid.

Experiments with Mixtures of Carbon Monoxide and Hydrogen

In Figure 3 are plotted the partial results of a series of runs made with carbon monoxide and hydrogen in which the space velocity was varied. These runs represent closely comparative data, since they were carried out continuously over the same catalyst and with the same entering gas mixture, the catalyst temperature not varying more than 5° C. during the entire series. The activity of the catalyst had previously been tested and found not to vary appreciably over a far longer period than represented by these runs.

Inspection of the curves in Figure 3 brings out three points of interest:

(1) There is considerable methanol in the final product even for the longer times of contact. Assuming the thermodynamic data used above to be reasonably correct, equilibrium was therefore not established in these experiments, since calculations based on the free-energy values given in Figure 1 show that at 400° C. the amount of methanol in equilibrium with the higher alcohols is almost negligible.

(2) Ethyl alcohol is present in lower concentrations than any of the other alcohols identified. Assuming a stepwise reaction mechanism whereby the higher alcohols are built up from lower ones, the low percentage of ethanol in the products suggests that the controlling reaction is the conversion of methanol to ethyl alcohol. Ethyl alcohol, once formed, is apparently rapidly converted to the higher alcohols. This conclusion is further substantiated by the previous work of Frolich and Lewis (*15*) showing the existence of a "critical temperature" in the synthesis of higher alcohols from carbon monoxide and hydrogen. Keeping the rate of gas flow constant and gradually raising the temperature, they observed that the formation of substantially pure methanol was suddenly interrupted by the appearance of alcohols higher than ethyl. This "critical temperature," which could be duplicated within a few degrees Centigrade, evidently represented the temperature at which the rate of conversion of methanol to ethyl alcohol became appreciable.

(3) The analysis of the product for aldehydes and ketones by titration showed the presence of ketones in very small amounts only. This was confirmed by the boiling points and refractive indices of the low-boiling fractions. Likewise the quantities of acids present were quite small. These results indicate that the decomposition of acetic acid into acetone and the subsequent reduction of acetone and higher ketones to iso-alcohols do not take place to any appreciable extent over this catalyst. It might be pointed out that, since the acids occur mainly combined with the alcohols in the form of esters, these esters could also be formed by the condensation of the corresponding aldehydes, as follows:

$$2CH_3CHO = CH_3CH_2OOCCH_3 \qquad (9)$$

This reaction (*7*), as well as the condensation of higher aldehydes, is thermodynamically possible at the temperatures and pressures employed. The patent literature also contains claims to this effect (*18*, *26*, *27*).

Experiments Using a Mixture of Liquid and Gas Saturator Experiments

Several series of experiments were carried out in which carbon monoxide was bubbled through methanol. Owing to the difficulties encountered in the manipulation of the saturator, however, these experiments (*3*) did not permit of quantitative interpretation, but were valuable in serving as a criterion for later work. The products obtained and the proportions of methanol in the product indicated that the same type of product could be obtained starting either with hydrogen and carbon monoxide, or with methanol and carbon monoxide, and that methanol was the intermediate product in the formation of higher alcohols.

A mixture of methanol vapor and hydrogen over the same catalyst yielded higher alcohols, but in lesser amounts than with a mixture of methanol and carbon monoxide. In the case of hydrogen a considerable proportion of water was always found in the product, while with carbon monoxide and methanol little or no water was present. This point will be reserved for further discussion.

Bomb Experiments

A series of experiments using the reactor as a closed bomb was carried out with the idea of obtaining additional preliminary information. The experiments were made at maximum temperatures varying from 400° to 450° C. and with times of contact varying from 15 minutes to 2 hours. While the results were not quantitative owing to the small free volume of the reactor, the following facts were brought out:

Table I—Partial Data from Experiments Using a Catalyst Composed of Basic Zinc Carbonate, Basic Manganese Carbonate, and Potassium Chromate, (Zn:Mn:Cr = 1.0:1.1:1.3)

Run	Reactants	Temp.	Pressure	Space Velocity	H_2O in Liquid Product	Mol Fraction Entering Liquid	Per Cent of Carbon in Entering Liquid to Liquid Products: Acids	Aldehydes	MeOH	EtOH	PrOH	BuOH	Higher alcohols	Per Cent of Carbon in Entering Liquid to Gaseous Products: CO_2	Unsatd.	CO	CH_4
		° C.	Lbs./sq. in.		%		%	%	%	%	%	%	%				
1	Methanol and hydrogen	450	2400	620	28.6	0.542	0.2	0.2	1.9	0.4	1.3	5.7	0.7	22.6	5.3	53.8	8.0
19	Methanol and hydrogen	400	2950	1400	8.3	0.333	2.6	0.3	41.0	6.1	7.4	5.3	..	12.1	3.8	21.4	...
2	Ethanol and hydrogen	450	2300	890	46.1	0.112	Trace	7.5	..	3.1	..	10.7	3.7	23.4	42.7	9.1	...
8	Ethanol and hydrogen	300	2800	910	0.0	0.120	1.1	0.7	..	78.0	..	..	..	5.9	11.8	2.5	...
11	Ethanol and hydrogen	400	2850	2650	20.4	0.085	0.7	3.4	..	38.6	..	27.0	8.4	2.3	19.6	..	...
10	Methanol, ethanol, and hydrogen	425	2250	900	36.6	0.111	...	...	2.1	12.5	22.0	20.2	..	19.0	16.1	8.1	...
9	Methanol, ethanol, and hydrogen	375	2300	1000	6.8	0.206	5.8	7.3	14.6	30.5	15.2	10.8	..	8.7	2.7	4.4	...
12	Ether and hydrogen	400	2900	2320	4.5	0.061	0.2	0.7	..	10.1	..	6.2	8.4[a]	2.5	22.3	0.8	...
16	Acetic acid and hydrogen	400	3000	1680	44.0	0.105	0.6	9.9	..	31.8	20.0	8.9	..	15.1	8.2	2.3	3.2
17	Acetone and hydrogen	400	3000	1560	24.9	0.055	0.3	...	..	..	63.2	..	23.8[b]	2.7	3.1	..	...
18	Acetaldehyde and hydrogen	400	3000	1780	41.7	0.067	7.7	4.7	..	36.9	..	34.4	..	4.2	12.1	..	...
13	Methanol, water and hydrogen	395	3100	1880	28.9	0.193[c]	0.5	3.4	48.4	..	..	..	2.1	..	..	..	...
14	Methanol, water, and carbon monoxide	400	3000	1320	3.3	0.270[c]	0.7	2.1	38.7	2.8	2.2	2.9	1.8	..	..	..	...
15a	Water and carbon monoxide	400	2900	2060	100.0	0.778	Conversion of CO to CO_2, 91% (theoretical, 91.5%)							..	..	..	...
15b	Water and carbon monoxide	400	2900	2500	100.0	0.722	Conversion of CO to CO_2, 73.5% (theoretical, 87.5%)							..	..	..	...
20	Methanol and carbon monoxide	400	2950	1600	0.0	0.127	1.7	0.9	25.4	1.1	3.8	4.2	3.4	..	..	..	...
21	Methanol and hydrogen[d]	390	2750	2210	25.7	0.218	...	...	16.1	0.8	..	..	..[e]	2.8	12.9	2.7	2.9

[a] 48.8 per cent unconverted ether in product.
[b] 6.9 per cent unconverted acetone and 23.8 per cent higher boiling polymerization and condensation products of acetone.
[c] Mol fraction of methanol.
[d] Catalyst consisted of aluminum oxide prepared from aluminum methylate.
[e] 61.8 per cent dimethyl ether in product.

(1) Methanol, even in the presence of a high partial pressure of hydrogen, suffered partial decomposition into carbon monoxide and hydrogen when placed in contact with a wide variety of metallic oxide catalysts. Over typical higher alcohol catalysts liquid products were formed resembling closely those obtained from carbon monoxide and hydrogen. Over a dehydrating catalyst such as aluminum oxide, prepared according to Adkins (*1*) from aluminum methoxide, considerable dimethyl ether was obtained together with small amounts of higher alcohols.

(2) Ethyl alcohol in the presence of hydrogen, and over metallic oxide catalysts such as used in the later experiments, showed a decided tendency to form higher alcohols.

(3) Diethyl ether in the presence of hydrogen and over the same catalyst suffered alteration with the formation of unstable higher boiling compounds.

Although in (1) no information was obtained regarding the ether rearrangement theory, yet in (3) the indications were that diethyl ether might be instrumental in the formation of higher alcohols. The behavior of ethers was further investigated in later experiments. The formation of higher alcohols in (2) again indicated that ethanol, in addition to methanol, is an intermediate product in their formation, and that these higher alcohols are therefore produced by the stepwise or successive formation of alcohols of increasing molecular weight.

Standard Runs

With the foregoing experiments as a guide, a series of experiments was made in which the liquid material was injected into the entering gas stream by the flow method previously described. A partial list of the results and calculations is given in Table I. Figures 4 and 5 represent the results of a continuous series of experiments over the same catalyst with an initial mixture of methanol and carbon monoxide at different rates of flow. Figure 4 shows the itemized conversion of methanol to the various liquid products, while Figure 5 gives the summarized conversion into both gaseous and liquid products.

At varying rates of contact the proportions of the individual alcohols in Figure 4 indicate the stepwise formation of the higher alcohols from the lower ones. When the vapors are in contact with the catalyst for a short time, the lower alcohols, such as ethanol and propanol, form a considerable proportion of the liquid product. As the time of contact is increased the proportion of ethanol decreases and the propanol increases to a maximum and then decreases. With the decrease of lower alcohols there is in general a rise of the succeeding higher alcohols. These curves resemble those obtained from a carbon monoxide–hydrogen mixture in Figure 3 and clearly show that the mechanism of higher alcohol formation is the same whether one starts with a carbon monoxide–hydrogen mixture or a carbon monoxide–methanol mixture. The only rational explanation of this observation is that methanol is the primary product in the stepwise synthesis of higher alcohols, and this conclusion is further confirmed by Figure 5.

Referring to the experimental data and calculated results in Table I, the addition of hydrogen to methanol (run 19) suppresses the decomposition of methanol to a greater degree than carbon monoxide (run 20). According to the Fischer mechanism this addition of hydrogen should result in a yield of higher alcohols much less than when carbon monoxide is added to methanol, since the partial pressure of carbon monoxide is almost negligible in the former case. On the other hand, if the condensation mechanism is controlling, the yield of higher alcohols should be increased, since there is more methanol available for higher alcohol formation. Actually 18.8 per cent conversion of the meth-

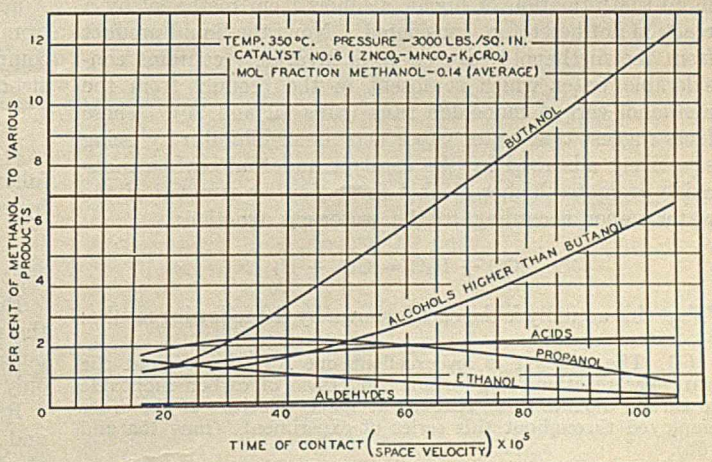

Figure 4—Effect of Variation in Time of Contact on Liquid Product Obtained from Methanol and Carbon Monoxide

anol to higher alcohols was obtained in run 19 with methanol and hydrogen, while in run 20 with methanol and carbon monoxide the conversion was only 12.5 per cent.

From these results it appears that the formation of higher alcohols from methanol is not dependent primarily on carbon monoxide addition to form acids and their subsequent reduction by hydrogen. Rather, the formation of higher alcohols from methanol in the virtual absence of either hydrogen or carbon monoxide lends support to the condensation mechanism, since neither enters into the reaction.

It is also significant that acids are formed to the same extent in the presence and in the absence of carbon monoxide, as shown in the results from these two runs. Since these acids occur mainly in the form of esters, they are in all probability formed by the condensation of aldehydes, as illustrated by Reaction 9. This condensation of aldehydes is furthermore demonstrated in a later experiment.

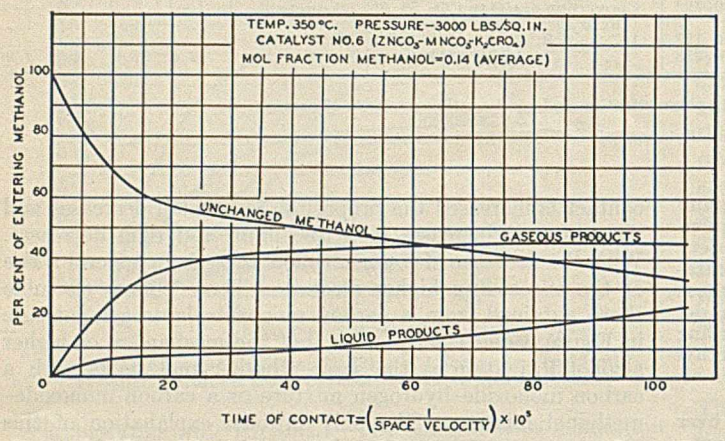

Figure 5—Effect of Variation in Time of Contact on Percentage Conversion of Methanol to Various Products

On the basis of the condensation mechanism there should be a rough proportionality between the yield of higher alcohols and the undecomposed methanol. Calculations show that the yield of higher alcohols obtained from run 20 with methanol and carbon monoxide is much greater than would be called for by such a proportionality. In other words, carbon monoxide enters into the mechanism to promote the formation of higher alcohols from methanol by a reaction not heretofore considered. Now, the liquid product from the methanol-hydrogen runs invariably contains considerable water which is absent in the product from the methanol–carbon monoxide runs (runs 19 and 20). These facts suggest that water vapor acts as an inhibitor by being selectively adsorbed by the catalyst and that carbon monoxide promotes higher alcohol formation by removal of the water vapor according to the water-gas reaction:

$$CO + H_2O = CO_2 + H_2$$

That this actually is the case is shown by the following results:

(1) The catalyst is an excellent one for carrying out the water-gas reaction, equilibrium conversion of carbon monoxide to carbon dioxide being reached at space velocities of the order employed throughout this series of experiments (runs 15a and 15b).

(2) The addition of water to a mixture of methanol and hydrogen reduces by 90 per cent the yield of higher alcohols as compared with that obtained from a mixture of methanol and hydrogen alone (runs 13 and 19).

(3) When water is added to a mixture of methanol and carbon monoxide, the reduction in yield of higher alcohols is only 22 per cent (runs 14 and 20).

(4) The exit gases from the runs in which carbon monoxide is employed invariably contain unusually high percentages of carbon dioxide.

(5) Under the experimental conditions employed a mixture of carbon dioxide and hydrogen yields methanol but no higher alcohols. In this case the water formed as a primary product in the reaction $CO_2 + 3H_2 = CH_3OH + H_2O$ inhibits the formation of higher alcohols from the methanol. That this inhibiting effect of water vapor has been observed in other catalytic processes is so well known that it need not be discussed further.

More positive information regarding the mechanism of higher alcohol formation is obtained from the runs using liquid materials other than methanol. For example, a mixture of ethyl alcohol vapor and hydrogen when passed over the catalyst gives a liquid product consisting mainly of butyl alcohol and water, part of the ethyl alcohol being dehydrated to ethylene. A maximum conversion of 27 per cent of the ethyl alcohol to butyl alcohol was obtained at 400° C. (runs 2, 8, and 11). Several patents published since this work was started claim similar results (*30*). This direct formation of butyl alcohol alone from ethyl alcohol in the absence of carbon monoxide is a strong point in favor of the condensation mechanism.

Runs 9 and 10 still further confirm the condensation theory: A mixture of methanol and ethyl alcohol might be expected to give the whole series of alcohols with a preponderating amount of propyl alcohol, and this is actually seen to be the case.

It has already been suggested that the over-all condensation of lower alcohols to higher alcohols may occur in two steps with intermediate dehydration of the lower alcohols to ethers, followed by rearrangement of the ethers to the corresponding higher alcohols. Although the passage of methanol vapor over a purely dehydrating catalyst, such as aluminum oxide, prepared from the methoxide does produce dimethyl ether (run 21), no direct evidence of intermediate ether formation was obtained from the results of any previous experiments in which the methanol was passed over a higher alcohol catalyst. In an attempt to clarify this point, run 12 was made with diethyl ether as the starting material. Diethyl ether was chosen in view of the difficulty of preparing, metering, and recovering dimethyl ether in the large quantities required. From the table (run 12) it will be seen that the main products are ethyl, butyl, and higher alcohols. A material balance and stoichiometric analysis of the results from this run indicate, however, that the main reaction is complete decomposition of the ether to ethylene and ethyl alcohol,

$$(C_2H_5)_2O = C_2H_5OH + C_2H_4$$

followed by the formation of butyl alcohol and higher alcohols by condensation reactions of the type:

$$2C_2H_5OH = C_4H_9OH + H_2O$$

Runs 16, 17, and 18 were carried out to determine whether the reduction of acids, aldehydes, and ketones play an important part in the building up of higher alcohols. The only other reactant in these experiments was hydrogen.

Run 18 shows that acetaldehyde is reduced to ethyl alcohol and the ethyl alcohol subsequently condensed to butyl alcohol. It should be noted, however, that ethyl acetate is also formed to a considerable extent, evidently by the reaction:

$$2CH_3CHO = CH_3COOC_2H_5$$

The exceptionally high concentration of combined acetic acid in this experiment confirms the suggestion previously advanced to the effect that acids are formed mainly by the

condensation of aldehydes, and not by the addition of carbon monoxide to alcohols. Acetone gives chiefly propyl and higher alcohols, but no ethyl or butyl alcohol, as might be expected (run 17).

When interpreted in light of the two last mentioned experiments, run 16 shows that acetic acid is converted almost quantitatively into acetaldehyde and acetone, which then in part undergo further reduction to ethyl alcohol and propyl alcohol. Condensation of the ethyl alcohol thus formed may account for the butyl alcohol present in the product.

Conclusions

In previous papers from this laboratory (*9*, *12*, *14*, *16*) there has been presented considerable evidence for the formation of formaldehyde as an intermediate product in the high-pressure synthesis of methanol from carbon monoxide and hydrogen. In other words, this work points to the formation of methanol in two steps:

$$CO + H_2 = HCHO$$
$$HCHO + H_2 = CH_3OH$$

It has now been shown that higher alcohols are in turn formed from methanol by a process of stepwise condensation, as exemplified by the reactions:

$$2CH_3OH = C_2H_5OH + H_2O$$
$$CH_3OH + C_2H_5OH = C_3H_7OH + H_2O$$
$$2C_2H_5OH = C_4H_9OH + H_2O$$

The theory of the condensation mechanism is supported by a number of concordant and comparative results. At the same time it is realized that the formation of the complex mixtures of organic compounds, which usually result from carbon monoxide and hydrogen over a composite catalyst such as that used in these experiments, may not be explained by a single primary reaction. Each of the metallic oxides composing the catalyst have been shown by Sabatier (*25*), Adkins (*2*), and numerous other investigators to have dual catalytic properties. In view of the results of the above experiments, however, it is evident that the more important reaction over the catalyst used is one of condensation and dehydration, with the reactions proposed by Fischer (*10*) taking place concurrently but to a minor degree. The extent to which either mechanism proceeds will be influenced by a change in the catalyst composition and other experimental conditions, such as carbon monoxide content in the entering gas mixture, etc.

On the basis of the present experimental work with a catalyst composed of the basic carbonates of zinc and manganese together with potassium chromate (Zn:Mn:Cr = 1.0:1.1:1.03), the following conclusions may be drawn:

(1) Methanol is an intermediate product in the high-pressure synthesis of higher alcohols from carbon monoxide and hydrogen.

(2) The higher alcohols are formed chiefly by successive condensations of lower ones. The controlling reaction in this formation of higher alcohols is the condensation of methanol to ethyl alcohol: $2CH_3OH = C_2H_5OH + H_2O$.

(3) It is possible that ethers are intermediate products in the synthesis of a higher alcohol by the condensation of two molecules of lower alcohols. Although the formation of methyl ether from methanol observed by Brown and Galloway (*6*) points in this direction, the writers have obtained no evidence that the reaction proceeds through the ether step. The information available is therefore considered insufficient to warrant any definite conclusion in regard to this point.

(4) The ratio of carbon monoxide to hydrogen is an important factor in the synthesis of higher alcohols. Although the condensation mechanism calls for the 1:2 ratio of these gases required for the synthesis of methanol, it is generally agreed that carbon monoxide should be present in excess in gas mixtures used for the synthesis of higher alcohols. Apparently the chief function of this excess carbon monoxide is to remove from the catalyst surface the water liberated by the condensation of the alcohols. The carbon monoxide reacts with the water according to the water-gas reaction, $H_2O + CO = H_2 + CO_2$, and this accounts for the high percentage of carbon dioxide resulting as a by-product in the synthesis of higher alcohols.

(5) The relatively small amounts of acids formed are largely present in the product in the form of esters. Although acids may be formed by the addition of carbon monoxide to an alcohol, as exemplified by $CO + CH_3OH = CH_3COOH$, the evidence points to the production of esters directly by polymerization of aldehydes, as illustrated by the reaction $2CH_3CHO = CH_3COOC_2H_5$. The intermediate formation of aldehydes by dehydrogenation of alcohols is favored by the low partial pressure of hydrogen in gas mixtures rich in carbon monoxide.

Owing to the many difficulties and possible sources of errors in the identification and quantitative determination of the higher alcohols, the writers have refrained from discussing their results in the light of the data obtained on the structure of the alcohols formed under varying experimental conditions.

Acknowledgment

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Adsorption of Methane and Hydrogen on Charcoal at High Pressure[1]

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Adsorption isotherms of methane and of hydrogen on charcoal have been determined over the pressure range of 1 to about 150 atmospheres at temperatures of 25° and 100° C. for hydrogen. The amount of gas adsorbed increased markedly with pressure, approaching a saturation value at 80-100 atmospheres. At 25° C. the maximum adsorption is approximately 12 and 4 liters per 100 grams of charcoal for methane and hydrogen, respectively.

Experiments with mixtures of methane and hydrogen under pressure at 25° C. have shown that charcoal adsorbs methane preferentially to the practically complete exclusion of hydrogen. The amount of methane adsorbed is approximately equivalent to that which would be adsorbed if the gas were present alone at a pressure equal to its partial pressure in the mixture.

THE problem of separating methane and hydrogen was recently encountered in this laboratory. The mixture of the two gases was available at a pressure of approximately 200 atmospheres and, after removal of most of the methane, the hydrogen was to be used in a process operating at that pressure. Owing to the high cost of compression, the best solution would therefore be to carry out the separation without releasing the pressure. Among the methods of accomplishing separation, the removal of the methane from the cycle gas by adsorption presented itself as having interesting possibilities.

The use of adsorption on charcoal for recovering volatile solvents such as benzene (*5*) and for producing natural-gas gasoline (*3*) has long been practiced. Although the successful application of this principle to the stripping of wet natural gas is due to the selective adsorption of the higher hydrocarbons, it is well known that the adsorptive capacity of charcoal for methane is small at atmospheric pressure (*1*). It therefore remained to determine whether pressure would materially increase the adsorption of methane and favor its retention in preference to hydrogen to such an extent as to make the method of any practical value to the present problem. To this end a study was made of the adsorption of methane and hydrogen, individually and in admixture, on charcoal at high pressures.

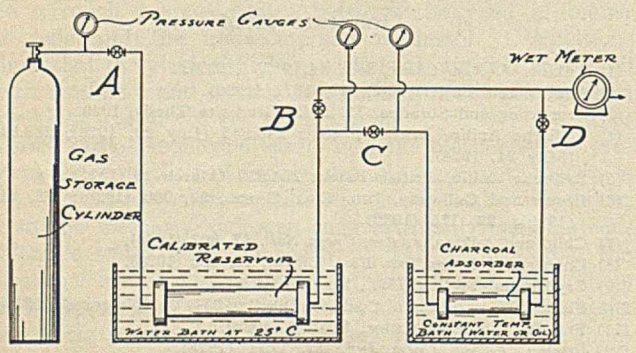

Figure 1—Apparatus for Determination of Adsorption Isotherms at High Pressure

Adsorption Isotherms of Hydrogen and Methane on Charcoal

The apparatus used to determine the adsorption isotherms at elevated pressures is shown in Figure 1. It consisted of a 5-liter gas storage cylinder, a 200-cc. reservoir, a 60-cc. adsorption chamber with carefully calibrated gages, valves, etc., as indicated.

The reservoir was first calibrated with the gas to be studied. This was accomplished by filling it with gas from the storage cylinder to about 200 atmospheres, closing valve *A*, and bleeding the gas slowly through valve *B* to the wet meter. Pressure readings on the reservoir and volume readings on the wet meter were taken simultaneously until the pressure in the reservoir dropped to atmospheric. These data were plotted and used later to determine the volume of gas bled into the adsorption chamber from the reservoir.

In starting a run the calibrated reservoir was again filled with gas to 200 atmospheres. The adsorber was charged with 27 grams of activated charcoal[3] of bulk density 0.47 and actual density 1.85[4] and evacuated completely. Gas from the reservoir was then bled into the adsorber through valve *C* until the pressure on the reservoir dropped 100 pounds per square inch (6.8 atmospheres). Valve *C* was closed and after about a minute, the time necessary to arrive at a constant pressure in the adsorber, pressure readings on both adsorber and reservoir were recorded. This operation was repeated; that is, successive portions of the gas were introduced from the reservoir into the adsorber with a pressure drop of 100 pounds per square inch (6.8 atmospheres) on the reservoir in each case, until the pressure on the adsorber equaled that on the reservoir. In most of the experiments the reservoir dropped from 200 to about 120 atmospheres, while the adsorption chamber increased from 1 to about 120 atmospheres. From these data and the calibration data previously obtained on the reservoir, the

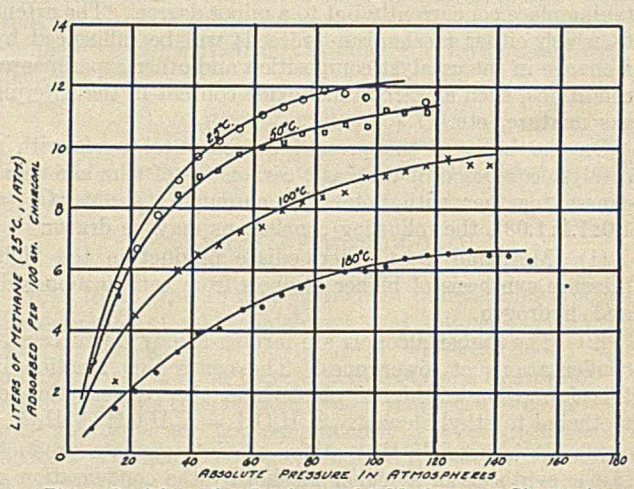

Figure 2—Adsorption Isotherms for Methane on Charcoal

[1] Received August 29, 1930.

[2] Present address, Standard Oil Development Co., P. O. Box 276, Elizabeth, N. J.

[3] Charcoal from the Carbide and Carbon Chemicals Corp., used as received.

[4] Determined by evacuating a weighed quantity of charcoal and measuring its real volume by kerosene displacement.

total volume of gas in the adsorber at the various pressures was figured and plotted on rectangular coördinate paper with pressure as the abscissa and volume as the ordinate.

To calculate the amount of gas adsorbed on the charcoal, the volume of gas in the free space had to be determined. This was accomplished by replacing the charcoal in the adsorber with an equivalent volume of copper shot (127 grams, density 8.98) and going through the procedure outlined above. These two sets of data were plotted on the same paper and the difference in gas volume in the adsorption chamber with charcoal and with copper shot for any one pressure was considered the volume of gas adsorbed on the charcoal at that pressure.

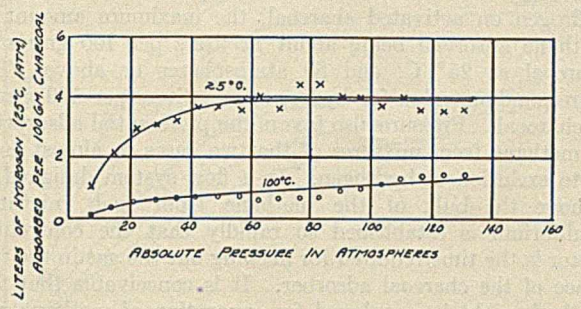

Figure 3—Adsorption Isotherms for Hydrogen on Charcoal

During the experiments and calibrations the temperature of the reservoir was maintained constant at 25° C. and that of the adsorber at any desired value.

The isotherms for methane at 25°, 50°, 100°, and 180° C. and for hydrogen at 25° and 100° C. are given in Figures 2 and 3, respectively. Most of these curves were checked by duplicate experiments. It will be seen that the adsorptive capacity increases markedly with pressure, approaching a saturation point at 80–100 atmospheres. At 25° C. this saturation value is 12 and 4 liters per 100 grams of charcoal for methane and hydrogen, respectively. It is significant that at 25° C. the amount of methane adsorbed at any one pressure is 2.5 to 3 times that of hydrogen at the same pressure, while at 100° C. methane and hydrogen are adsorbed roughly in the ratio of 9:1.

The adsorption of the two gases at these pressures does not follow the Freundlich adsorption isotherm (*4*), although the curves are represented as straight lines when plotted according to the Langmuir equation (*2*). McBain and Britton have recently shown that the same relations hold for the adsorption of nitrogen, nitrous oxide, and ethylene over the lower end of the pressure range studied in these experiments (*2*).

Figure 4 shows that the rate of decrease in adsorptive capacity with temperature is very nearly the same for both methane and hydrogen over the range studied. In the neighborhood of 150° C. the adsorption of hydrogen at 120 atmospheres is negligible, indicating that methane can be separated from hydrogen in this temperature region by simply passing the mixture of the two gases over activated charcoal.

Preferential Adsorption of Methane from Mixtures of Methane and Hydrogen under Pressure

In studying the adsorption of methane-hydrogen mixtures a dynamic method was employed. Methane-hydrogen mixtures of known composition were passed at a rate of about 30 liters per hour over the charcoal in the adsorber at the desired pressure until the analysis of the gas leaving the adsorber was the same as that entering. The apparatus employed was essentially the same as that shown in Figure 1, with the exception that the adsorber was of about 120 cc. volume containing 52 grams of charcoal and that the calibrated reservoir was eliminated from the set-up. When equilibrium had been established, as indicated by exit analyses, the gas-storage cylinder was shut off and the gas from the adsorber was bled out into a calibrated holder by releasing the pressure followed by heating of the chamber to 400° C. to remove the last traces of the adsorbed gas. From the volume of the gas and its analysis were calculated the amounts of hydrogen and methane present in the chamber at equilibrium.

The charcoal in the chamber was replaced by an equivalent volume of copper shot and the gas mixture was bled into the reactor to the pressure employed in the charcoal experiment. This gas was then released and measured to determine the volume of mixture in the free space. Since, in the above experiments with charcoal, at the time of dynamic equilibrium the inlet and exit analyses were the same, it follows that the composition of the gas in the free space was that of the original mixture. Therefore, the volume and composition of the gas in the free space at equilibrium being known, the amounts of hydrogen and methane in the free space could be determined and, by subtracting these values from the total hydrogen and methane in the adsorber as obtained in the experiment with charcoal, the values for the hydrogen and methane adsorbed were obtained.

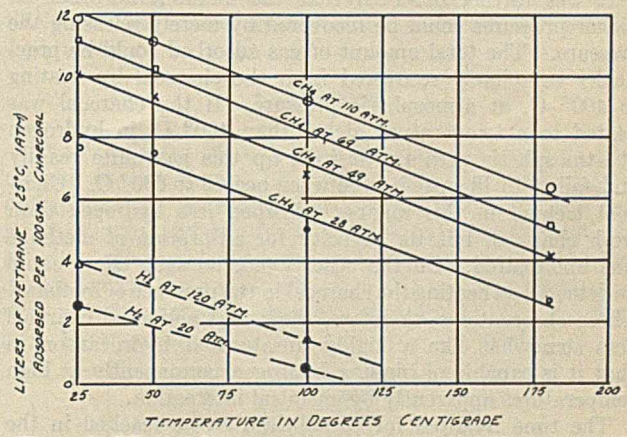

Figure 4—Effect of Temperature on Adsorption of Methane and Hydrogen on Charcoal

Figure 5 presents graphically the results of four experiments at 25° C. with methane-hydrogen mixtures of different compositions at several pressures. On this plot are presented the methane and hydrogen isotherms together with points indicating the observed adsorption from the various mixtures. The points are somewhat scattered, indicating a high percentage of error. This, however, is not surprising, considering the indirect method employed in obtaining the results. It will be noted that in no case, not even at the highest partial pressures, was any hydrogen adsorbed on the charcoal, and that the methane adsorbed was approximately the same as that which would have been adsorbed had it been used alone at its partial pressure in the mixture. It appears, therefore, that over the range of pressure and gas composition investigated methane is adsorbed by charcoal to practically the complete exclusion of hydrogen.

Miscellaneous Observations

A series of experiments made to study the adsorption of mixtures of hydrogen and methane at atmospheric pressure showed that in all cases hydrogen was adsorbed along with the methane. Owing to the small amounts adsorbed, the results of this work, as well as of determinations made of the adsorption isotherms for the two gases separately

at subatmospheric pressures, are not presented here. However, when seen in connection with the data obtained at high pressure, these results bring out the interesting point that pressure favors the preferential adsorption of methane on charcoal.

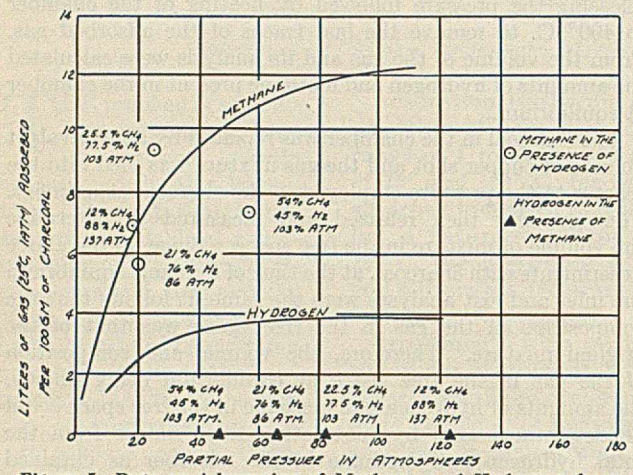

Figure 5—Data on Adsorption of Methane and Hydrogen from Mixtures of Two Gases at 25° C.

It was further observed that the methane adsorbed at higher pressures could be recovered by merely releasing the pressure. The total amount of gas adsorbed could be practically completely recovered from the charcoal by heating to 400° C. at atmospheric pressure. If the charcoal was heated to a temperature higher than 400° C. in hydrogen at atmospheric pressure, it took up this gas quite readily and failed to liberate it even when heated to 600° C. Charcoal treated in this manner adsorbed less hydrogen than fresh charcoal, but its capacity for adsorption of methane was unimpaired. On the other hand, no such effect could be detected on heating the charcoal in the presence of methane. These observations, therefore, show that activated charcoal acts somewhat like a highly unsaturated hydrocarbon in that it is capable of binding hydrogen permanently at high temperatures apparently by chemical interaction.

The time required for equilibrium to be reached in the high-pressure flow experiments with mixtures of methane and hydrogen is exceedingly short. It may be expected that some hydrogen is initially adsorbed, particularly toward the exit end of the chamber, where the gas has already been deprived of a substantial amount of its methane content by contact with the charcoal, and that a certain time is required for this adsorbed hydrogen to be displaced by methane. This interchange of the two gases must take place very rapidly, however, because equilibrium was always established in the time required for flushing out the gas contained in the free space of the reactor, no matter how high the gas velocity.

Conclusions

The results of these experiments show that pressure materially increases the specific adsorption of methane and hydrogen on activated charcoal, the maximum amount of methane adsorbed being about 12 liters per 100 grams of charcoal at 25° C. and 80 atmospheres or above. The corresponding value for hydrogen is 4 liters per 100 grams of charcoal. Pressure also favors the preferential adsorption of methane from mixtures of the two gases to almost complete exclusion of hydrogen. In a flow system designed to remove the bulk of the methane from such mixtures, equilibrium is established so rapidly that the controlling factor is the time required for flushing out the gas in the free space of the charcoal adsorber. It is conceivable that this method might be employed for separation of methane and hydrogen on a commercial scale, particularly where the enriched hydrogen is to be used at high pressure.

Acknowledgment

This method of separating methane from hydrogen was suggested by W. K. Lewis, who also took an active interest in directing the experimental work. The data reported here represent part of the results obtained in an investigation conducted by the Research Laboratory of Applied Chemistry, and the writers are indebted to several members of the laboratory staff for their participation in the work.

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(1) International Critical Tables, Vol. III, p. 250.
(2) McBain and Britton, *J. Am. Chem. Soc.*, **52**, 2198 (1930).
(3) Oberfell and Alden, "Natural Gasoline," p. 294 (1924).
(4) Walker, Lewis, and McAdams, "Principles of Chemical Engineering," p. 645 (1927).
(5) Walker, Lewis, and McAdams, *Ibid.*, p. 715.

Specific Heats of Gases at High Pressures

III—Results for Nitrogen to 150° C. and 700 Atmospheres[1]

B. H. Mackey[2] and Norman W. Krase

Department of Chemistry, University of Illinois, Urbana, Ill.

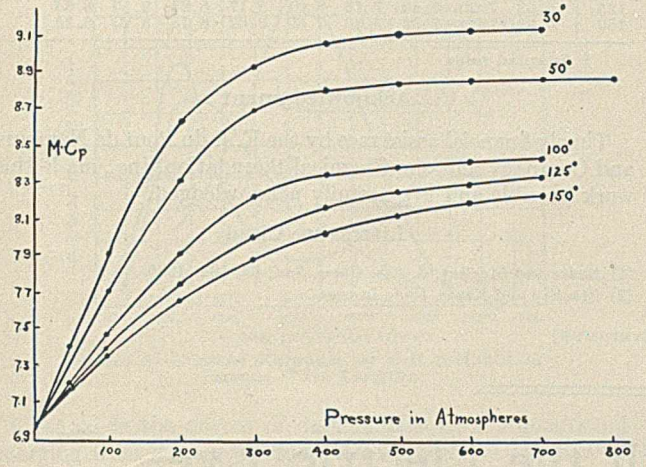
Methods of measurement and calculation of the specific heats of gases as a function of temperature and pressure have been developed, and the results for nitrogen up to 150° C. and 700 atmospheres are presented. Below 100° C. and above 400 atmospheres the effect of pressure on the heat capacity of nitrogen is small, the isothermals exhibiting a pronounced tendency to flatten out parallel to the pressure axis. At higher temperatures this tendency is not so marked. Data at higher temperatures are needed and this laboratory contemplates continuing the work in this direction on nitrogen and other gases.

In two previous papers (*1,2*) the authors have described apparatus and methods of measurement and calculation of specific heats at constant pressure at both ordinary and elevated temperature. The present paper summarizes the results for nitrogen to 150° C. and 700 atmospheres pressure. For a complete understanding of the method and measurements reference to the preceding papers is suggested.

Since the accuracy of each specific heat measurement depends on so many individual measurements, it is necessary to know the probable error in each and the corresponding

[1] Received September 2, 1930.
[2] Present address, Dupont Ammonia Corp., Charleston, W. Va.

effect on the final value. Certain quantities, such as the rate of gas flow, gas-temperature rise, heat input, etc., enter directly and the same error appears in the final value for C_p. Other quantities such as the absolute pressure and absolute gas temperature enter more or less indirectly and their effects may be evaluated by analyzing the finished data. Certain other individual quantities, such as thermocouple calibrations and systematic errors in the measuring instruments, do not affect the shape of the C_p isothermals but only their absolute position.



MC_p–Pressure Isothermals for Nitrogen

Experimental Conditions

The nitrogen used in all these experiments was purchased from the Linde Air Products Company and was their regular grade of atmospheric nitrogen considerably better than 99 per cent pure. De-oxidation over heated copper wire reduced the oxygen content to something less than 0.3 per cent according to analyses made from time to time by the yellow phosphorus vapor method. Carbon dioxide and water were removed by passage over soda lime and caustic in the pressure purification tower. No analysis was made for argon content, but this was probably quite low.

The pressure regulation was accurate to about an atmosphere during the experiments at low pressures. One atmosphere changes the value of C_p about 0.1 per cent in the low-temperature, low-pressure experiments. At higher pressures such a change has a smaller effect.

The error introduced by the electrical meter readings may be as high as 0.3 per cent, but this is unlikely as both the ammeter and voltmeter were calibrated against a potentiometer and the calibrations were good to about 0.1 per cent.

The gas-flow measurements were probably about as accurate as the power measurements. The rate was checked to 0.1 per cent by the stop watch and the weight of gas passed in calibration was accurate to 1 gram in a total of 600 grams.

The thermocouple calibrations were probably good to a little better than 0.1 per cent. As stated before, an error here affects only the absolute value of the specific heats. The C_p isothermals extrapolate so convincingly to the accepted value at 1 atmosphere that it is very unlikely that a large error of this type can be present.

The errors introduced by the potentiometer circuit are probably small. All connecting wires and switches are of copper, as is the entire galvanometer circuit. Correction is made for any small contact e. m. f. by shorting the potentiometer circuit through a copper resistance and correcting for the deflection. The gas-temperature readings were probably not reliable to much more than 0.2 per cent at the lower pressures, since there is usually more fluctuation here, but those at the higher pressures were usually good to the limit of sensitivity of the galvanometer, which was about 0.2 microvolt.

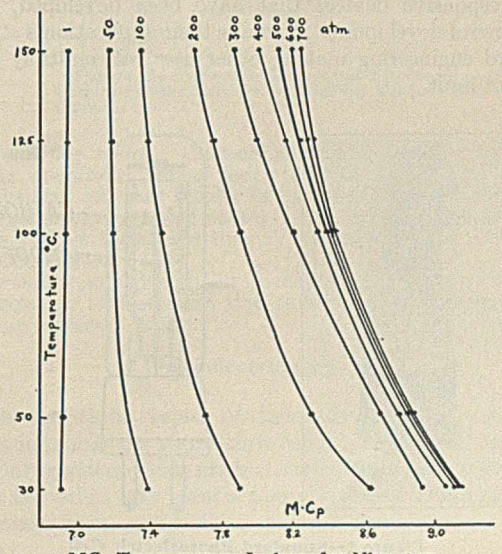
The conduction losses are probably not known to a very high degree of accuracy, but since they are quite small the possible error is very likely less than 0.1 per cent. This allows an error in this correction of about 20 per cent at the highest temperature used, and since only the change in temperature gradient between a calibration with no heat input and a regular experiment actually enters, it is unlikely that the error rises above this.

The calorimeter calibration with no power input (*2*) makes a blanket correction for the Joule-Thomson effect, the effect of the electric fields, all thermal leakage, and partially for the thermal conduction along the inlet tubes. This calibration is reliable to about 0.1 calorie at the high temperatures and considerably more than this at the lower ones.

The error due to faulty technic in operating the apparatus, of course, varies with the amount of care taken. It is possible to check individual results to within 0.5 per cent consistently. Some experiments fall outside of this limit, but almost always there is a logical explanation for the discrepancy. The authors believe that the values offered may be relied upon to within 0.5 per cent for the most part. Some of the values at the lower pressures, where the difficulties are larger, may not fall within this limit, but it seems unlikely that any of the results can be in error by as much as 1 per cent.

Calculations

The calculation of MC_p from the data obtained by this method is very simple. The total heat input is found by multiplying the product of the corrected voltmeter and ammeter readings by the factor 0.2389 to convert joules to calories. The conduction and miscellaneous losses are determined by the method described in the previous paper and their sum is subtracted from the gross input. The gas flow in mols per minute is found by dividing the product of the



MC_p–Temperature Isobars for Nitrogen

indicated rate and the weight of gas passed during calibration by the product of the cubic feet of gas passed during calibration and the molecular weight of the gas. The gas-temperature rise is found by multiplying the e. m. f. given by the "difference" couples by the factor taken from the standard thermoelectric curve and the calibration correction. The molal specific heat is then found by dividing the net

heat input by the product of the rate times the gas-temperature rise.

Results

The accompanying table and graphs give all the results derived from the investigation. All the values have been carefully checked except a few at the highest pressures which fall exactly on the curves. No measurement was made at 50° C. and 50 atmospheres. The upper pressure limit was set by the ability of the gas-storage system to stand a pressure about 200 atmospheres above the pressure in the calorimeter. Since the system was designed for 1000 atmospheres, no data could be taken above 800 atmospheres. Average values have been shown for the most part, but in a few instances certain experiments have been given more weight because of a closer agreement with the rest of the results.

It is readily seen that up to 100° C. an increase in pressure above 400 atmospheres has little effect on the heat capacity of nitrogen and that at all temperatures shown a pressure considerably above 1000 atmospheres would be necessary to cause significant changes in the values. There is no immediate need for data at still higher pressures, but values at temperatures up to 450° C. are of industrial interest and present plans contemplate extension of the measurements in that direction.

Molecular Heat of Nitrogen at Constant Pressure

Temp.	Pressure in Atmospheres									
	1[a]	50	100	200	300	400	500	600	700	800
° C.										
30	6.91	7.41	7.92	8.64	8.94	9.07	9.12	9.14	9.16	..
50	6.92	..	7.72	8.32	8.70	8.81	8.85	8.86	8.88	8.89
100	6.94	7.21	7.48	7.92	8.23	8.35	8.39	8.43	8.45	..
125	6.95	7.20	7.40	7.76	8.01	8.17	8.26	8.30	8.35	..
150	6.96	7.19	7.36	7.66	7.89	8.02	8.13	8.20	8.25	..

[a] Accepted value.

Acknowledgment

Timely financial assistance by the E. I. du Pont de Nemours and Company and the Chemical Foundation, Inc., made this work possible and is gratefully acknowledged.

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(1) Krase and Mackey, *J. Am. Chem. Soc.*, **52**, 108 (1930).
(2) Mackey and Krase, *Ibid.*, in press.

[End of Symposium]

Process Control with the Electric Eye[1]

C. A. Styer and E. H. Vedder

Westinghouse Electric & Manufacturing Company, East Pittsburgh, Pa.

THE photoelectric cell, perhaps best known through its relation to the "talkies," has already found some applications in the chemical industries in spite of being a comparatively new tool to the chemical engineer and process operator. As these men gain acquaintance with the light-responsive devices that have been developed, or are in course of development, to make their application a straightforward engineering matter, other uses will multiply almost without limit.

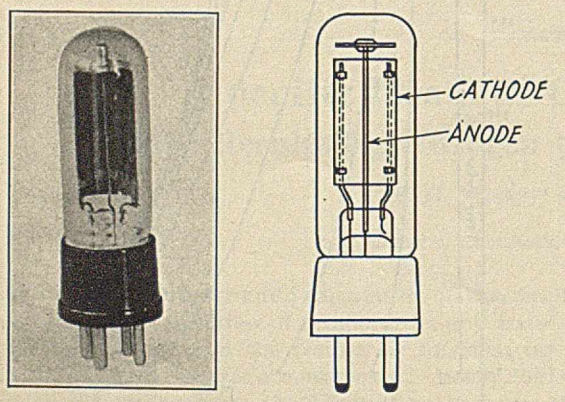


Figure 1—Standard Photoelectric Cell

This is peculiarly so in the chemical and process industries, because the "electric eye," as the photoelectric cell is frequently called, so adequately satisfies two great needs characteristic of most chemical processes—namely, a means for quick analysis and a means for control—that is at once automatic and continuous, perhaps instantaneous, in its response and in exerting its controlling action. With reliable facilities available for quick analysis and automatic control, the industrial chemist and process man are in a fair way to convert many of their batch processes to continuous ones and thus bring about the production economies that characterize the latter.[2]

Whether it is in connection with a continuous or a batch process, or with the non-chemical operations invariably associated with the production and handling of materials, such as counting bags of ammonium sulfate discharging from a chute, use of the electric eye is in many cases much less expensive than that of the human eye it replaces. But putting aside for the moment its important economic ad-

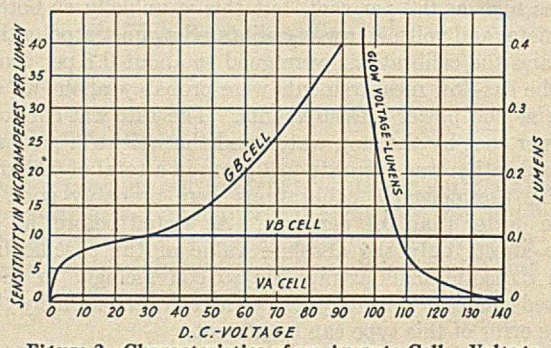


Figure 2—Characteristics of an Average Cell. Voltage per Unit of Light Flux and Glow Voltage-Illumination Curve

[1] Received July 28, 1930.

[2] An interesting discussion of the economic significance of substituting continuous for batch processes and of the relation of quick methods of analysis and automatic control to such conversions is to be found in a recent paper by H. H. Dow, president of the Dow Chemical Company [Ind. Eng. Chem., **22**, 113 (1930); and in abridged form, *J. Soc. Chem. Ind.*, **49**, 38 T (1930)].

vantage, photoelectric "observation" is more reliable than human observation in many cases where the latter is now used. More than this, the freedom of the photoelectric cell from fatigue, its ability to measure (and record if desired) differences in degree as well as "see" them, and its capacity for accurately following the progress of very rapid or very slow processes combine a range of abilities that surpass those of the human eye and operator for many industrial chemical operations.

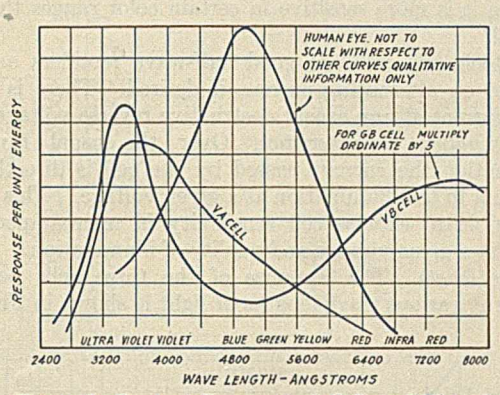


Figure 3—Current Response of Cell to Light of Various Wave Lengths

Changes in the degree of discoloration of a vegetable oil emerging from a filter press, in the turbidity of overflow of paper-pulp wash water, in the refractive index of a petroleum distillate, in the optical rotation of a sugar solution, and in other optical properties now employed in routine analysis and process control are photoelectrically measurable under works conditions. Other physical properties, such as specific gravity, pressure, temperature, and viscosity, are automatically measurable by photoelectric means, with the advantage that the vitiating effects of opposing forces and loss motions that characterize other automatic means for measuring the small forces and movements usually available from the changes are eliminated. Besides being weightless and frictionless, a beam of light does not corrode or dissolve.

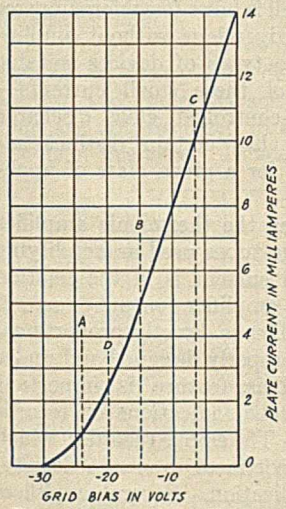


Figure 4—Amplifier Characteristics

The wide range of applicability of photoelectric analysis and control not only depends on the wide range of properties amenable to measurement, but also, and perhaps equally, it rests upon the power of photoelectric methods to give instantaneous indications or records and thus eliminate the delays incident to sampling and analysis. Coördinate with the instantaneous characteristic is that of continuity, which makes possible the determination photoelectrically of true time and space averages of fume in a duct section, for example, without the errors inherent in intermittent and discontinuous sampling methods.

Uses and Applications

The photoelectric cell is potentially applicable wherever light may be produced or affected in any of its characteristics by the changes which occur in chemical or physical processes and operations. In connection with these it is adaptable for indicating, recording, signaling, or controlling their condition or progress and for safety purposes. This field includes many cases where, for lack of other responsive devices, the human eye has of necessity been employed and in addition many others where the power of human observation or the required manual coördination is inadequate to the task.

A brief list of some of the numerous industrial applications illustrates the above general statement:

Smoke recorder, a permanent record of smoke density in convenient form impossible to obtain by ocular comparison with smoke charts. The record is continuous in degree of smoke density variation as well as in time throughout night and day.

Counting hot ingots. The electric eye "sees" the piece and thus avoids the excessive wear and tear on mechanically contacting devices for this service.

Counting delicate goods, such as sheets of paper, where mechanically contacting devices damage the goods.

Signaling presence of smoke in unattended substations and *automatically operating fire-extinguishing equipment* in warehouses. It provides continuous duty versus intermittent watchman service and does not have to wait for fire to develop sufficient heat to actuate alarm or release protective equipment.

Elevator control. Photoelectric leveling allows the elevator to swing in the shaft without trouble due to varying clearances in electric and magnetic circuits.

Suppressing commutator flashover, detecting the trouble and removing the converter from the line before the flashover has assumed damaging proportions.

Clear water level indicator in septic tanks.

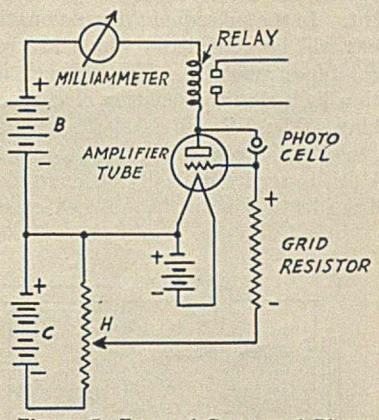


Figure 5—Forward-Connected Photo-Cell Amplifier Circuit for Use on Direct Current

Steel-mill flag switch. Controls automatic shearing and mill reversing operations where shock due to high-speed impact on mechanical switches results in excessive maintenance cost.

Detecting breaks in paper making. The photoelectric detector gives an audible signal and thus avoids necessity for continual visual observation.

Paper cutting, at a given point by mark on paper, thus avoiding inaccuracies in measurement due to slippage over mechanical measuring surfaces.

Photoelectric Cells

There are three types of light-sensitive devices—viz., the selenium cell, the photo glow tube, and the photoelectric cell. Only devices using photoelectric cells will be discussed here as the other two possess many inherent characteristics which make them ordinarily unsuitable for industrial applications.

A photoelectric cell is a light-sensitive device which, if connected to a circuit of the proper voltage, will permit a current to flow only when the cell is illuminated from a suitable source. The photoelectric cell (Figure 1) consists essentially of an anode and a cathode sealed into either an evacuated space or one filled with gas at a very low pressure. The cathode is of a material which has the property of emitting electrons when illuminated by light of the proper

wave lengths. After the electrons have been emitted from the cathode they will be accelerated toward the anode if a voltage of the proper polarity and magnitude is applied between the two electrodes.

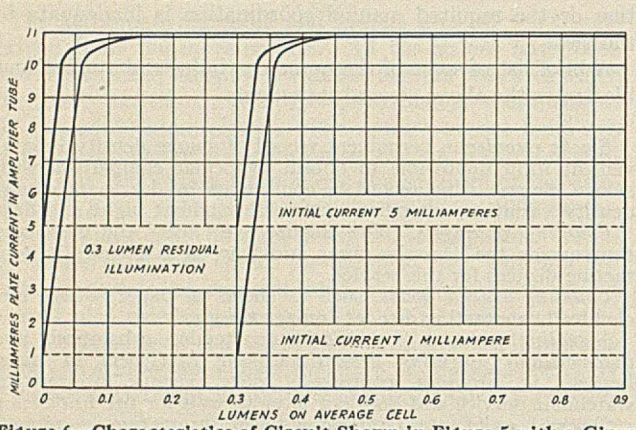


Figure 6—Characteristics of Circuit Shown in Figure 5 with a Given Grid Resistance

There are two general types of photoelectric cells—vacuum and gas-filled. In appearance they are identical, but in characteristics they are very different. In each of these general groups there are many types of cells, having various values of response per unit of light energy at different wave lengths of light. In the subsequent discussion, three different types of tubes will be considered which are representative of the general types available. The VA cell is a vacuum-type cell with a light-sensitive coating of caesium on a magnesium backing. The VB cell is also a vacuum cell with caesium as the sensitive metal, but processed differently from the VA cell to secure radically different characteristics. The GB cell is identical with the VB cell except that it is gas-filled.

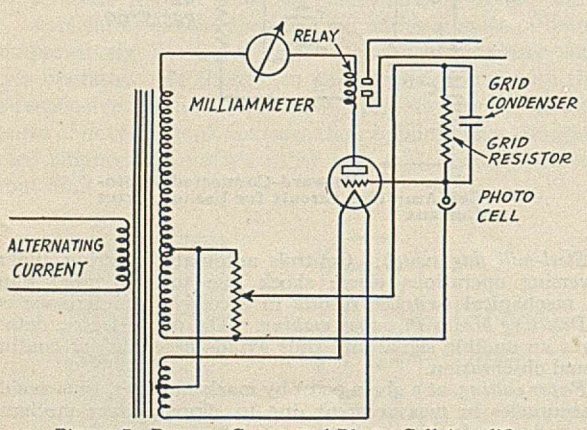


Figure 7—Reverse-Connected Photo-Cell Amplifier Circuit for Use on Alternating Current

The *sensitivity*—i. e., the current per light unit—is dependent on the voltage between the cathode and anode, as shown in Figure 2. Almost complete saturation of the VB cell is obtained at 30 volts. In other words, changes in the applied voltages above 30 have practically no effect on the current passed by the cell for a given quantity of light falling on it. Below 30 volts there is essentially no difference between the VB and GB cells. The point at which the two curves begin to diverge is at that potential at which the electrons leaving the light-sensitive surface of the gas-filled cell reach a velocity high enough to ionize the gas through which they pass. Ionization results in an additional or secondary flow of current which accounts for the difference between the curves for the VB and GB cells at the higher voltages.

The limiting voltage which can be applied to the gas-filled cell GB for various illuminations on the cell is shown in Figure 2. One essential of all designs of commercial apparatus is that the conditions necessary to initiate a glow discharge shall never be produced in service. A glow discharge quickly alters the sensitivity of the cell.

The VA cell is much less sensitive to the light obtained from the usual incandescent lamp than are cells VB and GB, as shown by its response curve. This cell is of value largely because it is more sensitive in certain color ranges than the VB cell.

Photoelectric cells are good half-wave rectifiers and can be used on alternating current if desired. There is no reverse current at any except destructive reverse voltages.

Illumination characteristics. Over the usual range of illumination the current passed by the cell is directly proportional to the illumination at a given voltage. This makes it possible to express cell sensitivity in microamperes per lumen at a given voltage and quality of illumination.

Wave length. The response of the three cells per unit energy at various wave lengths of light is shown in Figure 3.

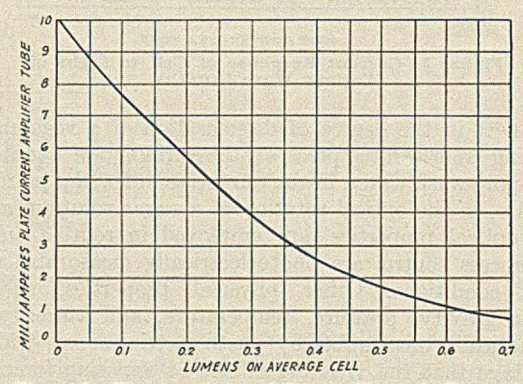


Figure 8—Characteristics of Circuit Shown in Figure 7 with a Given Set of Circuit Constants

Amplification of Cell Impulses

The current of a photoelectric cell is but a few microamperes and is too small to operate sturdy relays without amplification. In general there are two types of devices suitable for the effective amplification of these small currents—thermionic amplifiers and grid-controlled glow discharge tubes. Each type of amplifier has certain distinct advantages which make it suitable for a given class of applications.

The essential difference between the thermionic amplifier and grid-controlled glow discharge tubes used as amplifying devices for the photoelectric cell current is in the relation between cell illumination and amplifier output current. The output of a thermionic amplifier is directly proportional to the light falling on the cell, if properly designed and under correct operating conditions. This feature is important in applications requiring continuous indications or records of a given light effect on the cell. The smoke recorder, which requires an amplifier output proportional to smoke density, is one example of this type of application. Several amplifiers can also be used in cascade in various ways to secure enormous amplifications.

Glow discharge devices of the grid-controlled type when operated from photoelectric cells are essentially relaying tubes; that is, current through the tube begins or stops at a certain cell illumination and its magnitude is usually constant and unrelated to the cell illumination. With the proper circuit some degree of proportionality between light on the cell and output current of the tube can be obtained.

However, these tubes are most valuable merely for relay action.

The amplifier tube, when supplied with direct current, is the most sensitive means of light-current amplificiation now available. It can be supplied with alternating current and made self-rectifying, thus retaining the proportionality of current to light on the cell, but at the same time decreasing the cost and also the sensitivity of the amplifier.

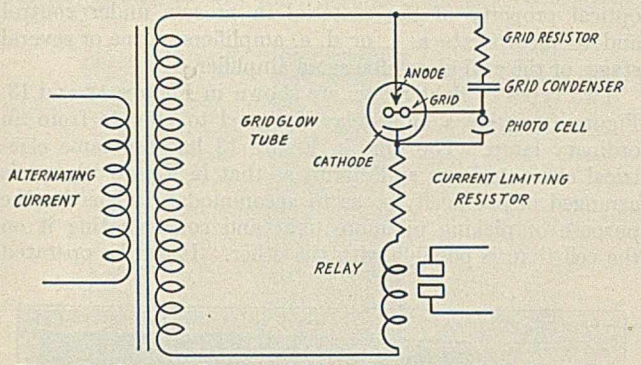


Figure 9—Reverse-Connected Light-Controlled Grid Glow Tube Circuit

The photo-cell and glow-discharge-tube combination is best suited to such operations as counting, relaying, and many types of automatic control. It is the cheapest amplifier combination inherently and is also comparatively simple in construction.

Photoelectric Cell and Thermionic Amplifier Tube

There are many circuits using the thermionic amplifier with direct or alternating current and one or more stages of amplification. The amplifier can also be so connected that the output current either increases or decreases with an increase of illumination on the photoelectric cell, whichever is desired. The circuits in which the output current increases with an increase of illumination on the cell will be known as forward circuits. Those in which output current decreases with an increase in illumination on the cell will be known as reverse circuits.

The forward circuit for use on direct current will be taken here as an example for detailed explanation. A few other circuits and their characteristics are also shown, although they are not discussed in detail. Figure 5 shows a typical circuit of this type. In addition to supplying plate potential

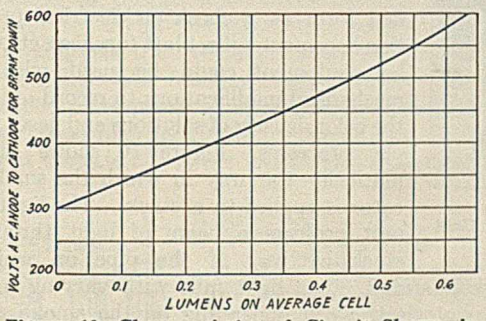


Figure 10—Characteristics of Circuit Shown in Figure 9 with a Given Set of Circuit Constants

and grid bias for the amplifier, the voltage of battery B plus the voltage from the filament to point H act as the source of potential for the photoelectric cell. When the photo cell is dark, the grid of the amplifier tube will be at a negative potential with respect to the filament as determined by the setting of potentiometer H, such as point A in Figure 4. This is on the assumption that zero grid current is flowing through the grid resistor, which will be nearly the case if the amplifier tube has been properly manufactured and tested. When light falls on the cell, a current flows from the positive terminal of the B battery through the meter and relay to the anode or positive terminal of the photoelectric cell. From this point the flow is through the cell, grid resistor, and then to the point H of the potentiometer and negative end of the C battery. The current flow results in a voltage drop over the grid resistor in such a direction as to cause the grid to become more positive with respect to the filament as indicated by the signs beside the grid resistor in Figure 5. Owing to this change in grid bias, to such a point as B in Figure 4, an increased current will flow through the amplifier tube.

The current change in the output of the amplifier will be linear with respect to light under proper circuit conditions, since the response of the photoelectric cell is linear with respect to light. The characteristic of the amplifier tube shown in Figure 4 is linear except at the two extremes of bias voltage. It remains only to operate the amplifier on the straight part of its characteristic and to use a grid resistor whose resistance does not change with the change of voltage.

Figure 6 shows the characteristic curve of the circuit in Figure 5 plotted with plate current of the amplifier as a function of lumens on the photo cell for various initial current settings and residual illuminations. The initial amplifier currents are determined by arbitrary settings of the point H.

Figure 11—Photoelectric-Cell Amplifier Unit

The operation of the reverse circuit is not radically different from that described above. A few connections to the photo cell have merely been reversed in such a way that illuminating the cell causes the grid of the amplifier tube to become more negative with respect to the filament instead of more positive, as was the case for the forward circuit.

Figure 7 shows a reverse circuit for use on alternating current. The operation of the a. c. circuit is not very greatly different from that of the d. c. circuit in Figure 5. The main point of difference is that the amplifier tube and photo cell each acts as its own rectifier. The resulting amplified current is half-wave pulsating direct current. The resulting characteristic curve with milliamperes output plotted as a function of lumens on an average VB cell is shown in Figure 8.

Photoelectric Cell and Grid Glow Tube

One grid-controlled glow discharge tube suitable for the amplification of photo-cell impulses is the grid glow tube. The grid glow tube is a three-electrode glow discharge tube

which passes a quantity of current depending on the potential of the grid electrode with respect to the anode. If the grid is sufficiently negative with respect to the anode, no current will be allowed to flow from anode to cathode. Thus the grid glow tube acts as a very sensitive relay which can be controlled by the photo cell. A vacuum photo cell is used with this combination, since the voltage is high enough to cause a gas-filled cell to glow and thus be ruined.

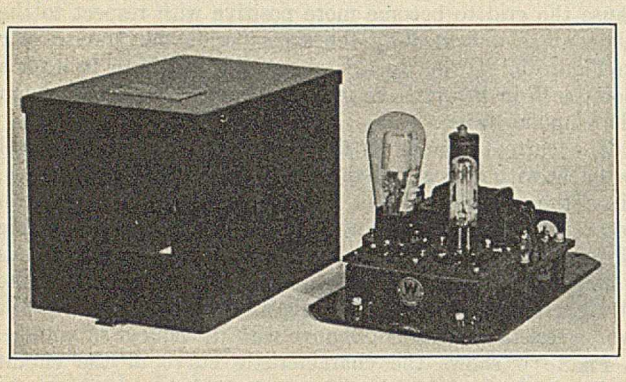


Figure 12—Light Relay for Short Spacing Equipped with a Grid Glow Tube for Amplification

Figure 9 shows the reverse circuit of this type. It is seen that the photo cell and condenser act as an impedance potentiometer which controls the potential of the grid depending on the illumination on the photo cell. Figure 10 shows the resulting characteristic of this combination. It is seen from the curve that this circuit gives a discontinuous characteristic. In other words, as the light is varied slowly a point is reached where the glow tube either passes a definite current or passes no current depending on a very small change in light on the cell.

Photoelectric-Cell Amplifier Unit

A convenient piece of apparatus incorporating any one of the three types of amplifier circuits mentioned above is the photoelectric-cell amplifier unit shown in Figure 11. The photo-cell and amplifier-tube combination for either alternating or direct current and the photo-cell and grid-glow-tube combination can easily be mounted in it with slight differences in construction. The unit is a very flexible device which can be used effectively for experimental work because of its adaptability and as the nucleus of a final design.

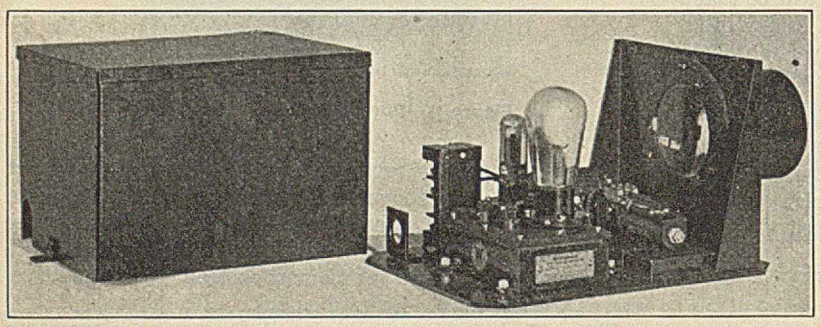


Figure 13—Light Relay for Use with Directed Light Beam Equipped with a Grid Glow Tube for Amplification

The unit is made moisture- and dust-proof by effectively sealing all joints with gaskets. All the leads between the photo cell and the amplifier or grid glow tube are concealed in the unit together with grid resistors and condensers.

Light Relays

Light relays can be built in almost any desirable mechanical form and can accommodate almost any desirable circuit and optical system. The number of kinds is so great that it would be very difficult to design a complete line which would fit all the needs for automatic relaying and control equipment of the light-sensitive type. They can be built as the demand arises for operation by changes of practically any optical property of the material in process under control and to incorporate a. c. or d. c. amplifiers of one or several stages or the grid glow tube as an amplifier.

Two types of light relays are shown in Figures 12 and 13. Figure 12 shows a light relay designed to operate from an ordinary lamp. The unit in Figure 13 has the same electrical characteristics and circuit as that in Figure 12, but is arranged mechanically so as to accommodate a lens for the purpose of picking up more light and concentrating it on the cell than is possible with the other. It can be operated with a projector type of light source, as shown in Figure 14, up to several feet. Both of these light relays use the circuit shown in Figure 9, incorporating the grid glow tube as the amplifier. These light relays are particularly adapted to automatic control and counting at high speed.

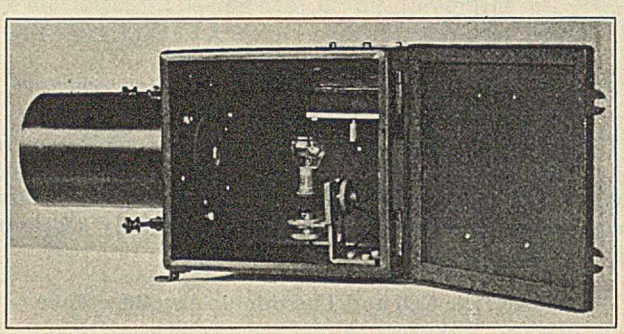


Figure 14—Projector Light-Source Unit

Smoke-Density Indicators

Smoke-density indicator (Figures 15 and 16) is an example of the use of a light-sensitive device as a calibrated piece of apparatus for the purpose of keeping a record or giving an indication of certain phenomena. This apparatus has been proposed in the present or modified form as a check on electrical precipitation in cement mills, blast furnaces, etc. Similar equipment could be used with slight mechanical modifications to record or indicate the color density of solutions and gases in various processes. Figure 16 shows diagrammatically the way in which the smoke indicator is applied to a stack. The light source unit projects a beam of light through the stack by way of the pipe on which the units are mounted. The light falls with varying intensity on the photoelectric cell depending on the smoke density. The beam of light is intercepted by the smoke at the center of the stack for a short section which is representative of the conditions throughout the rest of the stack. Figure 17 shows two charts representing extremes of conditions as obtained on two different installations.

Life and Constancy of Tube Devices

The life and constancy of tube devices is probably one of the first things which come to the mind of the potential

user of them. It is a common misconception that anything in a glass tube is not reliable. It should be realized that all long-distance telephony depends on large numbers of amplifier tubes in repeater stations along the line. Similarly, properly designed and manufactured light-sensitive devices will operate dependably for long periods of time. The tubes themselves will have an average life of about one year of continuous operation 24 hours a day. Standard Mazda lamps operated at less than normal voltages give adequate

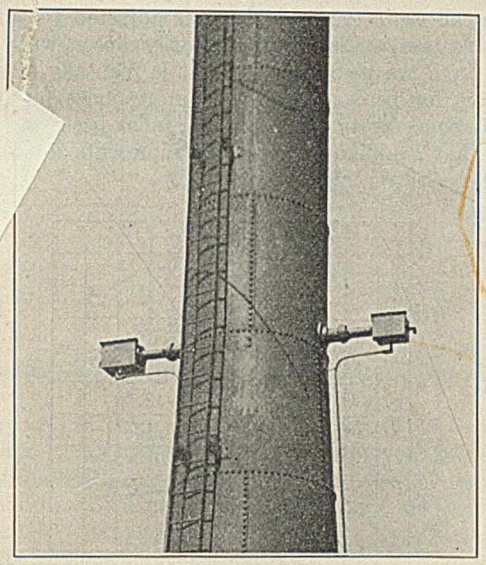


Figure 15—Smoke-Recorder Installation

light and have a life comparable with the other tubes. The amount of adjustment required will depend entirely on the type of service required of the apparatus. If accurate indicating or recording is required, it will probably be necessary to check the calibration once each week or two or, in cases of extreme accuracy, every day. For relaying operations such as counting, where complete interruption of the light beam is obtained, no adjustment may be found necessary over the life of the tubes. It is, of course, necessary to keep the optical equipment clean if the apparatus is in a dirty position.

Speed of Operation

The speed of operation of light-sensitive equipment is limited only by circuit and mechanical relay characteristics, since the photoelectric cell is instantaneous in response to change of light. The familiar talking movie is an example of the speed of response which can be obtained where the frequency is as high as 10,000. Objects can be accurately counted at the rate of 300 per minute and automatic relaying

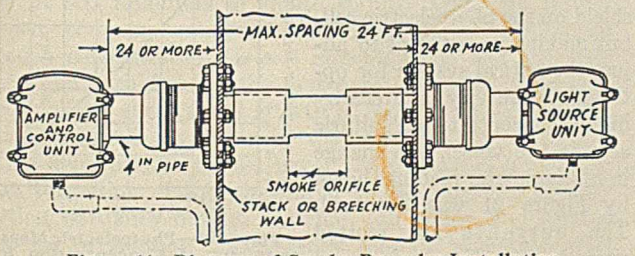


Figure 16—Diagram of Smoke-Recorder Installation

can be performed in $^1/_{30}$ second after the light impulse is received. Indications depend only on the inertia of the instrument for their speed, since the amplifier can easily be made to respond to 0.001 second. Thus it is seen that in many cases this apparatus will be more speedy than any at present available.

Plant and Process Control

Some of the illustrative applications listed earlier under the section "Uses and Applications" exist in one or another of the process industries; all of them are directly applicable or immediately suggest obvious adaptations to the particular needs of the chemical plant and process. Generally the chemical works is located where it does not need to concern itself with the amount of smoke emitted, but the smoke recorder is nevertheless valuable as a means for improving and sustaining boiler-plant economy. Moreover, if fuel economy is a matter of little moment to the engineer who is worrying about nitrous oxide losses from the Gay-Lussac towers of his chamber acid plant, it is equally of little moment to the photoelectric cell, whether it is on the watch for smoke or nitrous oxides, for it "sees" the latter unerringly, day or night. Clogging of a spray nozzle in the chambers themselves is another important trouble that frequently goes unnoticed for some time, upsetting conditions within the chambers, and besides is occasionally difficult to locate. With an electric eye "watching" the spray such trouble will be promptly detected and located.

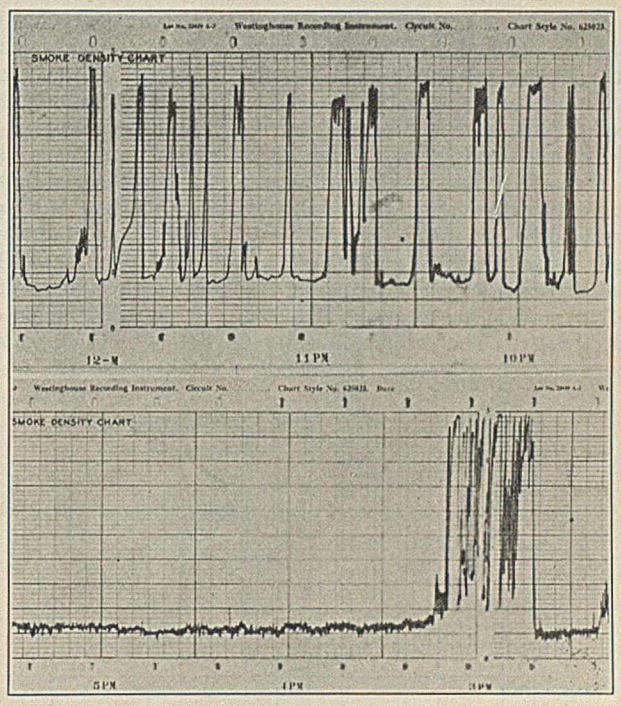
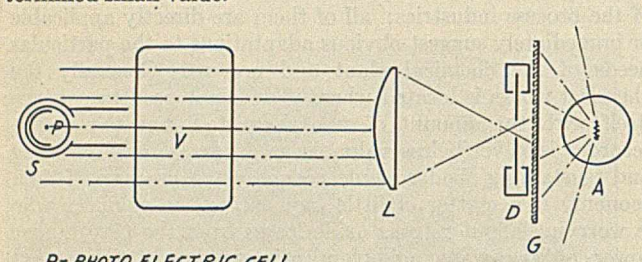


Figure 17—Smoke-Density Records

Rather than trust to the observation and judgment of attendants to start the ventilating fans in plants where accumulations of poisonous fume or explosive dust intermittently occur, the fans are kept running all the time, with consequent waste of power. A beam of light traversing the room or ventilating duct and impinging upon a light relay will allow the fans to idle at reduced speed or at rest until a predetermined concentration of obstructing particles has diminished its intensity and caused the relay either to operate a signal or to speed up the fans.

The turbidity of thickener overflow is a measure of the losses in the continuous concentration of metallurgical slimes and of water-borne solids generally. A photoelectric turbid-

imeter will measure instantaneously and continuously the loss of solids and can be applied to maintain that balance between rate of feed and overflow turbidity giving maximum economy of thickener operation. A closely related application is found in freeing sulfite paper pulp from black liquor, where light relays are used to terminate the operation when discoloration of the washings has fallen to a predetermined small value.



P-PHOTO ELECTRIC CELL
S-LIGHT SHIELD
V-CONTAINER FOR LIQUID
L-LENS
D-IRIS DIAPHRAGM
G-GROUND GLASS
A-21 C.P. AUTOMOBILE HEADLAMP

Figure 18—Diagram Showing Arrangement for Measuring Transmission

Some Quantitative Illustrations

In the following paragraphs some illustrative measurements of photo-cell and amplifier response to phenomena with which the chemist and engineer are familiar are given. These are offered in anticipation of two difficulties which, up to this point, may have confronted the reader who has been endeavoring to visualize the use of photoelectric methods of analysis or control in his own process. One of these is that the illustrative applications already cited perhaps lack a sufficiently quantitative character to convey a satisfactory idea as to whether the changes in the particular material and process with which the reader is concerned are of an order of magnitude that can be detected and measured photoelectrically. The second difficulty is that of relating such abstractions as lumens, foot-candles, and perhaps the numerical limits of spectral bands to the reader's own visual impressions of phenomena or conditions in the plant or process. If this is so, perhaps the terms in which the following results are expressed will relieve any sense of unfamiliarity.

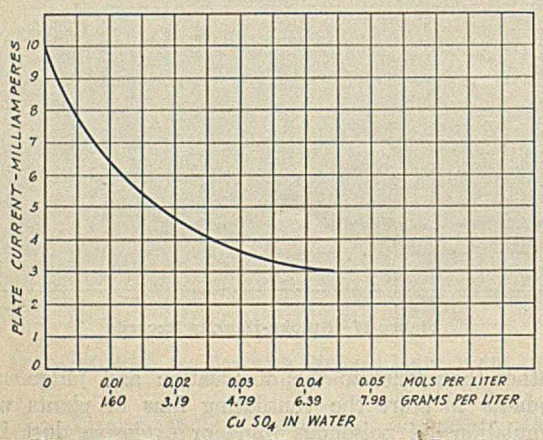


Figure 19—Photoelectric Measurement of Dissolved Copper Sulfate—Low Concentrations

All of these illustrative tests were made with a vacuum type photoelectric cell and amplifier energized and metered as diagrammed in Figure 5. Figure 18 indicates the arrangement of light source and approximate optical path employed in taking the data for Figures 19, 20, 22, [illegible] 23. Figure 24 shows the arrangement used for takin[illegible] data on refractive index shown in Figure 21.

The solutions under observation were cont[illegible]d in a narrow beaker or a glass jar shaped to crudely [illegible] angular form about $2^1/_2 \times 3^1/_2$ inches in plan. The light [illegible]rce was a ground-glass plate illuminated by an ordinary [illegible]-candle-power automobile headlamp and the amount o[illegible]ght was controlled by a camera diaphragm. Light [illegible]ing the diaphragm was roughly collimated by a $2^1/_2$-in[illegible] diameter lens. In all cases the grid bias was adjusted t[illegible]llow the amplifier to pass 1 milliampere (arbitrarily chosen) [illegible] all light shut off from the photo cell, so that in mentall[illegible]aluating the curves for percentage change in response [illegible] a given change in concentration or refractive index it should be kept in mind that 1 milliampere actually represents zero [illegible] stimulus of the photoelectric cell.

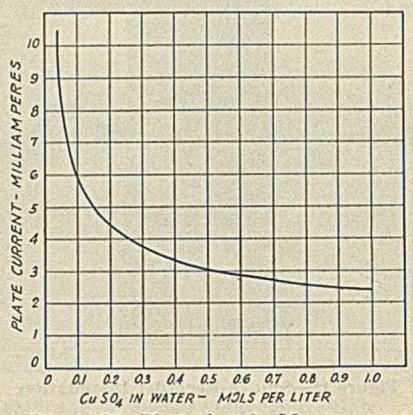


Figure 20—Photoelectric Measurement of Dissolved Copper Sulfate—High Concentrations

Figure 19 was taken by first adjusting the diaphragm to make the meter read full scale (10 milliamperes), with the light passing through water, and then adding copper sulfate to produce the concentrations shown. It will be noted that the equipment, as thus set up, is most sensitive to changes in concentration in the region of lower concentrations. Lest the impression be gained from this curve that the method is applicable only to changes in small concentrations, Figure 20 is shown, which indicates how, by choosing another combination of solution thickness and diaphragm opening, a ten- to twenty-fold range in concentration can be covered with the same equipment.

Dependence need not be placed upon change in color density, for refractive index may be the property upon which to base photoelectric control. Arranging the crudely rectangular vessel as indicated in Figure 24 so as to refract light toward the aperture in the light shield on the photoelectric cell, but making no attempt to adjust the optical system for optimum sensitivity, and changing the concentration of sulfuric acid in the vessel, the change in milliammeter reading shown by Figure 21 was obtained. The currents are plotted against refractive index and the magnitude of effect suggests at once the great possibilities of photoelectric analysis and control of solutions whose colors do not change or whose changing color is not a basis for control.

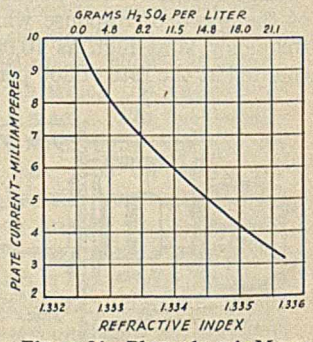


Figure 21—Photoelectric Measurements of Concentration by Refractive Index

Using an ordinary portable milliammeter with a 5-inch scale graduated to 0.1-milliampere divisions and employing an optical system as inefficiently arranged as this one was, Figure 21 shows the possibility of reading changes in refractive index of from 0.00002 to 0.00006, averaging 0.000046 for the entire curve, and of estimating even smaller changes. Substitution of standard recording or controlling instruments for the indicating one is possible with no loss in sensitivity.

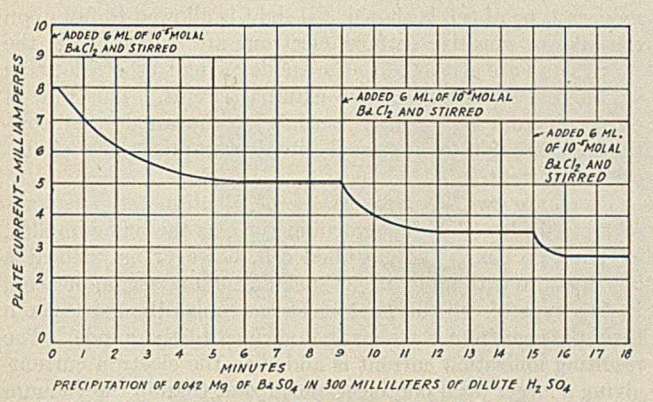


Figure 22—Measurement of Suspended Solid Concentration

By way of indicating the use of refractive properties for density and mass measurements of dissolved substances, a few typical substances are tabulated together with the approximate changes in specific gravity and of percentage concentration that accompany changes of 0.00004 in the refractivity of their aqueous solutions.

Aqueous Solution	Approx. Change in Density	Approx. Change in Concn. by Weight
		Per cent
NH_4Cl	0.00006	0.02
$CaCl_2$	0.00014	0.014
H_2SO_4	0.0003	0.04
C_2H_5OH	0.0014	0.7

Refractometric analysis is, of course, no new thing that light-sensitive devices have made possible. The significant point is that photoelectric equipment, that is adequately simple and permanent in adjustment for works application, makes possible the continuous refractometric analysis of a continuously changing mixture and extends refractometry to the needs of process operation such as that of the continuous metering of dissolved substances in flowing solutions or of the vapor content of a vapor-gas mixture either at rest or in motion. As an example of the possibilities of vapor-phase metering, the above-mentioned change of 0.00004 in refractive index corresponds to a change of about 5 per cent of acetone vapor in an acetone-air mixture.

Figures 22 and 23 illustrate the field of turbidity measurement and precipitation control. Figure 22 shows the history of precipitation of three 0.014-mg. portions of barium sulfate in 300 milliliters of dilute sulfuric acid. As is well known, the appearance of barium sulfate from solutions of such concentrations is not instantaneous and the freedom from turbidity for the first quarter-minute is evident. Then follows the gradual growth of solid in suspension at a diminishing rate, as shown by the flattening out of the first or left-hand portion of the curve. At the end of 9 minutes, after formation of solid appeared to be complete, another portion of dilute barium chloride was added and further decrease in solution transparency due to increasing solid formation is followed by the falling current. At the end of 15 minutes this was repeated. Inequality of the three parts of the history is due to at least two causes—one being that the change in transmissibility per unit of solid formed diminishes with increasing concentration of solid, and the other that after the twelfth or thirteenth minute the amount of solid and particle size had reached such proportions as to make removal of solids from the light path by settling a factor tending to offset the light-obstructing effect of increasing solid formation.

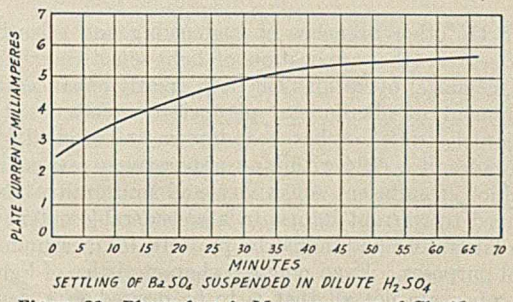


Figure 23—Photoelectric Measurement of Clarification Progress

Following the eighteenth minute the mixture was vigorously stirred to put all settled barium sulfate in suspension, and then settling was followed photoelectrically as shown by Figure 23.

Figures 22 and 23 represent cases where increasing turbidity diminishes the light received by the photo cell. Other measurements, not illustrated, in which the photo cell was placed so as to receive, not directly transmitted light, but light scattered from particles in suspension, gave increasing illumination of the photo cell with increasing turbidity and showed that measurement of scattered light is a practicable alternative.

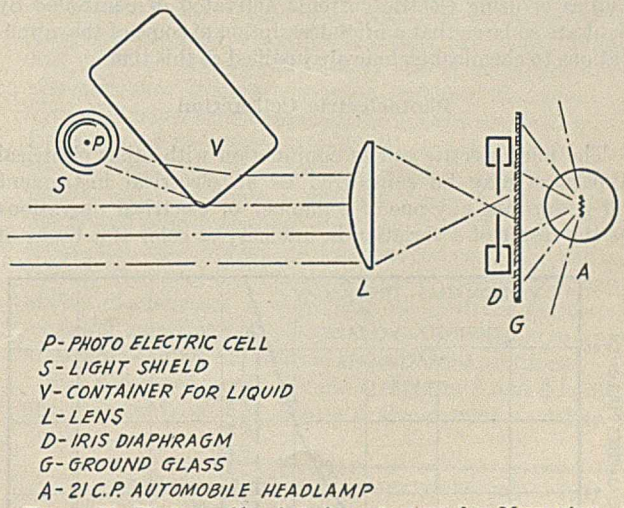


Figure 24—Diagram Showing Arrangement for Measuring Refractive Index

The availability of standard equipment together with the simplicity of manipulation evident in the description of procedure followed in taking data for these curves will, no doubt, indicate to the reader who wishes to apply this tool to his own needs that horse sense and ingenuity, rather than a diploma in optics or electric circuit theory, are sufficient prerequisites to a successful start.

Acknowledgment

The authors wish to express their appreciation for the work done by E. D. Wilson, of the Westinghouse Research Laboratories, in obtaining the color sensitivity characteristics shown in Figure 3.

Photoelectric Cells in Chemical Technology[1]

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As in other branches of engineering and scientific research, the application of light-sensitive devices to chemical operations has been greatly enhanced by the development of alkali-metal photoelectric cells. Although the photoelectric effect has been known and studied for several decades, it is only within a comparatively few years that a product of sufficient sensitivity and uniformity has been developed to warrant its use to a considerable extent in research laboratory and industrial projects, for measurement or control purposes. Even now the characteristics of light-sensitive tubes are not all that is to be desired in a device of this nature, but for some purposes their use can be depended upon to give satisfactory and consistent service. The possibilities of using electric currents activated or controlled by light are so large that a brief description of some of the applications to chemical technic are justified at this time.

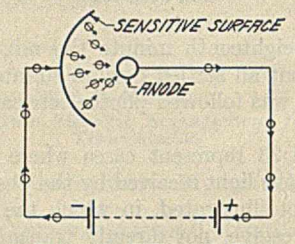

Figure 1—Schematic Drawing Illustrating Action of a Photoelectric Cell

Photoelectric Cell Action

The photoelectric cell in conjunction with other electrical apparatus may be considered as an electrical instrument for performing any one of a number of electrical operations as the result of a variation in intensity or color of a beam of light. The cell, which in some respects is similar to a radio tube, depends for its action upon the emission of electrons from a sensitive surface of an alkali metal or alkali-metal hydride.

In Figure 1 a schematic illustration of the action of a modern type of cell is shown. If light is allowed to fall upon the interior sensitive surface, electrons are emitted from the surface and are attracted to the anode owing to the polarizing action of the battery in the external circuit. This flow of electrons from the sensitive surface to the anode and continuing through the external circuit comprises the photoelectric current.

There are two general classes of alkali-metal or alkali-metal hydride cells. The vacuum type, as the name implies, contains no gas. The gas-filled cell, however, is filled at a low pressure with an inert gas such as helium, argon, or neon. In this type of cell the photoelectrons ionize the inert gas in their passage from the sensitive surface to the anode. The resulting ionization current is added to the electron current, giving a larger total photoelectric current than in the vacuum type of cell. Photoelectric cells of maximum sensitivity are therefore of the gas-filled type.

The magnitude of the current in the gas-filled cell depends upon the specific surface sensitivity, color of light, the volume, pressure, and nature of the inert gas, the cell voltage, and the total light flux entering the cell. In the vacuum cell the current depends only upon the surface sensitivity, color, and amount of light, and to a certain extent upon the cell voltage. As there is no ionization in the vacuum cell, the sensitivity does not materially increase after the saturation voltage is reached, and the cell is not critical with respect to operating voltage. This characteristic is illustrated in Figure 2 (type AV). Where highest sensitivity is not required, the vacuum cell can be used to advantage. However, the sensitivity of modern vacuum cells is only one-fourth to one-fifth that of gas-filled cells, and the latter are used where sensitivity is of more importance than absolute constancy.

The principal characteristics of typical cells are shown in Figures 2 and 3. In Figure 2 the specific cell sensitivity in micro-amperes per lumen is plotted against cell voltage. As the voltage of the gas-filled cell (type A) is raised, the sensitivity of the cell increases rapidly until the curve rises almost vertically. If the voltage is raised above this critical point, the cell "spills over" into a state of cumulative ionization or

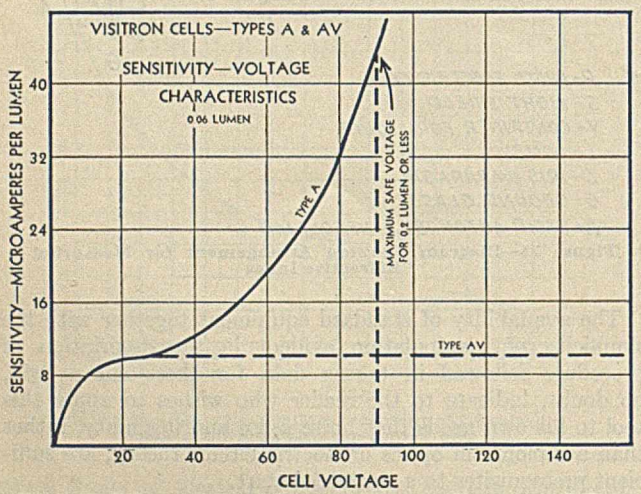

Figure 2—Voltage-Current Characteristics for Vacuum and Gas-Filled Cells

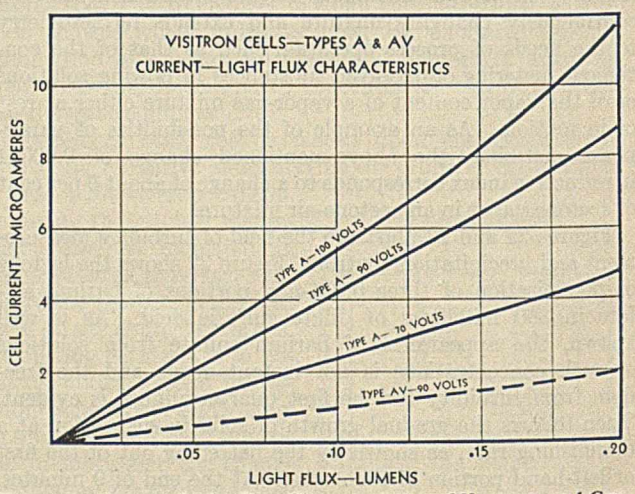

Figure 3—Current-Light Flux Characteristics of Vacuum and Gas-Filled Cells at Various Operating Voltages

[1] Received July 10, 1930.

glowing. In this condition the cell is inoperative and is subject to serious damage. The maximum safe operating voltage of the gas-filled cell depends upon the amount of light energy entering the cell. With greater light intensity the operating voltage must be lower to prevent cumulative ionization.

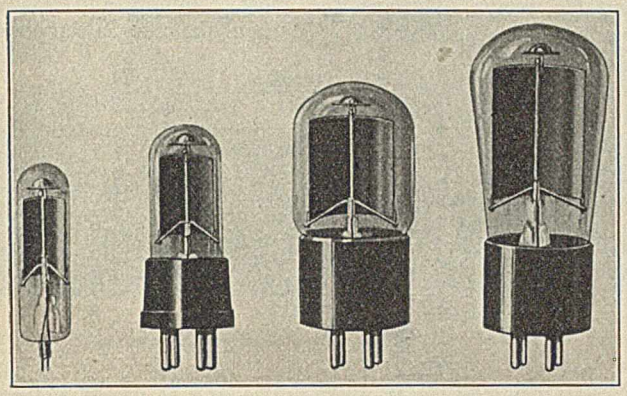

Figure 4—Four Standard Sizes of Visitron Type A and AV Photoelectric Cells

Figure 3 shows the linear light-flux cell current characteristics for different operating voltages. Here again the increase of cell sensitivity with cell voltage will be noted.

The ratio of the micro-ampere output per lumen of light flux at a definite cell voltage is a measure of cell sensitivity at that voltage. To make possible comparisons between different cells having different voltage ratings the specific cell

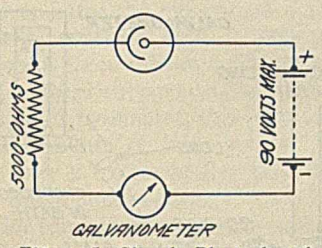

Figure 5—Simple Photoelectric Photometer Circuit for Measurement of Light from Various Sources

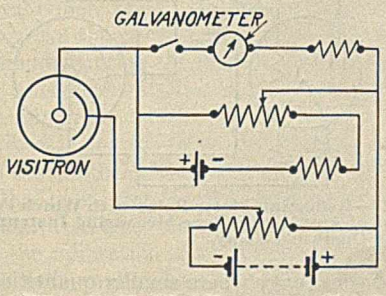

Figure 6—Modified Photometer Circuit in Which Greater Sensitivity May Be Obtained in Measuring Increments of Change of Light

sensitivity is expressed in micro-amperes per lumen at 10 per cent below the light glow voltage (for a definite amount of light flux such as 0.2 lumen).

Figure 4 shows modern forms of photoelectric cells which can be obtained in either gas-filled or vacuum types.

Photoelectric Cell Circuits

The types of circuits in which photoelectric cells can be used may be divided into two general classes: (1) circuits in which the photoelectric current itself is used to actuate a sensitive electrical instrument, such as a galvanometer; and (2) circuits in which the photoelectric current actuates a radio-tube amplifier, thereby increasing the magnitude of the current which can be used to control a meter, relay, or other electrical device.

In the first classification the circuits of Figures 5 and 6 can be used in the measurement of optical properties of various materials. As an example, the arrangement of apparatus shown in Figure 7 in conjunction with one of these circuits can be used for the determination of light transmissive power, reflecting power, or absorption factor of metals, glass, tiles, other ceramic materials, paints, varnishes, and various cellulose products. By using the proper color filters and accessory calibration apparatus, the color characteristics of such

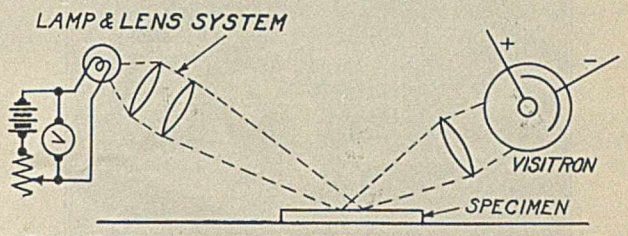

Figure 7—Arrangement of Optical Apparatus for Measuring Reflecting Power of Various Materials Such as Metals, Paints, Varnishes, Etc.

materials can also be studied. Figure 8 shows the response of the human eye as well as the photoelectric cell to various colors of light.

In addition to the use of this photometer type of circuit for the determination of physical properties of materials, this arrangement has many applications as a light-measuring instrument in studying actual chemical processes. Thus the end point of various reactions in which the criterion is the disappearance or change of color, degree of transparency, or change of colloidal properties can be quantitatively determined by means of the photoelectric cell in place of the human eye. (Figure 9) Among many such applications is the measurement of liquid ingredient densities, proportions of liquid and solid ingredient mixtures, thickness of paper-mill stock, etc. Such apparatus, when properly adjusted and maintained, eliminates the dependence upon personal judgment or ability of operators to determine such critical factors. By means of amplifier and relay circuits it is possible to provide automatic control of titration and similar operations.

The difference in the circuits of Figures 5 and 6 is mainly one of sensitivity. In Figure 5 the current variation can

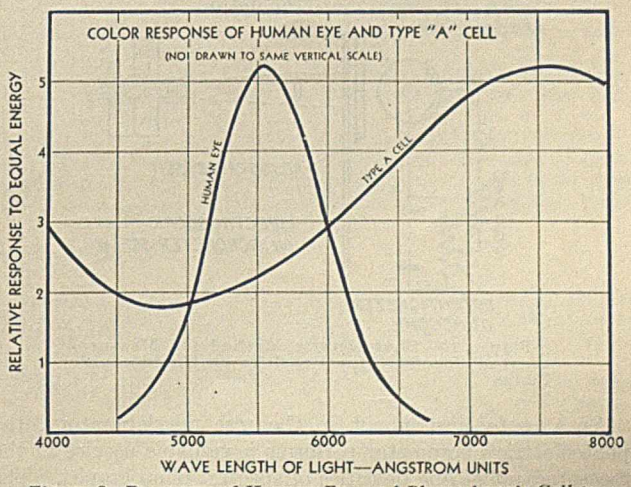

Figure 8—Response of Human Eye and Photoelectric Cell to Various Colors of Light

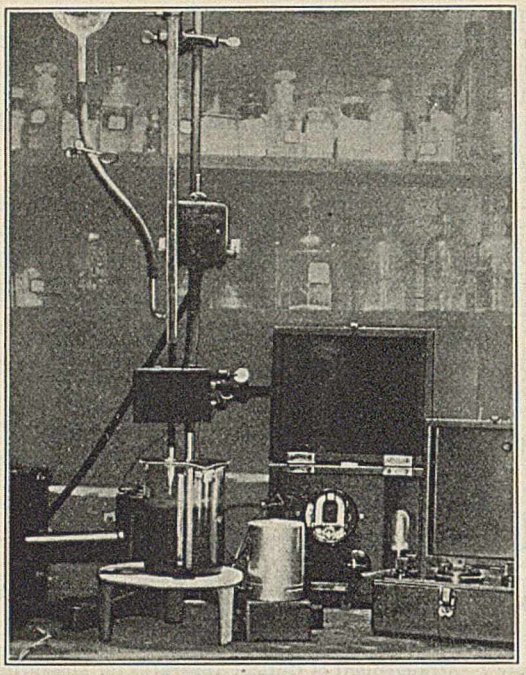

Figure 9—Arrangement for Automatic Electrical Indication of Titration of Chemical Mixtures

The mixture in the beaker changes color or light-transmitting power when the correct amount of standard solution from the buret is admitted. A beam of light passing through the mixture to a photoelectric cell causes a relay to operate when the critical point is reached. This relay controls the valve on the buret, shutting of the standard solution.

only be measured as a percentage of the full-scale deflection of the meter which is usually a low-range micro-ammeter or reflecting galvanometer.

Note—In the determination of the end point of a reaction there may be a certain amount of transmitted light during the entire reaction which gradually increases as the end point is reached. The measurement to be made is the change of light rather than the total quantity.

In Figure 6, however, the current variation may be made full scale by balancing out the constant current component. By using properly calibrated rheostats or resistance boxes this method may be used as a "null method," which is conducive to greater precision and ease of manipulation. In this form the balancing circuit is essentially a potentiometer, and a commercial instrument of this type may be used.

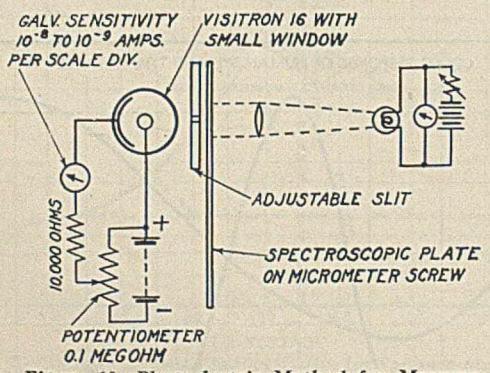

Figure 10—Photoelectric Method for Measurement of Spectral Line Densities on Photographic Plates

As a useful instrument in the research laboratory, the photoelectric photometer performs a valuable service in the measurement of line densities of spectral photographs. The plate is mounted as shown in Figure 10 between the cell and a source of light. The relative line densities can readily be determined from the corresponding cell currents.

Photoelectric Relays

In the second classification of circuits are many and varied arrangements of vacuum-tube amplifiers with which the photoelectric current may be measured or used to control suitable relays. Perhaps the most common and easily managed is that of Figure 11. Without the relay in the plate

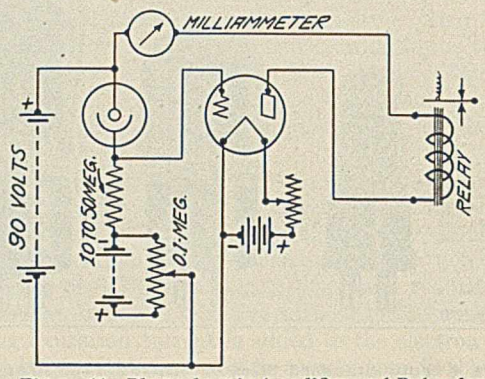

Figure 11—Photoelectric Amplifier and Relay for Controlling Any Electrical Circuit by Means of Light

circuit of the tube, this device can be used in the same manner as the circuit of Figure 5, in this case measuring the amplified current rather than the actual photoelectric current. With the relay in the circuit, properly adjusted to operate on a predetermined current margin, any local power circuit or electrical apparatus may be controlled.

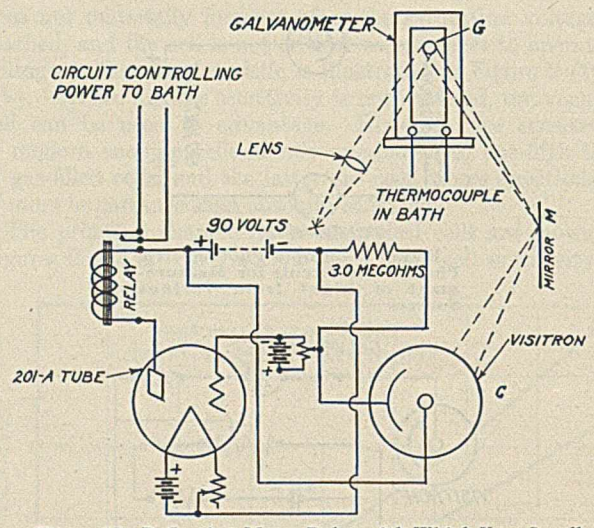

Figure 12—Reflecting Meter Relay with Which Very Small Deflections of Any Mirror-Type Measuring Instrument Can Be Used to Operate a Relay

For greater sensitivity where smaller quantities of light are available, multi-stage amplifiers are necessary. As the current to be amplified is unidirectional and usually continuous—i. e., not rapidly pulsating—the stages of the amplifier must be resistance-coupled. As it is somewhat more convenient to amplify a current pulsating at some moderate audio frequency such as 500 or 1000 cycles—the beam of light may be "chopped" by a rotating disk having open sectors in its periphery. An alternative method is to superimpose an electrical oscillation on the steady current circuit. The more convenient resistance-condenser coupled amplifier using common A and B batteries can then be used.

One of the most useful applications of the photoelectric relay circuit is that shown in Figures 12 and 13. The arrange-

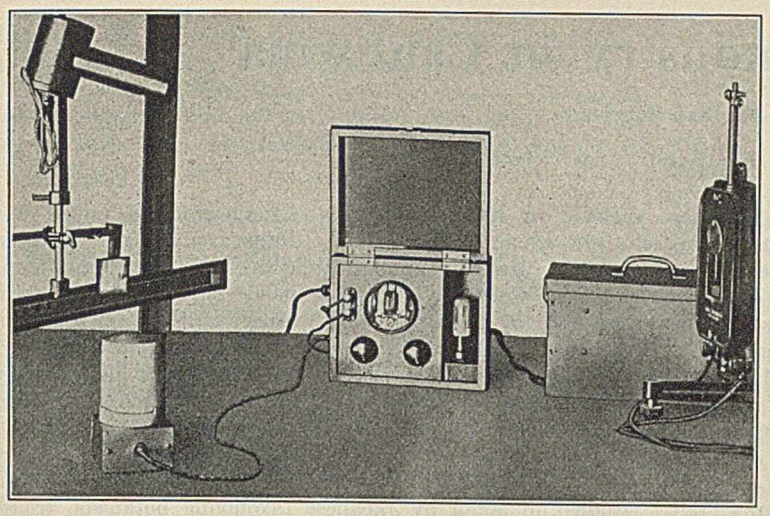

Figure 13—Assembled G-M Sensitive Photoelectric Relay in Use

ment is known as a reflecting meter relay and in the circuit shown is applied to a constant-temperature bath control. However, this device is capable of controlling any kind of an electric circuit by very small deflections of the mirror of a galvanometer, electrometer, or other reflecting instrument. The beam of light from a lamp, such as an automobile headlight bulb, is focused on the galvanometer mirror, *G*, to the stationary mirror, *M*, from which it is reflected to the cell, *C*. The system is so adjusted that with a very slight deflection of *G* the beam of light will move off of or on to the sharp edge of the mirror, *M*. The photoelectric current produced is amplified and operates the relay which controls the heater in the constant-temperature bath in this particular case. By means of two or more mirrors additional relays may be operated and as many circuits controlled. Using the thermocouple as a radiation pyrometer, this relay can be operated on infinitesimal amounts of heat energy. As the photoelectric cell has only a trigger action, this apparatus can be assembled with the minimum effort in calibration and can be depended upon for consistent service with little attention.

The applications of the photoelectric relay to counting, timing of objects, and safety devices are obviously great in number. Figure 14 shows a photoelectric safety device attached to a punch press. In fact, wherever light is the medium of control the photoelectric cell can generally be applied. Before attempting the development of such apparatus it is wise to consider carefully the limitations and complications in the apparatus which may be necessary. These are briefly described in the following paragraphs.

Wherever the photoelectric cell is used for the quantitative measurement of light intensity, it is necessary to provide some form of standardized test from which a check can be made at intervals on the calibration of the circuit, for even the best of photoelectric cells cannot be depended upon to give absolutely uniform results over long periods of time. Furthermore, if amplifier tubes and batteries are components of the equipment, further changes in calibration must be checked.

With a gas-filled cell a decrease in sensitivity can generally be corrected (within limits) by raising the cell voltage. This is equivalent to increasing the slope of the linear characteristic shown in Figure 3 to its original value. In the case of a vacuum cell the voltage has but little effect and correction must be made either in the intensity of the light source or some other part of the circuit. Furthermore, in quantitative applications great care must be exercised in providing a constant source of illumination. Otherwise, the entire effect to be measured may be obscured by fluctuations in the light source. For example, a 3 per cent change in voltage applied to a tungsten filament lamp may produce from 10 to 15 per cent change in total light emission. However, where the cell is used for limited lengths of time and check tests are made, gratifying results may be obtained in many lines of endeavor in the chemical field. As a relay device it will find increasing application in the many branches of industry in which the chemist is working today.

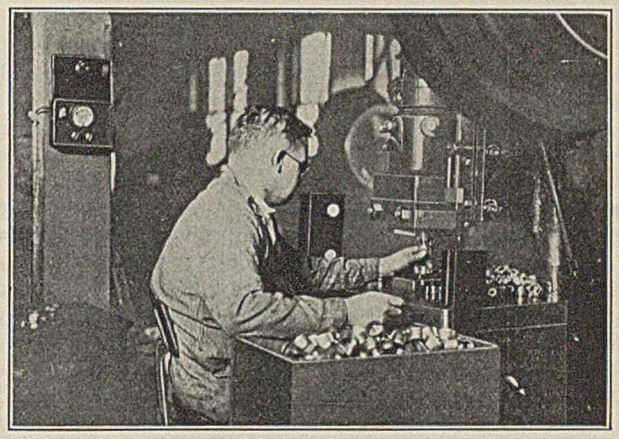

Figure 14—Photoelectric Safety Device Shown Assembled on Punch Press

The beam of light and photoelectric cell are mounted in the metal case at the left of the operator. A mirror is mounted at the right. Any interruption of the beam of light focused on the mirror and reflected to the cell actuates the relay, which prevents the operation of the press.

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Dust Explosion in Starch Plant to Be Investigated—David J. Price, principal engineer in charge of the chemical engineering division of the Bureau of Chemistry and Soils, U. S. Department of Agriculture, has been detailed to assist the Staley Starch Manufacturing Company in the investigation of the explosion which occurred in its starch plant at Decatur, Ill., on September 20. The explosion resulted in the loss of five lives and injuries to several other workmen.

Department engineers considered the starch plant at Decatur to have been well equipped with dust-explosion prevention devices and well maintained and operated. It is anticipated that the investigation will develop new facts regarding dust-explosion prevention that will make a valuable contribution to the knowledge at present available on this important subject.

This is the fifth explosion which the Department of Agriculture has been called upon to investigate since August 20. The department is conducting special research investigations to develop methods of preventing loss of life and property as the result of dust explosions in industrial plants.

The Agar Industry in California[1]

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University of California at Los Angeles, Calif.

The standard Japanese technic in the industrial preparation of agar from Gelidium sea moss has been adapted to modern American plant practice, in San Diego, Calif., by the American Agar Company. Following the discovery of extensive beds of moss on the Pacific coast, a modernized process, featuring artificial refrigeration and efficient washing, has been developed. The relations of chemical and physical structure of agar to new problems of manufacture and use are discussed.

According to legend, a Japanese emperor and party, traveling in the mountains, were marooned in a snowstorm, and accepted the hospitality of a peasant family. Anxious to offer the best, the humble host prepared an abundance of his choicest delicacy, seaweed jelly.

Much of the food was left over, and had to be thrown out. This was an unprecedented act in thrifty Nippon, but it led to discovery. The discarded jelly lay upon a shrub where it froze during the night. Immediately thereafter came a thaw, and the householder was surprised to see the frost-bitten jelly collapse, the watery part leak away, and the remainder shrink to a glistening, crinkly, papery mass of trifling weight.

Fortunately the mountaineer was bitten by the research bug at this point. He discovered that the dried jelly could be restored to dessert form, good as new, if it were merely heated again with water and cooled.

In this way, says the legend, arose the great agar industry of Japan. To this day operations are conducted much like those credited to the mountaineer. Sea moss is taken to the mountains for the December–February period, and advantage taken of the succession of frosty nights and clear sunny days. The moss is extracted with boiling water for several hours, and the extract strained through a coarse medium. The congealing to jelly form, freezing, thawing, de-watering, and drying follow the idea given in the story. Unfortunately, of course, contamination of the product is inevitable, to say nothing of a seaweed odor which naturally persists through the process. The product is, nevertheless, valuable and much prized as a part of oriental diet.

California Takes Notice

The discovery by Japanese fishermen of agar-bearing sea moss in quantity on the Los Angeles harbor breakwater led to a small establishment in simple oriental style in the near-by town of Glendale. It was quite obvious that California had plenty of sunshine by day, but not enough frost by night, for application of the standard Japanese process. Hence came the call for artificial refrigeration. As a result the operations attracted the attention of American industrial experts. The enterprise was re-financed and moved to commodious quarters in San Diego, a point more centrally located with respect to raw material. Here now is found the only agar plant on the western hemisphere. It is almost needless to say that an entirely new assembly of modern machinery has been developed to meet the situation.

Sources of American Agar

The principal source of agar on American shores is the maroon-red marine alga *Gelidium cartilagineum*, shown in the illustration. It is very commonly collected in small sprays by vacationists on beaches of southern California, as at Laguna Beach and other popular resorts. The plant grows on rocks in tuft or bushlike masses in the more turbulent waters from low tide mark down to 60 feet depth. Other species of Gelidium are also used, but these usually are scant in quantity or give inferior products. In the orient certain other varieties are found in good commercial quantity. Products of still lower quality come from allied genera, but these are not made on the American side.

These plants have been studied in detail by Japanese taxonomic botanists, whose publications, some of which are out of print, are almost the only source of information in the field. Apparently nobody on this side of the Pacific has taken up the *Rhodophyceae* as a serious botanical problem. The new agar industrialists are thus at a loss to identify some of the moss offered for sale. It is likely that there are varieties quite unknown in Japan. More particularly is felt the lack of knowledge of locale, life habits, etc., which would greatly aid the industry from the scientific side.

The agar moss has been found as far north as Monterey, Calif.—not quite reaching San Francisco. Southerly it reaches Magdalena Bay, Mexico. The San Diego operators estimate that about half of the available supply, roughly figured, occurs below the Mexican line. The California industry is licensed under export tax to harvest the Mexican coast, and pays a small fee to the state of California for similar privileges in United States waters. Just at present a large part of the crop is coming from Cape Punta Banda, just south of Ensenada, Mexico, and from the Los Angeles harbor breakwater.

Harvesting Difficulties

The limited output of the moss harvesters is now the greatest problem of the California agar industry. At present $180 per ton is most gladly being paid at the door for crude air-dried moss. By the time the agar manufacturer washes out the salt, rejects the shellfish, and discards the pebbles which the moss fisherman forgot to discard, the intrinsic cost of the colloid itself runs high. Only one sixth to one fifth of the crude weed comes through as refined agar. This establishes an initial raw material cost of nearly 55 cents per pound at the start of the factory process.

It seems to be almost impossible to harvest the moss by machine, although a great deal of mechanical ingenuity has been expended on the problem. The rough seas which surge over the best moss beds are the undoing of complicated mowing machines. There seems to be nothing equal to diving and handpicking in deep water. In shallow situations special hooklike rakes are effective. The turbulence of the waters seems to be an essential point in the growth of the really valuable beds.

The labor problem is accordingly acute. Harvesting moss is no job for water-front loafers, but requires hale, hardy, and thoroughly industrious men who know the sea. The Japanese are just the people to handle the situation, and have a natural advantage in oriental production.

Possible Supply

The California operators estimate that a steady annual crop of 1000 to 2000 tons of moss could be harvested, count-

[1] Received August 2, 1930.

ing both the California and Lower California fields. This would take care of a considerable part of the world demand for agar. At present Japan produces nearly the entire world supply of the colloid. There will need to be new applications of the material before so great a new production can be taken care of.

The American Process

The dried, baled sea moss as delivered by the fishermen is washed with fresh water in open vats for 24 hours to eliminate most of the ordinary marine salts. It is then transferred by crane in iron dump baskets to one of five closed digesters, in which it is digested under steam heat for 6 hours in a fairly concentrated agar liquor prepared from the nearly-spent weed of a previous batch. Following a modified countercurrent principle, the weed receives two more extractions, 8 and 12 hours, respectively, first with dilute solution and finally with water.

The hot agar liquors, so prepared, are treated with both charcoal and Filter-Cel, and filtered at about 30 pounds pressure in an ordinary filter press. The clarified material congeals readily to a firm jelly upon return to room temperature. A variety of congealing containers has been used, but in any case the agar gel is fed with the aid of a pump to a shearing machine. The gel is received into standard ice cans in the form of short rods or similar fragments of pulp. This part of the process deviates from the Japanese method, where the jelly is extruded from a hand pump in a macaroni-like form, and is not cut up. As a result the finished Japanese product occurs in long strips instead of fine flakes as in American production.

Frozen Jelly

The cans filled with jelly are frozen in brine tanks in the manner common to commercial ice production. A 300-pound cake, so prepared, contains about 3 to 6 pounds of agar.

The cakes of frozen jelly are cut up finely in a rotary ice crusher, and the granular mass cautiously thawed in a stream of water leading to the washing and filtering apparatus. Care is taken to keep the temperature well below 10° C. throughout this thawing process. A rotary filter of special design handles the sludge of disintegrated pulp and rejects the considerable quantity of soluble material. The pulp still retains a quantity of water, which no doubt would retain salts; but the washing with fresh water dialyzes out most of these salts. The cutting up of the jelly, disintegration by expansion of ice crystals, and crushing of the ice blocks all combine to give an unusually fine state of division in the agar pulp. In this situation the process of dialysis is most effective, and the final product thus exceptionally free from soluble impurities.

A special dehydrator has been developed to handle the moist agar pulp. Two aluminum cylinders, 35 feet high and 3 feet in diameter, receive the wet flakes from a screw conveyer. An upward hot-air blast agitates the heavy pulp particles until they are light enough to rise over the top of cylinder No. 1. They then fall through a fabric pipe to cylinder No. 2, where the dehydration is finished. The final commercially dry agar is a fluffy mass of extremely low apparent density. As suggested in the illustration, the flakes roll and warp into crinkled masses which are very readily dispersed in hot water when desired for use.

For some applications even these agar flakes are too coarse, and a part of the product is ground and sifted to granular powders of varying fineness. On account of the toughness of agar, this operation is not so readily accomplished as with salts.

Further details, both of California manufacturing methods and application to foods, may be seen in a paper by Mackinnon (*3*).

Quality of Product

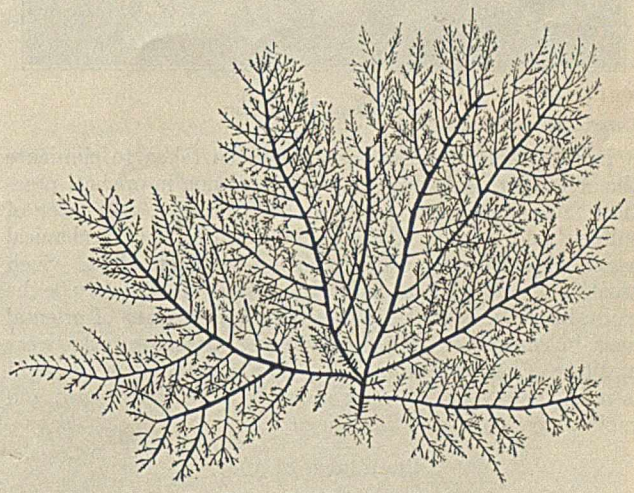
A real filtration of viscous agar liquor is practicable only with modern pressure equipment. The American agar is thus free from sticks, sand, etc., which may escape the relatively coarse screens of the oriental factories. Equally important is the effective thawing and washing process, in which the frozen jelly is drained so effectively that it loses the seaweed taste characteristic of so much of the old-world product.

On the other hand, the best No. 1 agar from Japan has a more beautiful, whiter appearance than the American product. This is due to the long period of sun bleaching, and the relative freedom from so much contact with iron vessels. American agar is grayish in tint. The whiteness of the oriental product is attained, however, at the expense of some chemical deterioration—probably hydrolysis if nothing else. The American product thus has a higher jellying power, and will absorb more water.

Chemical Structure

The material known in America as "agar" acquires its name as an abbreviation of the Malay term "agar-agar," which simply means jelly.

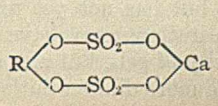
Although the chemical structure of agar is not known with certainty, and has been ignored generally in manufacture, it is likely to have considerable bearing in industrial research, both of preparation and applications, which is soon due.



Agar Sea Fern, *Gelidium cartilagineum*

A consensus of opinion identifies agar as a galactan, or polysaccharide in whose molecule numerous galactose units are united in a manner suggestive of the grouping of glucose nuclei in cellulose. A small proportion of other sugars complicates the situation, so that agar reactions have not been uniform in all research laboratories.

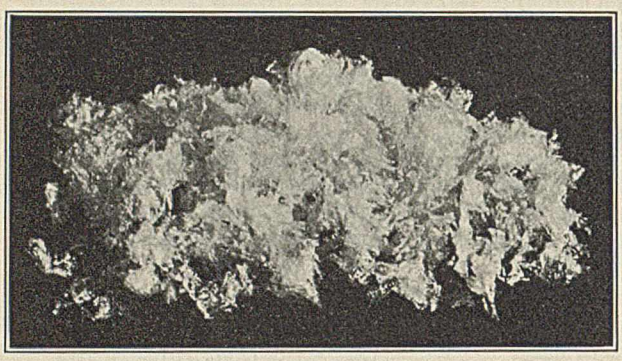
Combined with the carbohydrate mass is a small proportion, usually nearly 3 per cent of sulfur. This is apparently in the form of organic sulfate. Furthermore, calcium and magnesium form an essential part of the substance. Without these or similar bases the material is useless as a practical colloid. The firm bonding of all this material leads to the present assumption that the main carbohydrate molecular mass is combined as an ester with sulfuric acid. Inasmuch as but one of the two acid groups of sulfuric acid is esterified, the second is free to form a calcium salt, of the following general formula:



Further structural details have been described by Fairbrother and Mastin (*1*).

Chemical Behavior

It is not difficult to understand that agar, being a calcium salt, is rather stable in weakly alkaline solution, but might easily undergo simple ionic, and perhaps organic, reactions in acid media. This situation is probably related to one of the principal American applications of the colloid—viz., its use in the treatment of constipation. Taken into the alimentary canal, agar swells greatly, but is not digested. It furnishes a large volume of fecal matter and stimulates proper intestinal action without chemical irritation. Apparently the material passes out of the acid environment of the stomach long before any appreciable amount is hydrolyzed, and in the alkaline fluids of the intestines is not hydrolyzed at all.



American Flake Agar

In the California plant care has been taken to eliminate the acid treatment which has been common in oriental practice. Apparently the use of a little vinegar, and later of sulfuric acid, was considered in the orient to be of mechanical assistance in the preparation of a good-looking product. Such treatment, however, causes partial hydrolysis, and may be the cause in some cases of the inferior jellying power of oriental agar in contrast with the American. Moreover, the wear and tear of sun radiation by day and rain and snow by night is much harder on the agar molecule than the prompt and rapid processes used at San Diego.

Cloudiness of Agar

The slight opacity of agar gels has always thrown them into a position of disadvantage in competition with gelatin. Suspicion has been thrown on the alkaline-earth component as possible cause of the opacity, and experiments have been carried out to free the agar-acid by the admixture of hydrochloric acid to the ordinary colloid product. While this is readily accomplished, the jellying power of the material disappears and only a viscous liquid remains. Probably considerable hydrolysis occurs.

It is probable that hydrolysis is not the only cause of trouble in the attempt to eliminate the alkaline earths. It is quite possible that agar derives its principal virtue, that of high gel strength, from its structure as a salt of an acid of very great molecular weight. There are probably colloid-ion phenomena resembling those described by McBain in solutions of cold-water soaps.

The possibility of substitution of sodium or potassium for the alkaline earths in the agar salt group has been investigated to some extent (*2*), but has not yet reached industrial attention. Such substitutions may have an important bearing, not only on clarity of gels, but also on the viscosity and surface tension of the more dilute solution of the colloid.

Physical Behavior

As little as 2 grams of agar, dispersed in a liter of hot water, upon cooling will set to a jelly. Freezing destroys the jelly structure. Upon thawing, the shreds of agar which had lain between the ice crystals will absorb about four times their weight in water. If the temperature is kept low, however, no more water is absorbed. The swollen agar particles do not stick to each other, even upon being packed or squeezed tightly. Reheating promptly restores the jelly structure.

The more dilute mixtures, or sols, are quite viscous, but do not show a very low surface tension. This fact bears consideration in any attempt to substitute agar for some expensive high-class emulsifier. It is probably advisable to combine a substance of great power to reduce surface tension with agar in order to profit by the major virtue of the latter—viz., an increase in viscosity.

The power of agar to swell to large volume in cold water is a mark of its high quality, and has been the subject of colloidal research. It is claimed that the American product excels in this respect to a notable degree (*3*).

Research Problems

The elimination of the expensive freezing operation attracts interest, but so far without promise of commercial success. When the agar liquor is simply jellied and dried, a tough, horny material is produced. It forms relatively large masses, and is very difficult to crush or cut up. It is difficult to disperse it again in hot water. Furthermore, if a simple evaporation method were adopted, it might be necessary to dialyze the particles for a long time to get the undesirable salts out of the mass.

The use of glass or enameled industrial ware would undoubtedly permit the production of pure white or colorless agar, if a real demand should come for such material. Experimental batches of such character have been prepared in the San Diego laboratory. Agar is so highly absorptive that the slightest discoloration is easily acquired and quite obvious to the eye, although the actual percentage of colored impurity may be almost infinitesimal.

Applications

A large part of future investigation will concern applications of agar and by-products. Among these are the familiar petroleum-agar emulsions, which may be improved. In these mixtures the agar is used, not in its ordinary medicinal application, but rather in coöperation with gum arabic or like preparation as a protective colloid. With this aid the petroleum lubricant is kept dispersed in the alimentary canal and does not cause leakage. Unfortunately some concerns have led the retail purchaser to believe that he was getting a substantial amount of agar in these bottled proprietary medicines—an assumption not borne out by analysis.

Very much remains to be done in the investigation of the applicability of agar to salad dressing, table jellies, ice creams, confections, coating of textile fabrics, and in general any situation where thickening or gelation is desirable. The substitution of agar for a portion, not necessarily all, or some expensive colloid may be feasible without reduction of efficiency. Unlike pectin, agar requires no sugar to make it jelly; and a much smaller quantity of the colloid preparation will do the work. Unlike gelatin, it does not require special refrigeration to form a firm jelly.

Spent Weed

The considerable residue of spent weed is finding some use as a fertilizer, since the nitrogenous part of the sea plant is left

behind. Inasmuch as its sodium chloride has been almost entirely washed out, but not its lime content, it offers promise as an ingredient in mixed poultry food. Undoubtedly it may also serve the fiber-board industry.

Other Seaweeds

Common brown kelp, or seaweed, does not yield agar—at least not in appreciable quantity. It does yield, however, colloidal material of quite different character, such as the alginic products. The quantity of common weed is so enormous that a much greater industry could be developed if the market should require it. The initial development of this industry is already started in the San Diego district.

During the World War a considerable amount of aliphatic acid products, including acetic anhydride, acetone, propionic acid, and the like, were made near San Diego. The process involved fermentation of the weed. The processes are not economical with peacetime prices, however, and this industry is indefinitely suspended. It is quite possible, on the other hand, to produce the more unusual acids such as butyric, valeric, and higher members of the fatty series, in quantity from kelp.

Bibliography

Further details of the manufacture and purification of agar may be seen in publications by Fellers (*2*) and the Department of Commerce (*4*).

Literature Cited

(1) Fairbrother and Mastin, *J. Chem. Soc.*, **123**, 1412 (1923).
(2) Fellers, J. Ind. Eng. Chem., **8**, 1128 (1916).
(3) Mackinnon, *Food Ind.*, March, 1930.
(4) "Methods of Manufacturing Agar-Agar in Japan," in *Commerce Repts.*, October 10, 1927.

Dust Control in Phosphate Rock Grinding[1]

W. H. Gabeler

Davison Chemical Company, Baltimore, Md.

At the Baltimore plant of the Davison Chemical Company on Curtis Bay phosphate rock from the company's Florida sources is treated to produce superphosphate. The first operation after the raw material is unloaded to bins is the pulverizing of the rock for the acidulating process. The equipment for this purpose consists of twelve Raymond mills with air separators discharging to an intermediate storage bin. When placed in operation, there were two features which required adjustment. The first was the irregular load curve on the mill motor, which was corrected by providing mill feed control from a pick-up actuated by a solenoid in the mill motor line. The load curve on this motor is now uniform, to give maximum grinding capacity, which averages about 4 tons per hour.

The second feature of the system which required remedy was the dust discharge in the vent air from the cyclones. This vent air amounted to about 1000 c. f. m. per mill, and carried with it the extreme fines from the grinding operation which were not precipitated in the cyclone. The dust discharge from these twelve vents, shown partially in Figure 1, was a serious nuisance to the plant and neighborhood, as well as constituting an appreciable loss of material.

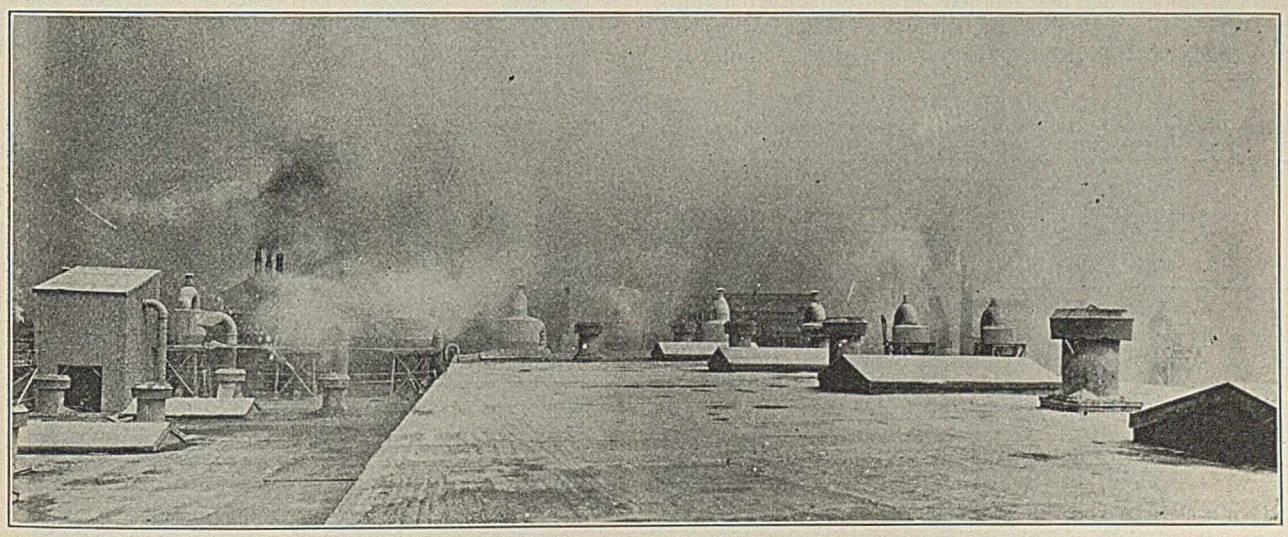


Figure 1—Dust Nuisance Created by Cyclone Vent Air before Installation of Air Filters

Preliminary Experiments

To remedy the dust discharge a number of experiments were tried, beginning with the simplest and least complicated methods. The first plan was to close off the vents and run the air-separation systems without excess air. Table I shows a few comparative operating data for one system operating venting and closed.

A number of objections to this system were revealed under operating conditions, of which the most serious was the increase in the moisture content of the circuit air, as the moisture in the material was liberated during pulverization. In a comparatively short time saturation was approached, and consequent condensation occurred in the exposed piping and cyclone.

[1] Received June 26, 1930.

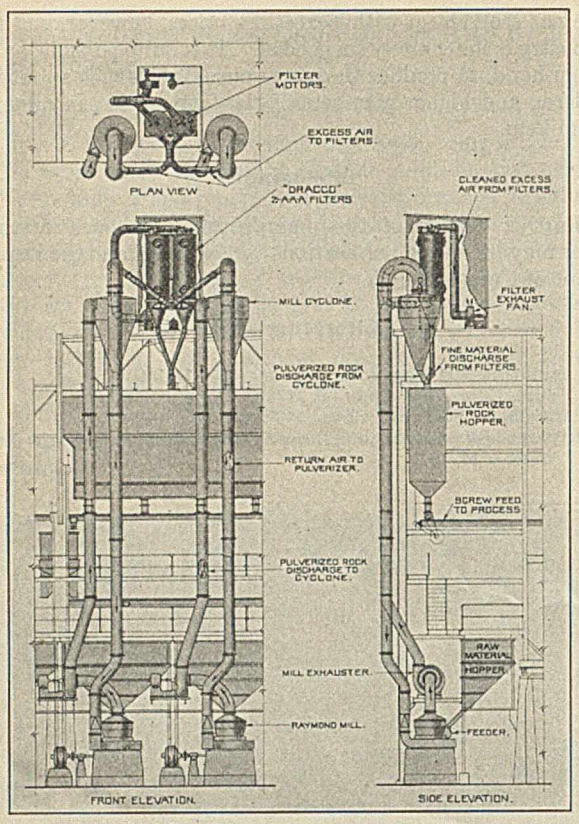


Figure 2—Special Arrangement of Dracco Air Filters Handling Excess Air from Two Cyclone Separator Systems

This caused the material to clog and build up sufficiently to make the operation very unsatisfactory.

Since this test showed the necessity of drawing off from the system a certain amount of excess air, the problem was to find the simplest and best method of recovering the dust burden in this air. A simple water spray in a horizontal pipe was first tried, but the material was not precipitated in any appreciable amount.

Table I—Comparative Operating Data for Raymond Mill and Air Separation System with and without Venting of Excess Air

	Relief Vent on Return Line from Cyclone			
	Closed		Open	
	Static pressure	Temp.	Static pressure	Temp.
	Inches H_2O	*°F.*	*Inches H_2O*	*°F.*
Inlet to mill	2.6	112	−0.1	100
Mill	−3.5	116	−7.2	105
Fan discharge	8.5	126	4.7	114
Inlet to cyclone	8.4	126	4.4	106
Outlet from cyclone	4.2	116	0.5	102
Return air, cubic feet per minute	6000		4330	
Rock ground, tons per hour	3.13		4.07	
Load on fan motor, amperes	30.0		32.4	

It was then considered possible that a small-diameter cyclone might accomplish the result, and the connection was made to one vent. The exceeding fineness of the dust, however, made the cyclone efficiency too low to justify the installation. To test the possibility of wetting the particles in conjunction with centrifugal separation, water sprays were introduced in an effort to improve the dust precipitation. This effected but little improvement in the volume of dust discharge.

A wet washer was tried out as a final effort to collect the vent dust by mechanical means, but the results fell far short of satisfactory collection. It then became evident that high-efficiency filtration was necessary to produce required results, and a recommendation was requested from engineers and manufacturers of such equipment. Two plans were submitted, both using standard Dracco high-efficiency bag filters equipped with cotton-napped filter bags. The first was to group in one unit the collecting equipment for all cyclone vents, and the second, to erect a two-compartment filter for each set of two vents. This second plan was adopted, because it approached more closely unit operation of each mill, because it eliminated redistribution by screw conveyor of the collected material, and finally because it made possible the operation of a small test plant before the purchase of the complete equipment.

Filter Arrangement Adopted

Figure 2 shows the arrangement of the two-compartment Dracco filter to handle the excess air from two mill separation systems. The air volume through the two-compartment collector is 1800 c. f. m., or 900 c. f. m. excess air from each mill system. This has been determined to be the minimum quantity to provide proper static conditions, to prevent dust leakage in the piping, and to maintain a constant air balance. The static pressure at the intake to the filter is 1 inch positive, and at the filter exhaust fan 2 inches negative, giving a 3-inch drop through the equipment. A 5-horsepower motor is connected to the exhaust fan, but the average load is less than 2 horsepower.

Figure 1 shows the first filter unit erected and in operation at the extreme left, on mills number 1 and 2. The discharge from the exhaust fan is free from any visible solids, and the lack of dust at these points presents an interesting comparison with the discharge from the other vents. (Mills number 7 and 8 were not in operation when this photograph was taken.)

The collected material is discharged to the pulverized-rock hopper through a gravity discharge box. Tests show a recovery of 32 pounds per hour for two mills, which is 0.2 per

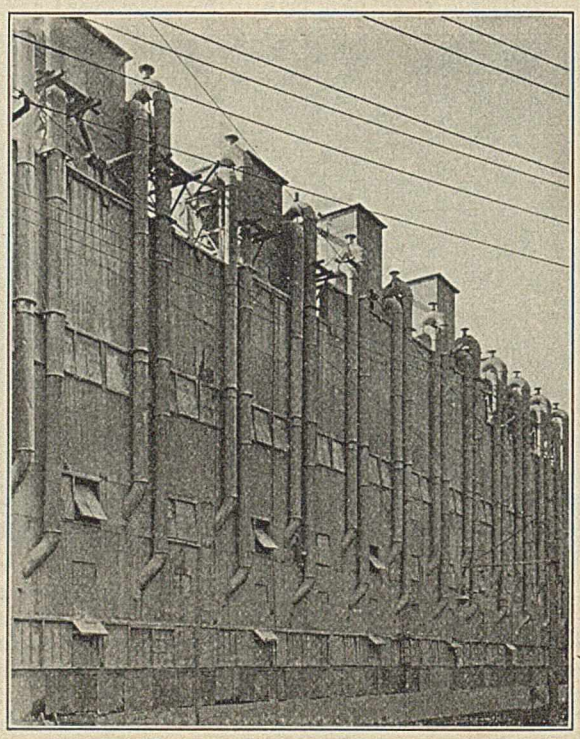


Figure 3—Photograph during Installation of Air Filters

The piping from the Raymond mills to the cyclone separators, as originally installed, has been modified only by the connection of excess air lines to the air filters as evident at the extreme upper left.

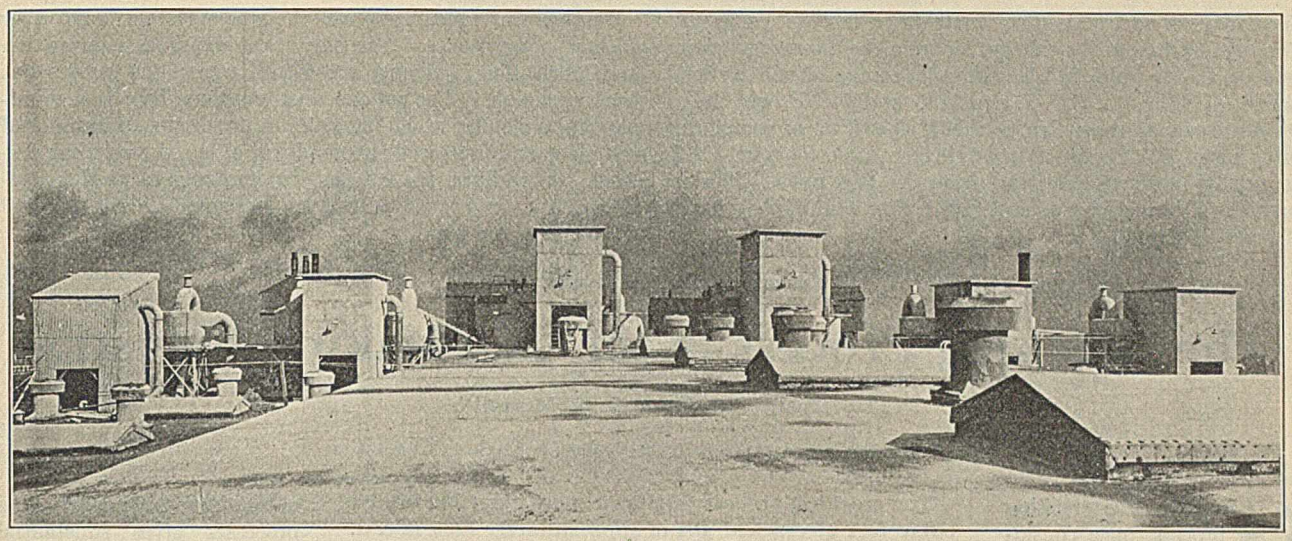


Figure 4—Dust-Free Operating Conditions Obtained with Air Filters Handling Excess Air from Cyclone Separators
Compare with Figure 1, which shows operating conditions before installation of the filters.

cent of the average mill capacity of 4 tons per hour. The performance of this first equipment proved completely satisfactory, and after a suitable test run was completed five additional units were ordered to equip all twelve mills. Figure 3 shows the equipment during erection, and Figure 4 shows the complete absence of dust in the filtered air.

Dust Recovery and General Efficiency

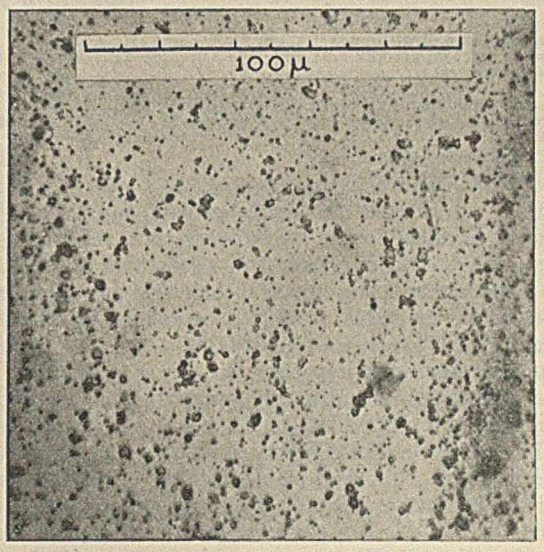
The recovery from the complete collecting installation amounts to a little less than a ton a day ($9^1/_2$ hours) of extremely fine phosphate rock. Table II gives comparative screen tests of the material recovered from the mill cyclone and from the filter equipment. The material precipitated in the mill cylcone is already very finely ground—more than one-half through a 200-mesh screen—but the dust which is carried through to the filters is almost powder. Only 3.5 per cent is coarser than 200-mesh and five-sixths of it pass through a 300-mesh screen. At the left of Figure 5 is a microphotograph of the material collected in the cyclone and at the right is a microphotograph of the dust collected in the filter.

The rock particles from the cyclone vary from 5 microns to over 100 in size, the average running between 30 and 40 microns. The two large particles in Figure 5 are between 50 and 60 microns in diameter. The dust particles from the filters average well under 2 microns in diameter, and a substantial proportion of the dust is literally smoke fine. A consideration of these facts explains the failure of the mechanical and spray collectors to collect the vent dust, and the success only of a filter embodying a positive filter medium.

Table II—Comparative Screen Tests on Material Recovered in Mill Cyclone and in Air Filter

Material Collected	Material through Various Screens			
	100-mesh	150-mesh	200-mesh	300-mesh
	%	%	%	%
In mill cyclone	91.9	81.9	67.0	51.3
In air filter	99.9	99.5	96.5	83.9

Material collected in mill cyclone. × 500



Material collected in Dracco filters. × 500

Figure 5—Comparison of Particle Size of Material Collected in Mill Cyclone Separator and in Air Filter, Respectively

A recovery of 32 pounds per hour from an air volume of 1800 c. f. m. gives a dust concentration in this vented air of 2.05 grains per cubic foot, assuming a collecting efficiency of 99 per cent. This efficiency seems to be attained easily,

since there is no visible dust whatever in the fan discharge. The temperature of the exhaust air from the filters was taken as 110° F. dry bulb, 94° F. wet bulb, compared with atmospheric conditions of 82° F. dry bulb and 71° F. wet bulb. On the basis of these figures the 1800 c. f. m. of vented air carry away 124 grains of moisture per cubic foot, or 191.3 pounds of moisture per hour, from the two mills. This is equivalent to removing as moisture 1.2 per cent of the weight of material ground.

The current consumption of the whole system is not over 15 horsepower hours. The only labor required is inspection and lubrication, and over a 6-month period the service has been negligible. The serious dust nuisance has been eliminated completely, which has both improved the appearance of the plant and increased the good will of the surrounding district. In addition the 0.2 per cent recovery of product formerly lost has proved a distinct increment in the over-all efficiency of the plant.

The Cracking Process in the Gas-Making Industry[1]

Gustav Egloff and J. C. Morrell

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The cracking process produced more than 250 billion cubic feet of cracked gas of approximately 1250 B. t. u. per cubic foot during the year 1929.

The gas from the cracking process is an enriching one suitable for blending with water gas and producer gas, and the coke produced is highly suitable for water gas or producer gas production.

The cracking process can be operated so as to produce maximum yields of gas and minimum yields of gasoline, or maximum yields of gasoline and minimum production of gas, dependent upon the market requirements.

GAS from the cracking process, once considered by the refiner largely as a loss, is now occupying a unique place among petroleum products. More than 250 billion cubic feet of cracked gas were produced during 1929. This gas has distinctive properties, and is finding a market in enriching gases for domestic and industrial use and as a raw material for chemical synthesis of such substances as alcohols and glycols and their derivatives.

Table I shows the relative production of various kinds of gases, both natural and artificially produced. It is interesting to note that the combined volume of gas from the petroleum stills and from the cracking process is greater than the entire manufactured-gas output of the country, and it is safe to predict that the production of gas from the cracking process will increase at a rapid rate.

Table I—Production of Gas in 1929

	Billion cubic feet
Natural gas[a]	1800
Gas from petroleum distillation	270
Gas from the cracking process	250
Carbureted water gas[b]	255
Oil gas[b]	32.4
Manufactured gas, total (includes carbureted water gas, coal gas, oil gas, and coke-oven gas distributed by gas companies)	514

[a] U. S. Department of Commerce.
[b] American Gas Association.

In less than two decades the cracking of heavy oils has grown from an incident in the oil industry to a major refinery operation. From practically zero production in 1912 cracked gasoline has gained in importance until it now represents one-third of the total of 17 billion gallons gasoline produced during 1929 in the United States.

The cracking process is important to the gas industry. It will not only supply a substantial proportion of gas of high calorific value for enriching purposes, but will function also as a balance in cracking liquid products, such as gas tars and coal tars. Cracking plants located in refineries near populous districts are already being utilized to enrich gases of low fuel value. The gas from the cracking process with approximately 1250 B. t. u. per cubic foot permits the enriching of gases, such as water, blast furnace, producer, and coke-oven gas. In some communities the supply of gas consists of a mixture of coke-oven and producer gas enriched with gas from the cracking process. The cracking of tars from some gas-making processes gives substantial yields of motor fuel in addition to high B. t. u. gas and coke.

The cracking process operated in conjunction with a gas-making plant will produce gas from any hydrocarbon material such as tars or oils. An economic balance can be maintained as a function of maximum yields of gasoline, or gas production from the cracking process. This is dependent upon the peak demands of each commodity during the year. The gas plant of the future will be a distributor of high-antiknock motor fuels in addition to cracked gas.

Composition of Cracking-Still Gases

Gas from cracking stills is characterized by a relatively high content of olefins. These give it high illuminating values, and in addition make it a suitable material for the preparation of chemical derivatives. The percentage of hydrocarbon groups present in cracked gases varies widely as a function of the charging stocks and temperatures and pressures used. By proper regulation of the cracking process the percentage of components present in the gas may be varied almost at will. Table II shows some approximate analyses of gas from the cracking process.

Table III shows typical analyses of a number of gases from the cracking process.

Gas Produced from Cracking

The amount of gas produced per barrel of charging stock varies quite widely. Gas formation is particularly high in non-residue operation when producing distillate and coke as the only other products. The gas production depends on the nature of the oil and the conditions of the cracking operation, such as temperature, pressure, and time. In Table V are shown the yields of gas produced by cracking different oils using the non-residue type of operation.

Flexibility of Cracking Process

The primary use of the cracking process at the present time is the conversion of petroleum into gasoline. No one method of operation will fit all the economic demands made upon the refining or gas industry. The process must be so flexible that oil of any type can be cracked into products in greatest demand. This condition is fulfilled by the cracking process, whose adaptability is such that it may be operated for maximum yields of gasoline, furnace or Diesel oil, residual oil, coke, and gas. The process may be operated so as to

[1] Received April 19, 1930. Presented before the Division of Gas and Fuel Chemistry at the 79th Meeting of the American Chemical Society, Atlanta, Ga., April 7 to 11, 1930.

Table II—Analyses of Gases from Cracking Process

Charging Stock	Gravity	Composition						Sp. Gr.	Calorific Value
		$H_2S + CO_2$	C_2H_{2n}	O_2	CO	H_2	$C_nH_{2n+2} + N_2$		
	° A. P. I.	%	%	%	%	%	%		B. t. u. per cu. ft.
Midcontinent gas oil	35.6	0.5	12.8	0.2	0.1	3.9	82.5	0.894	1123[a] gas (mixed 1220)
Midcontinent kerosene distillate	38.4	0.5	14.0	0.3	0.2	5.4	79.6	0.851	1123[a]
North Texas kerosene distillate	39.5	0.0	8.7	0.6	0.4	11.1	79.2	0.660	1395
Midcontinent fuel oil	26.9	1.0	9.0	0.5	0.5	4.4	84.6	0.847	1702[b] gas
Midcontinent topped crude	28.9	0.7	8.3	1.1	0.2	3.8	86.9	0.900	1680[b]
Ranger topped crude	26.8	0.4	8.4	0.5	0.0	4.4	86.3	0.850	1562
Healdton crude	29.6	1.6	5.1	0.4	0.3	5.2	87.4	0.802	1427
Montana topped crude	38.4	0.0	5.2	0.6	1.4	10.2	82.6	0.722	1600[b]
Kentucky fuel	25.5	0.61	2.21	0.61	2.24	3.06	91.27	0.806	...
Mexican distillate	26.3	6.4	5.8	1.9	0.2	6.1	79.6	0.807	1368
Mexican gas oil	21.0	0.1	9.9	1.4	0.3	4.3	84.0	0.827	1600[b]
Panuco residuum (Mexico)	9.7	13.1	4.1	1.0	0.9	5.0	75.9	0.898	1265
Panuco residuum (Mexico)	9.7	10.5	4.6	1.3	0.5	6.6	76.5	0.873	1238
Panuco residuum (Mexico)	9.7	7.2	3.7	0.4	0.5	3.4	84.8	0.908	1326
Panuco residuum (Mexico)	9.7	13.9	8.3	1.1	0.6	3.4	72.7	0.960	1284
Panuco crude	12.6	11.82	6.32	1.02	0.63	5.58	74.63	0.928	1302
Panuco crude	12.6	12.15	7.47	0.92	0.61	4.56	74.29	0.917	1326
Venezuela fuel	13.4	7.34	9.10	1.92	2.04	6.60	73.00	0.956	1264
Venezeula fuel	13.4	9.32	3.74	0.93	3.01	3.11	79.89	0.884	1300
Tarakan crude (Borneo)	18.2	0.6	5.2	0.3	0.3	4.0	89.6	0.784	1317
Tarakan crude (Borneo)	18.2	0.4	5.8	0.6	0.2	5.6	87.4	0.787	1388

[a] Gas from cracked distillate receiver.
[b] Gas from cracked distillate separator.

produce maximum quantities of gas. Viscous oils may be used as charging stock and cracked but lightly in order to lower their viscosity and cold test so that they will flow readily through pipe lines. The manner in which the process is used will depend upon market conditions and the charging stock available for cracking. Various tars from coal, shales, lignite, peat, or wood may be used also for charging stocks. The operation may be controlled to produce maximum yields of any product desired without modification of the cracking unit in principle or equipment.

Table III—Analyses of Gases from Cracking Process

	%	%	%	%	%	%	%	%	%	%	%
Ethylene	0.6	1.9	2.2	2.5	2.7	4.0	4.7	6.3	27.0	28.0	32.4
Propylene	11.7	0.8	15.2	5.0	7.6	6.8	6.1	12.0	16.0	19.0	16.8
Butylenes	4.7	7.4	3.9	0.3	6.5	2.6	2.0	7.1	9.0	..	5.4
Amylenes	..	..	..	0.2	..	..	..	..	..	..	1.1
Butadiene	..	..	..	...	..	..	..	..	1.0	..	0.7
Higher olefins	..	..	..	...	..	..	..	..	..	3.0	3.7
Hydrogen	3.0	1.9	2.0	...	3.0	5.0	5.6	1.7	7.0	..	..
Paraffins	80.0	88.0	77.7	...	80.2	81.6	81.4	72.9	40.0	..	..

Table IV—Analysis of Midcontinent Cracked Gas

	Per cent		Per cent
Hydrogen	2.9	Hexane	Trace
Methane	64.5	Ethylene	2.9
Ethane	16.0	Propylene	1.9
Propane	6.7	Butylenes	1.3
Butanes	2.9	Higher unsaturates	Trace
Pentanes	Trace	Hydrogen sulfide and carbon dioxide	0.3

A detailed analysis of gas from the cracking of a Midcontinent fuel oil is also shown in Table IV.

The residual oil method of operation of the cracking process may be carried out continuously for a period of thirty days or more, producing high yields of gasoline, a fuel-oil residue passing all market specifications, and an insignificant amount of coke, the amount of coke produced per barrel of charging stock ranging from a trace to a few pounds. The volume of gas produced may be 800 cubic feet per barrel more or less, as desired.

The cracking operation may also be so controlled that only cracked gasoline, coke, and gas are produced. This mode of operation produces the maximum yield of gasoline, gas, and coke. The gas production may exceed 1200 cubic feet per barrel of oil cracked. With high-temperature operation of the cracking process the amount of gas per barrel of oil will be over 2000 cubic feet while making high yields of gasoline. The operation may also be varied to crack overhead products of the process of intermediate boiling range such as reflux condensate in a separate heating element. This will permit higher temperatures and increased gas yields. Other changes in the arrangement of the process may also be made to meet requirements.

Table V—Gas Production in Cracking Representative Oils

Source of Oil	Gravity	Gas	Motor Fuel	Furnace or Diesel Oil	Coke
	° A. P. I.	Cu. ft./bbl.[a]	%	%	Lbs./bbl.[a]
FUEL OILS					
Panhandle, Tex.	29.5	425	65.5	11.4	45
Caddo-Bull Bayou, La.	28.6	388	67.8	12.2	28
Midcontinent	27.4	517	61.2	17.9	41
Muskegon, Mich.	26.1	620	60.1	16.5	77
Rosecranz, Calif.	25.7	517	58.0	21.2	38
California	25.6	670	61.2	17.3	44
Eastfield, Ark.	23.6	476	60.9	15.5	53
North Texas	22.7	499	61.6	12.5	31
Wyoming	22.4	576	59.8	9.9	60
Oregon Basin, Wyo.	22.2	700	56.6	11.5	77
Kentucky	22.0	640	60.8	14.6	48
Pondera, Mont.	21.1	865	49.3	15.0	72
Ventura, Calif.	20.1	368	57.2	15.8	33
McCamey, Tex.	19.9	624	59.1	13.5	63
Alamitos, Calif.	19.5	698	42.7	8.5	62
California	17.2	855	48.8	15.9	89
California	16.7	637	48.2	14.6	103
Texas	8.9	427	30.6	3.2	138
GAS OILS					
Pennsylvania	38.8	570	71.9	6.8	24.8
California	38.6	350	64.8	16.8	12.9
Eldorado, Ark.	34.7	255	60.7	21.5	30.0
California	33.7	250	47.1	38.9	14.7
Texas	27.3	330	48.6	32.2	29.3
California	23.2	628	56.4	13.9	33.6
CRUDE OILS					
Nacome, Tex.	22.5	644	58.8	16.5	43
Cole Bruni, Tex.	17.9	608	61.7	21.3	21
Posecreek, Calif.	15.4	838	46.3	21.3	86
Maricopa Flats, Calif.	15.4	785	52.1	19.7	42
Maricopa Flats, Calif.	13.7	874	48.2	21.3	73

[a] 42 gallons per barrel.

The accompanying photograph shows the arrangement of a modern cracking plant.

Uses of Cracking-Process Gas

At present the major use of gas from the cracking process is for refinery fuel. However, several city gas companies are purchasing cracked gas from refineries for enriching purposes. The gas has an average calorific value of 1250 B. t. u. per cubic foot when stripped of gasoline, and some values are as high as 1600 B. t. u. per cubic foot. The extent to which gas from cracking surpasses other commercial gases in heating value is shown in Table VI.

Table VI—Approximate Calorific Values of Various Commercial Gases

	B. t. u. per cu. ft.
Cracking-still gas	1250
Natural gas	1000
Crude-oil distillation gas	1000
Carbureted water gas	550
Coke-oven gas	550
Water gas (blue gas)	310
Producer gas from coal or coke	140
Blast-furnace gas	100

Gas from Cracking of Low-Temperature Coal Tars

There are projects now under way in which the gas obtained from low-temperature carbonization is being blended with water gas and distributed by public utility companies for domestic use. This gas has a calorific value of approximately 850 B. t. u. per cubic foot. One low-temperature carbonization plant is in commercial operation with an approximate capacity of 600 tons per day.

Cracking of Tar Acids from Low-Temperature Coal Tar

The tar acids produced by low-temperature carbonization have been converted by the cracking process into lower boiling tar acids useful as disinfectants, antiseptics, wood preservatives, and for the manufacture of resins from the condensation of phenols and aldehydes.

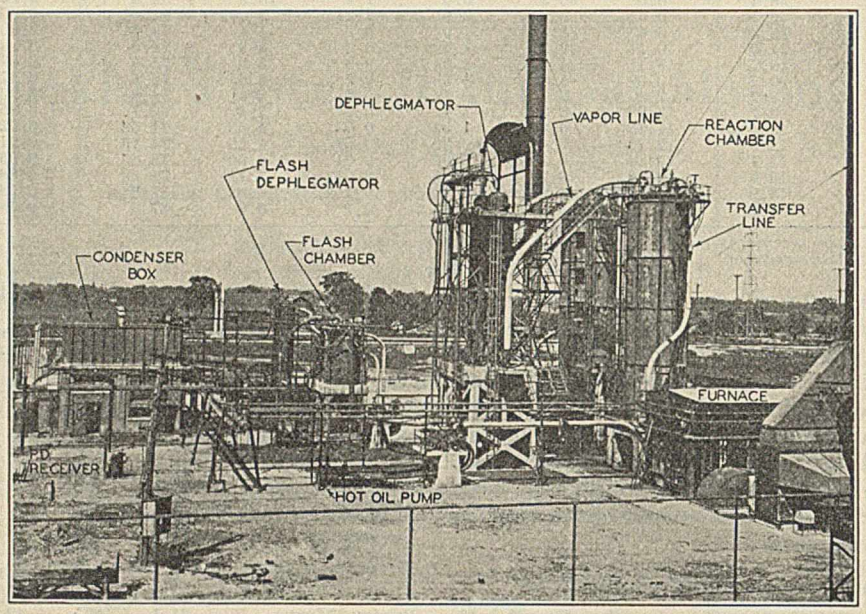
When tar acids separated from low-temperature coal tar were cracked, approximately 1000 cubic feet of gas per barrel of charge were obtained. The use of approximately 15 to 20 per cent of water or steam during the cracking operation produced approximately 1900 cubic feet of gas per barrel. The gas when no water or steam were present had the following composition:

	Per cent
Carbon monoxide	1.3
Carbon dioxide	0.8
Unsaturated hydrocarbons	1.2
Paraffin hydrocarbons	30.6
Hydrogen	39.2
Oxygen	2.0

The use of water and steam in conjunction with the operation, while producing practically double the gas, had very little observable effect upon the composition of the gas. The coke formation and yield of neutral oils were also increased.

The over-all results in the use of steam in the cracking of tar acids or low-temperature coal tars containing them is a large increase in gas formation, some increase in coke formation, and an increase in the formation of neutral oils—all at the expense of tar acids.

Another important factor having a direct bearing upon the cracking process is the creosote-oil problem caused by the increasing use of low-temperature carbonization processes and gas retorts which produce similar tars. The content of creosote oils in these tars meeting present specifications for wood preserving is much lower than that present in ordinary coal tars. The chief reason for this difference in gas tars is the use of steam in the vertical ovens and the withdrawal of the tar from relatively low-temperature zones. The present creosote-oil requirement of the United States is approximately 200 million gallons, of which 50 per cent is imported from abroad. Approximately 500 million gallons of coal tar, sufficient to supply the total requirements of creosote oil of the United States, are produced in this country.



Modern Cracking Plant

It is estimated that there are 3154 billion tons of bituminous coal in the world, of which the United States has approximately 1600 billion tons. By means of low-temperature distillation of this quantity of bituminous coal, 960 billion barrels of tar can be produced which under cracking conditions will yield approximately 240 billion barrels of motor fuel of high antiknock properties. The motor fuel produced from low-temperature carbonization and cracking, when operating a high-compression motor, will give more than double the mileage per gallon compared with ordinary gasoline using present-day motors. The superior quality of this type of motor fuel is due to the high percentage of aromatic and unsaturated hydrocarbons contained therein. The amount of gas that would be available by low-temperature carbonization of the total bituminous coals in the United States is 9,600,000 billion cubic feet. The amount of gas from cracking the tar derived from the coal would approximate 480,000 billion cubic feet, and this could be increased at the expense of motor fuel if so desired.

Table VII shows the production of gas and other products from the cracking of coal-tar and related oils.

Table VII—Cracking of Coal-Tar and Related Oils

Source of Oil	Gravity	Gas	Motor or Diesel Fuel	Furnace Oil	Coke
	° A. P. I.	Cu. ft./bbl.	%	%	Lbs./bbl.
Low-temperature carbonization	8.9	570	28.8	10.3	...
Straight-distillation acid oil from low-temperature carbonization	9.9	485	25.3	28.9	73
Intermediate-temperature carbonization	6.0	500	14.5	17.7	241
High-temperature coal tar	7.0	706	12.1	22.6	158
Kentucky cannel coal	25.1	577	42.1	22.6	106
Lignite tar	13.9	767	38.3	...	241
Lignite distillate	21.1	672	46.7	18.1	84
Brown-coal tar	9.2	835	28.6	...	96

The problems are, of course, more acute in Europe because they are directly affected by both angles. The solution of this problem lies in the cracking of the low-temperature coal tar and similar gas tars directly or in the cracking of the straight distillates or neutral oils obtained therefrom. The straight distillates may be extracted to remove any portion of tar acids desired for other purposes—e. g., the tar acids may be blended with petroleum products to make excellent wood preservatives.

Cracking of Gas Tars

The cracking of water-gas tars produces a relatively low yield of high-antiknock motor fuel, but a fair volume of gas is made as well as a high yield of coke. The coke, owing to its characteristic porous structure and low ash content, is especially suitable for gas making, either for water gas or producer gas.

Tar from vertical gas retorts which utilize steam, such as the Glover West retort, has properties both chemical and physical similar to low-temperature coal tar, and the results from cracking approach those obtained in the cracking of low-temperature coal tar—i. e., approximately 22 per cent of high-antiknock motor fuel and 600 cubic feet of gas per barrel of charge. Similar tars have been produced from modified Koppers coke ovens.

Apparently the use of steam in the retorts and the withdrawal of the tar from relatively low-temperature zones gives to the tars properties and characteristics of the low-temperature type, making them highly suitable for cracking for the production of both gas and gasoline.

Tar from Glover West Retort

The analysis of the tar from Chilean coal processed in a Glover West vertical gas retort and the results obtained on cracking follow:

Specific gravity	1.0497
Initial boiling point to end point (oil and water)	210° to 705° F.
Flash point (Cleveland open cup)	160° F.
Fire point (Cleveland open cup)	215° F.
Flash point (Pensky Marten)	146° F.
Furol viscosity at 122° F.	20 seconds
Cold test	+65° F.
% B. S. & W. (benzene centrifuge)	4.2
% Water (A. S. T. M.)	2.4

Over *Per cent*	Temperature ° F.		*Per cent*
5	340	Over	85.0
10	406	410° F.	8.0
20	464	437° F.	13.0
30	520	572° F.	36.0
40	585	Water	2.5
50	639	Coke, by weight	15.9
60	669		
70	705		
80	Superheated		
End point	705		

Table VIII summarizes the yield of unrefined products made by cracking coal-gas tar.

Table VIII—Yield of Unrefined Products

(Based on coal-gas tar)

	Motor Fuel End Point		
	392° F. *Per cent*	400° F. *Per cent*	437° F. *Per cent*
Water	4.7	4.7	4.7
Tar acids	9.6	9.6	9.6
Tar bases	2.3	2.3	2.3
Naphthalene	6.0	6.0	6.0
Motor fuel (free from tar acid, tar base, and naphthalene)	11.8	12.4	18.0
Pressure-distillate bottoms (free from tar acid, tar base, and naphthalene)	15.7	15.1	9.5
Coke and gas, including loss	49.7	49.7	49.7
Redistillation loss	0.2	0.2	0.2
Total	100.0	100.0	100.0

The products shown in this table were made without recycling any pressure-distillate bottoms. Additional gasoline may be obtained by recycling the bottoms. From each barrel of coal-gas tar cracked, 144 pounds of coke and 823 cubic feet of gas were produced. The unscrubbed gas had the following composition:

Specific gravity	0.8173
	Per cent
Carbon dioxide	2.1
Unsaturated hydrocarbons	5.6
Oxygen	2.1
Hydrogen	11.3
Carbon monoxide	0.8
Paraffin hydrocarbons	65.9
Nitrogen (by difference)	12.2
Total	100.0

Tars quite similar to low-temperature coal tars have been produced from modified Koppers coke ovens. Apparently the use of steam in the retorts and the withdrawal of the tar from relatively low-temperature zones gives to the tars properties and characteristics of the low-temperature type, making them highly suitable for cracking for the production of both gas and gasoline. The use of steam during the cracking process should greatly increase the yields of gas in accordance with the reactions shown with tar acids.

Water Gas and Producer Gas from Petroleum Coke

The most extensively manufactured gas is blue gas, sometimes called water gas, according to the following reaction:

$$C + H_2O = CO + H_2$$

The physical properties of coke from the cracking process make it an ideal raw material for the manufacture of blue gas. This coke has an apparent density of 0.9 to 1.1; a cellular and firm structure exposing maximum area to reaction with the steam; and contains from 5 to 15 per cent of volatile matter, from 80 to 90 per cent of fixed carbon, and 0.1 to 1.5 per cent of ash. The heating value is approximately 15,500 B. t. u. per pound, with a sulfur content depending upon the source of the oil from which it is produced. For example, from a Pennsylvania or Midcontinent oil the sulfur content will be usually less than 1 per cent, while from a Mexican or California oil it will vary from 1 to 5 per cent depending upon the kind of oil.

The utilization of coke from the cracking process for the manufacture of blue gas and the carburetion of this gas by gas from the cracking process is a practical and economic basis of manufacture.

Coke from the cracking process can also be used for making producer gas, which has for its basis the following reaction:

$$2C + O_2 = 2CO$$

Some tests were made upon coke of the following composition and calorific value:

	Per cent
Moisture	0.97
Volatile matter	9.35
Fixed carbon	89.01
Ash	0.67
B. t. u. per pound	16,042

The composition of the gas produced was as follows:

	Per cent
Carbon dioxide	5.25
Unsaturates	0.27
Oxygen	3.23
Hydrogen	13.40
Carbon monoxide	22.40
Methane	0.48
Ethane	0.33
Nitrogen	54.64

The gas had an average calorific value of 144 B. t. u. per cubic foot. The clinkerous slag was removed through a water seal at the bottom of the producer. The over-all hot gas efficiency of the process was between 90 and 94 per cent.

By operating the cracking process to produce coke and gas as the major products and by gasification of the coke in the manner described, the process will be chiefly a gas-making one.

Thermal Requirements and Operating Characteristics of the Urea Autoclave[1]

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The thermal requirements of, and the temperature distributions within, the autoclave used for the direct synthesis of urea from liquid ammonia and liquid carbon dioxide have been determined under both operative and non-operative conditions. The over-all autoclave reaction has been shown definitely to be exothermic for 35 to 40 per cent conversion of the reactants. Data are given for the corrosion resistance of a number of metals under operative conditions.

THE future commercial use of urea, either as a fertilizer or in the manufacture of synthetic resins, will depend in a large measure upon its economic production from ammonia and carbon dioxide. Autoclaving of these materials at temperatures of 135° C. and above and at pressures in the neighborhood of 100 atmospheres results in their partial transformation to urea according to the following equations:

$$2NH_3 + CO_2 = NH_2COONH_4$$
$$NH_2COONH_4 = (NH_2)_2CO + H_2O$$

Direct Synthesis of Urea

A continuous process for the synthesis of urea from liquid ammonia and liquid carbon dioxide has been developed at this laboratory and described by Krase, Gaddy, and Clark (*1*). A small unit for the production of 79.5 kg. (175 pounds) of urea per day has been designed, constructed, and successfully operated. In the pilot plant the anhydrous liquids are introduced separately into the base of the lead-lined autoclave by means of single-acting hydraulic-type pumps actuated by a common crankshaft. (Figure 1) The liquid ammonia is supplied directly to the pump from commercial containers. The liquid carbon dioxide usually requires preliminary drying, since in many cases it contains sufficient water to interfere with pumping. The drying is accomplished by passing the expanded gas through concentrated sulfuric acid and through wood charcoal. The carbon dioxide drying, compressing, liquefying, and storage units are shown in Figure 2. The converted mixture discharging from the top of the autoclave enters a still, where thermal decomposition of the unconverted carbon dioxide compounds of ammonia is effected. The urea is removed in aqueous solution while the ammonia and carbon dioxide pass to a regenerative system for separate recovery. The urea autoclave and still are shown in Figure 3. Introduction of the reactants at the base and withdrawal of the products at the top of the autoclave allow advantage to be taken not only of the decrease in density accompanying conversion but also of the increased efficiency of conversion to be expected by maximum loading density (*2*).

Scope of Present Work

Because of the almost complete absence of reliable data for estimating the over-all thermal requirements of the autoclave reactions, it seemed advisable to measure as accurately as possible in the pilot plant the heat change involved. With this information and with the available data on the heat losses through commercial autoclave lagging, the prospective manufacturer can readily calculate his steam cost for this part of the process. For the proper design of larger units it is also important to know something of the temperatures produced within the autoclave and of the resistance of commercially available alloys to the combined effect of erosion and corrosion by the reacting mixture under actual operating conditions. The present paper presents the results of several such experiments on the apparatus described above.

Experimental Procedure

The following method was employed for obtaining the energy requirements of the autoclave. With the autoclave filled with a mixture which had previously been brought to equilibrium at 153° C., ammonia and carbon dioxide were introduced in the molecular ratio of $2NH_3$ to CO_2, and the products withdrawn as in ordinary operation. Two rates of input corresponding to reaction periods of 2.31 and 1.83 hours, respectively, based on stream-line flow, and equivalent to the introduction of 110 and 139 gram-mols of carbamate per hour (200 and 250 pounds of NH_3 per 24 hours) were used in these experiments. After a steady condition had been reached, the energy consumption required to maintain the autoclave at 153° C. was determined. A blank or non-operative run was then made under the same conditions as before, except that no ammonia or carbon dioxide was added and no product withdrawn. This experiment measured the energy loss per unit time per degree temperature difference between the autoclave and the surrounding air due to convection, radiation, etc. From these data the heat evolved or absorbed per unit weight of urea produced was calculated.

Exclusive of the autoclave reactions heat was supplied to the autoclave by electric resistance coils about the mercury trap between the gage and autoclave and about the discharge valve, as well as by the steam jacket surrounding the autoclave. The steam jacket welded on the outside of the autoclave and the small steam port employed for heating the top head were connected in series. The discharge valve was heated externally to prevent freezing of the discharge port by the rapidly expanding gases passing through the outlet. The mercury trap inserted between the Bourdon tube of the autoclave gage and the autoclave head was heated to prevent solidification of the autoclave products.

For the purpose of measuring the heat consumption of the autoclave the temperature and quality of the incoming steam and the temperature and amount of the condensate discharged were determined. The quality of the steam was obtained by means of a throttling calorimeter. The energy consumed in the electrical heaters was determined separately for the discharge valve and the autoclave gage from wattmeter readings. The air temperature surrounding the autoclave was also recorded. Quite satisfactory results have been obtained in spite of several unavoidable but complicating factors, such as variations in the humidity and in the velocity of the surrounding air.

In operative runs it sufficed for the present purpose to weigh the reactants introduced into the autoclave and to determine the urea produced from the weight and analysis of the urea solution discharged at the base of the still. The unconverted carbon dioxide compounds of ammonia were vaporized by steam introduced directly into the urea solution on the base

[1] Received June 26, 1930.

plate of the urea still. This solution, in general discharging at about 100° C., contained from 35 to 40 per cent of urea by weight, with only negligible quantities of ammonia and carbon dioxide. In commercial practice it will probably be found more economical to operate this still under pressure without the direct introduction of steam to the mixture.

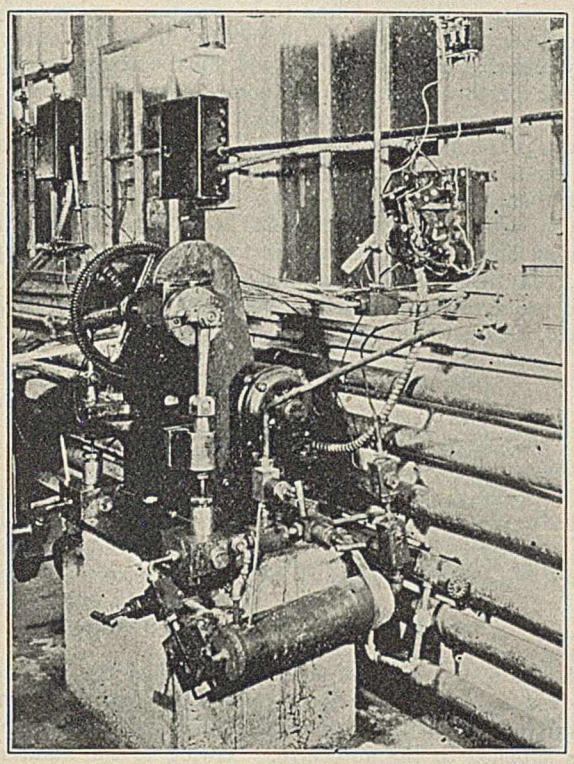

Figure 1—Liquid Ammonia and Carbon Dioxide Pumps

The urea could then be recovered in a molten condition. Davis and co-workers at this laboratory are at present engaged in obtaining equilibrium data that will be valuable in the proper design of such a recovery system.

The temperature distribution within the autoclave was determined by means of four No. 22-gage chromel-alumel thermocouples insulated from each other by close-fitting thin-walled glass tubes, the whole inserted in a thermocouple well constructed of 1.4-cm. o.d. and 0.6 cm. i.d. high-pressure steel tubing protected from corrosion by a 0.3 cm. lead coating. The thermocouple well extended through the top head of the autoclave and to within 1.9 cm. of the base. The thermocouple assembly with junctions 51.4 cm. apart could be raised or lowered at will, thus permitting determination of the temperatures at all points throughout the length of the autoclave.

A few of the metals which had been shown by the work of Thompson, Krase, and Clark (*3*) to be most corrosion-resistant to this system under static conditions, together with a few additional samples, were prepared for testing under actual operating conditions. These samples were drilled and mounted on a 0.3-cm. glass rod, with 0.6-cm. lengths of 0.9-cm. glass tubing separating them. Duplicate sets of samples were placed within the autoclave, near the top and bottom, respectively, and were supported by but were not in contact with the thermocouple well. This was accomplished by means of glass supports secured with lead wire.

Thermal Requirements of Autoclave

The mean values of the hourly heat losses obtained on two different non-operative runs of 3 and 4 hours each are shown in Table I. The mean of these values is 7.25 kg-cal. per hour per degree Centigrade temperature difference between the applied steam temperature and the average surrounding air temperature. The average deviation from the mean is 0.25 kg-cal., or 3.4 per cent.

Table I—Heat Consumption of Urea Autoclave. Non-Operative Experiments

Experiment	Temperature Difference	Heat Consumption	
	° C.	*Kg-cal./hour*	*Kg-cal./hour/° C.*
2	149.0	1106.6	7.43
	147.7	1068.5	7.23
	146.6	1125.5	7.68
	146.1	1100.3	7.53
4	144.8	1047.9	7.24
	143.1	941.4	6.58
	142.0	1005.6	7.08
		Mean	7.25

Table II—Heat Consumption of Urea Autoclave. Operative Experiments

Experiment	Temperature Difference	Heat Consumption	Urea Produced	Conversion	Heat of Reaction
	° C.	*Kg-cal./hour*	*Kg./hour*	*%*	*Kg-cal./kg. urea*
1	156.1	781.7	3.20	35.5	109.4
	155.6	732.6	3.30	40.2	119.8
	155.1	729.6	2.98	36.4	132.5
3	135.8	570.5	3.13	36.3	132.3
	133.6	550.6	3.06	36.4	136.6
	132.4	560.5	3.05	36.3	131.0
	132.2	535.5	2.99	34.7	141.5
	132.4	547.4	3.07	34.9	134.4
5	135.5	728.5	2.33	36.7	109.0
	134.3	691.1	2.37	34.9	119.2
	133.8	656.2	2.47	35.2	127.1
	132.5	621.4	2.49	40.1	136.2
	132.1	608.4	2.54	37.3	137.5
			Mean	36.5	128.2

During operative runs the heat consumption of the autoclave was considerably less than in non-operative runs. Applying the mean value of the heat consumption per degree Centigrade temperature difference to the data of the operative runs and referring the heat evolved to the weight of urea produced, the values given in Table II are obtained. Here the mean value of the heat evolved per kilogram of urea formed is 128.2 kg-cal. at 36.5 per cent conversion with an average deviation from the mean of 8.7 kg-cal., or 6.8 per cent. This

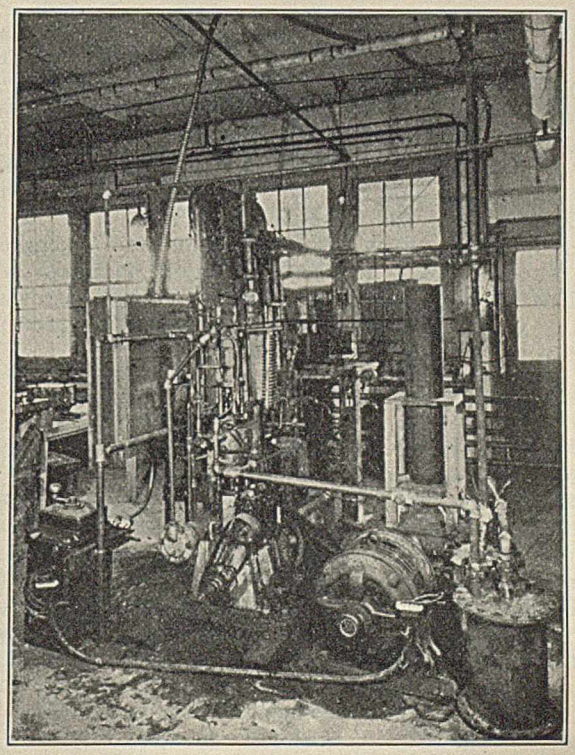

Figure 2—Carbon Dioxide Drying, Compressing, Liquefying, and Storage Units

mean value of 128.2 kg-cal. is equivalent to an evolution of 7700 gram-calories per gram-mol of urea produced at 36.5 per cent conversion from the reactants at 4.5° C. and 110 atmospheres pressure to the final state of the conversion mixture discharged from the autoclave at 65° C. and 1 atmosphere pressure.

Figure 3—Urea Autoclave and Still

Temperature Distribution within Autoclave

The temperature distributions throughout the autoclave during both blank and operative runs are compared with the applied temperature in Figure 4. During blank runs the temperature at the base of the autoclave was 146.5° C., or 5 degrees below the temperature of the remainder of the autoclave. This effect was due to conduction through the mountings and to radiation from the lower head which, although well lagged, was not provided with steam ports. In the operative runs the uniformity of temperature throughout the autoclave (166.8° to 168.6° C.) may be an indication of turbulent flow. The mean temperature of the reactants was 168.1° C., or 15 degrees above the applied temperature, indicating a strongly exothermic reaction.

Heat of Autoclave Reactions

An over-all hourly heat balance for the autoclave reactions may now be set up by the same method as that employed by Krase, Gaddy, and Clark (*1*), except that the proper corrections for the actually determined temperature of reaction and percentage conversion of the reactants may be included. If this is done, the over-all heat balance obtained for an input of 139 gram-mols of carbon dioxide is as shown in Table III.

In order to make a comparison between the calculated value of the reactions and the experimentally determined heat requirement of the autoclave, it is necessary to correct the latter for the heat change accompanying the change in state of the products from 168.5° C. and 110 atmospheres to 65° C. and 1 atmosphere. The heat change accompanying the discharge of the products from 168.5° C. and 110 atmospheres to 65° C. and 1 atmosphere is measured by the difference between the energy requirements of the discharge valve in operating and in non-operating runs. The real difference in energy requirements of the discharge valve cannot be measured directly, since heat is supplied to it both by an electrical resistance coil and by conduction from the autoclave. Experimentally, that portion of the energy increase supplied by the resistance coil was found to have a mean value of 51.0 kg-cal. per hour per kilogram of urea produced. If, as seems very probable, at least half the additional energy is supplied by the resistance coil, then the actual value of the total increase in energy requirements lies between 51.0 and 102.0 kg-cal. per hour and may be assumed to be 76.5 ± 25.5 kg-cal. per hour. The heat evolved in the formation of 1 kg. of urea then becomes 128.2 + 76.5 ± 25.5, or 204.7 ± 25.5 kg-cal., which is equivalent to 623 ± 78 kg-cal. for the net over-all liberation of heat within the autoclave for 36.5 per cent conversion of 139 gram-mols of carbon dioxide to urea. This result indicates that the calculated heat effect of 705 kg-cal. is close to the true value.

Table III—Over-All Hourly Heat Balance

	Kg-cal.
Heat liberated in autoclave:	
Formation of 139 gram-mols of ammonium carbamate...	5290
Conversion of 0.365 × 139 gram-mols carbamate to urea..	400
Heat absorbed in autoclave:	
Heat necessary for evaporating 278 gram-mols of NH_3 and heating to 25° C.	1425
Heat necessary for evaporating 139 gram-mols of CO_2 and heating to 25° C.	265
Heating 139 gram-mols of carbamate from 25° to 168.5° C.	725
Heat of fusion of 139 gram-mols of carbamate	2570
Net over-all heat liberated	705

Autoclave Operation without Steam

A later experiment was carried out in which the conditions of operation imposed in the above experiments were maintained except that after operation had been initiated no steam was supplied to the autoclave. Owing to the additional insulating effect of the steam jacket, the total heat requirement was only 81.5 per cent of that required in previous runs. The autoclave operated at an average temperature of 165° C. and at a slightly lower conversion efficiency. The energy distribution between the various sources for the two methods of operation is compared in Table IV.

Table IV—Distribution of the Energy Requirements in Operative Experiments

Source	Normal Operation %	Without Steam %
Steam	38.0	..
Gage heater	6.5	11.5
Valve heater	23.5	38.5
Reaction	32.0	50.0

Table V—Results of Corrosion Tests

Sample	Non-Ferrous Composition C %	Cr %	Ni %	Si %	Loss *Mg./sq. cm.*	Relative Penetration
1 Chromium					0.21 gain	0
2 Tantalum					0.10 gain	0
3 Duriron				14.5	2.4	1.0
4 Nickel					13.2	4.3
5 Illium G	0.5	21.5	58.5	1.4	12.5	4.4
6 Rezistal 4	0.23	18	22.5	2.9	37.0	13.9
7 Lead					67.4	17.3
8 Aluminum					55.4	59.9
9 Enduro KA 2	0.15	18.0	8.5	<0.75	308.0	114.3
10 Tin					506.0	252.1
11 Zinc					Complete solution	

Results of Corrosion Tests

The metal samples placed within the autoclave for corrosion testing were subjected to non-operative conditions for about 8 hours, to operative conditions for between 20 and 25 hours, and to the periods of preliminary heating and subsequent cooling attending each experiment. Since the total corrosion is the sum of the effects of these varying conditions, the results

are expressed as relative penetration referred to the least corroded sample as unity rather than on the usual "penetration per year" basis.

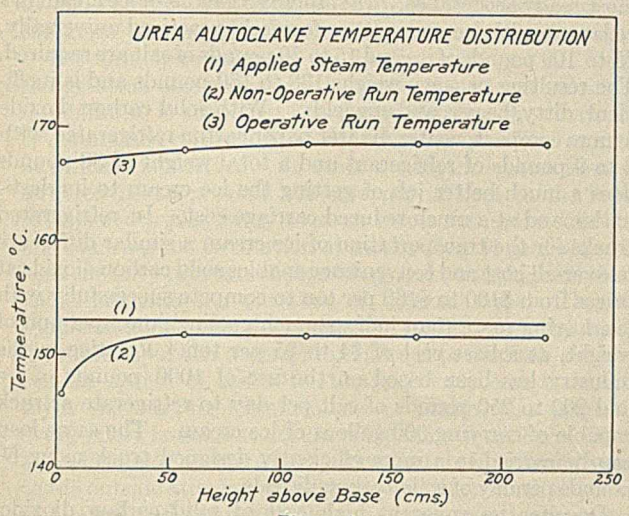

Figure 4

A comparison of these results with those obtained by Thompson, Krase, and Clark (*3*) indicates in a few cases a reversal in the relative resistance to corrosion under the more exacting requirements of actual operating conditions. In general the most corrosion-resistant alloys appear to be high-silicon chrome-nickel steels.

Autoclave Efficiency

No reliable conversion data for the urea-water-carbamate system have been published for temperatures above 155° C. The yields of urea in this system at temperatures above 150° C. are now being determined at this laboratory. The preliminary and unpublished results indicate the equilibrium at 170° C. to correspond to 47.8 per cent conversion to urea. Comparison of this value with the autoclave performance without respect to the reaction period allowed gives an operating efficiency of $\frac{36.5 \times 100}{47.8}$, or 76 per cent.

Conclusions

The over-all autoclave reaction has been established as being strongly exothermic both from the calculated over-all heat balance and from the experimentally determined heat requirements of the autoclave.

Proper design of large-scale equipment will reduce the steam consumption of the autoclave to a negligible value per kilogram of urea produced.

High-silicon chrome-nickel steels offer a high degree of resistance to both erosion and corrosion by the molten mixture. They are capable of being machined, and are strong and tough enough to withstand the pressures and temperatures employed in actual working conditions.

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The Growing Industry—Dry-Ice[1]

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JUST as a chance grain of sand in an oyster's shell forms the starting point of a pearl, so an idea is the nucleus for industrial development. Many other factors affect both pearls and industries, but a perfect pearl grows only on the right kind of a sand grain and an industry develops to an imposing extent only if it be based on the right idea in the beginning. The industry of commercial refrigeration by solid carbon dioxide (most widely known under the trademark "Dry-Ice") admirably illustrates this thesis.

Numerous attempts to apply solid carbon dioxide to the problems of refrigeration of foodstuffs amounted to nothing in the past because, among other things, their promoters failed to realize and to take into account the peculiar problems involved in making so extraordinary and so expensive a material practically usable. In 1924, Thomas B. Slate applied for United States patents on ideas, which if one is to judge from the results, were the correct ones on which an industry could be built. Although methods of preparation of solid carbon dioxide in useful form were not neglected in Slate's applications, he placed principal emphasis on utilization of the peculiar value of this material in maintaining low temperatures, and devised methods of putting it economically to work. Others before him had been looking for a time, which so far has failed to materialize, when solid carbon dioxide could be made and sold for a price directly competitive with ice, solid water.

[1] Received August 9, 1930. Presented before the Division of Industrial and Engineering Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

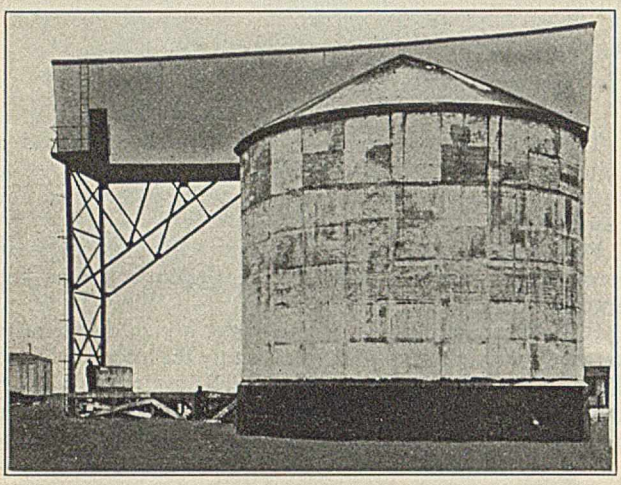
The wisdom of attacking the problem from Slate's angle has been borne out by the development in the intervening period of an industry of considerable proportions and by the working of a revolution in the refrigerated transportation of perishables. The first pound of solid carbon dioxide for commercial refrigerating purposes was sold by the DryIce Corporation of America in 1925. In 1929 production approached 15,000 tons, and the expected sales for the calendar year 1930, based upon figures for half of that period, will probably exceed double that figure, greater than the annual production of liquid carbon dioxide in the United States. This quantity of material is being produced in eighteen plants from coast to coast in the United States and distribution is being effected through twenty-seven sales outlets supplied from plants more or less remote by automobile truck and by a private railroad car line of forty cars devoted solely to this service. One could scarcely ask for more conclusive evidence than that under such circumstances.

Properties of Solid Carbon Dioxide

To understand this swift growth it is necessary to consider those peculiarities of solid carbon dioxide which have made its use practicable to so wide an extent. Statistically its properties are:

Specific gravity	1.56
Subliming temperature in carbon dioxide at 760 mm.	−78.6° C. (−109.6° F.)
Latent heat at subliming temperature	246 B. t. u. per lb.
Specific heat of gas (average)	0.193
Total refrigeration to 40° F.	273 B. t. u. per lb.

Like all thermal values, there is some uncertainty about these and disagreement among authorities. However, it is apparent that the available refrigeration per pound is nearly twice that of ice and that most of it is available at a temperature more than 140 degrees Fahrenheit lower than ice. On a volume basis the greater density of solid carbon dioxide gives it nearly three times the refrigerating effect of ice.



Regenerator of Special Construction for Storing Millions of Pounds of Dry-Ice

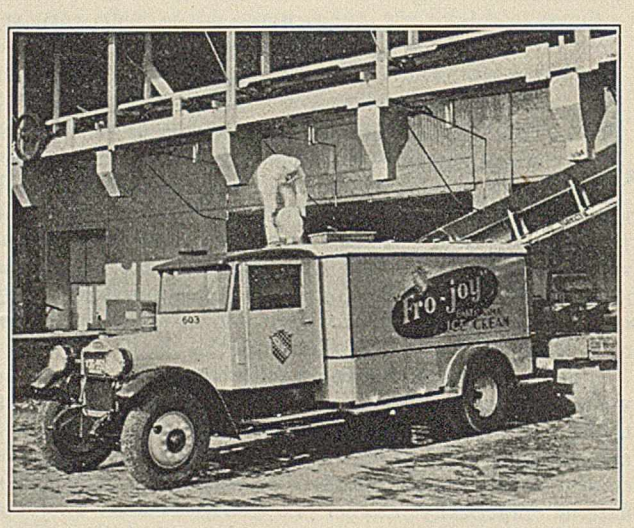
These physical facts would not permit effective competition for commercial refrigeration business with ice, but the sublimation of the solid to produce dry, cold carbon dioxide gas and the full utilization of its valuable properties have definitely placed solid carbon dioxide on the commercial map. It would be foolish to suggest that in some magical way solid carbon dioxide avoids the operation of the first law of thermodynamics and that some peculiar power of the heat units in it allows them to do many times more work than those in other materials without going farther to explain. Yet such an apparent anomaly is actually realized in daily practice.

Comparison with Ice Refrigeration

Gaseous carbon dioxide as generated from the evaporation of Dry-Ice is of course cold, and by virtue of the low temperature of its origin, extremely dry. It possesses a relatively low specific heat and an extraordinarily low heat conductivity. For the preservation of perishables by cold these conditions are quite ideal. First of all they make possible the use of insulated containers of much more efficient structure and materials than can be used where quantities of water or brine must be seriously considered. Not only can such materials as cellular paper and fiber be built into refrigerated containers for single service with no fear of destroying them or their value by water, but actually the treatment of insulation by the dry gas continuously removes moisture from it, moisture being the most prolific cause of insulation breakdown. The transfer of heat within the refrigerator is easily effected by means of the gas itself, whose low heat capacity assists materially in preventing overcooling. The replacement of air in the cells of insulation by the much better insulator, carbon dioxide, materially reduces heat leakage and the resistance to heat flow of the atmosphere of carbon dioxide within the refrigerator still further reduces the heat inflow and hence the refrigeration load.

Taking these factors into consideration, systems have been developed which for the performance of the same commercial task require a small fraction of the weight of solid carbon dioxide that would be theoretically required to do the same task using time-honored ice methods. To cite specific cases from average commercial practice, we may most easily turn to the ice-cream field, in which Dry-Ice refrigeration has found the most ready acceptance. In shipping 5 gallons of ice cream in a cedar tub with ice and salt, as formerly practiced universally, 75 to 100 pounds of ice and 15 to 20 pounds of salt are required. The resulting package weighs 138 to 150 pounds and is inefficient, dirty, heavy, and unwieldy. With solid carbon dioxide a more compact, neater, lighter paper carton refrigerated with 6 to 9 pounds of refrigerant and a total weight of 38 pounds does a much better job of getting the ice cream to its destination and at a much reduced carriage cost. In refrigerated trucks for the transportation of ice cream a similar difference in over-all cost and convenience enables solid carbon dioxide at prices from $100 to $160 per ton to compete successfully with ice, having more than half as much cooling power per unit of weight, at a base cost of $4 to $5 per ton. Practice in the industry has been based on the use of 1000 pounds of ice and 200 to 250 pounds of salt per day to refrigerate a truck capable of carrying 500 gallons of ice cream. The same load can be carried in a more efficiently designed truck using 60 pounds per day of solid carbon dioxide.

Despite the apparent high cost of solid carbon dioxide, the user realizes a definite over-all economy on its account. In carton shipments of ice cream as noted above over a distance of 60 miles there is an average net saving of more than 20 cents on each 5 gallons shipped with it as compared with the old brine methods. Larger savings result from longer shipments. In ice-cream trucking practice, the brine method requires a $3^1/_2$-ton chassis to carry a 500-gallon load, whereas the same load can be placed upon a $2^1/_2$-ton chassis if solid carbon dioxide is used as the refrigerant. On the basis of 60 miles per day there is an average net saving in direct cost of some $4 per day in favor of the latter in addition to numerous important indirect savings.



Small Amount of Dry-Ice Used for Maintaining a Safe Temperature in a Large Ice-Cream Truck

Refrigerating Problems Solved by Dry-Ice

No serious technical problem remains in the production of any temperature desired from that of the atmosphere down well below the range of any reasonable commercial requirements. A Dry-Ice refrigerator for maintaining a temperature of, say, 40° F. for a period of ten days or so without in the meantime recharging with refrigerant has been developed and numbers of these are in commercial use now where circumstances have justified it. The oft repeated question as to the use of solid carbon dioxide in domestic

refrigerators may be answered by pointing out that the problem at present is principally one of distribution. The economic one of general distribution of multitudes of small pieces to householders at low price is intimately connected with the more pressing problems of large-scale wholesale supply.

The principles adopted in making solid carbon dioxide refrigeration economical are based on the above. Design of refrigerators is such that the temperature of the commodity is maintained with as little departure as possible from that at which it is received. In other words, the system is so constructed as to prevent the entrance of heat to the lading. This is accomplished by more or less isolating the solid itself and allowing the circulation of carbon dioxide gas, whose low heat capacity prevents supercooling and whose high insulating value prevents the entrance of external heat. The ideal condition allows this gas circulation contact with the insulating material of the walls and permits it to displace air in the cellular spaces of the indulation. This scheme is modified to fit the varying circumstances of commercial usage, but every effort is made to insure complete utilization of the gas as an insulator and as a heat carrier before it is finally vented to the outside atmosphere carrying with it as much as possible of the unavoidable heat leakage. Appropriate arrangements are made for allowing the gas to permeate the lading or not as conditions require.

In handling perishables which are not damaged by too low temperature, such as ice cream, the perishable itself can frequently be used as insulation for the refrigerant. In this practice the outer insulated case is filled with the perishable and the refrigerant, insulated if necessary from the perishable to control its heat absorption rate, is placed in the center of the package. Here the continually generated gas moves outward through the lading carrying heat with it.

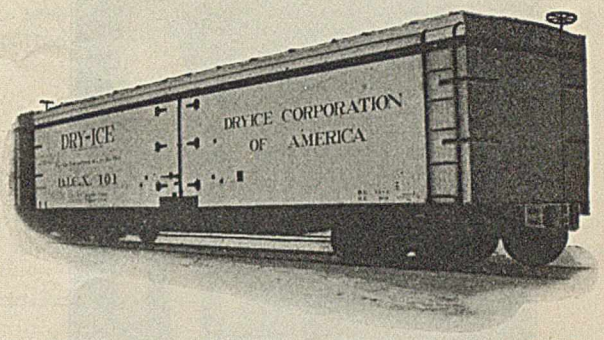
Many insulating materials not previously considered especially practicable on account of water absorption have been brought into great commercial prominence by the commercialization of this type of refrigeration. Kapok fiber, balsa wood, and several of the wood-fiber boards are proving highly useful.

For the solution of problems of cooling as distinct from those of maintaining a low temperature when once it is produced, solid carbon dioxide is economical only under special circumstances. In the form of Dry-Ice a dollar will buy at the present time 5460 B. t. u. available at 40° F., while the same dollar will buy 76,000 B. t. u. in the form of ice, nearly fourteen times as many. It is quite obvious, therefore, that for cooling large bulks of materials Dry-Ice ordinarily would be expensive. However, there are conditions of low temperature or absence of moisture where it is being used satisfactorily—as, for instance, in the freezing out of fats from alcohol extracts of pomades in the perfumery industry.

Effect of Gas on Materials Stored in It

One of the peculiarities of carbon dioxide which recommends it for many uses is the distinct germicidal effect of the gas and its salutary effect on the materials stored in it. The results of preliminary studies in this field have already been published (*4*). It was clearly shown that saturation of meat and fish with carbon dioxide materially reduces the rate of growth of many ordinary bacteria. Further work in the field has fully borne out this conclusion and has definitely shown that the factor of safety thus introduced into transportation of these perishables is of considerable value in preventing spoilage in cases of unforeseen delay in transit. No deleterious effect of carbon dioxide has been observed in commercial practice with any of these perishable materials which do not respire. The handling of pork, fish, poultry, milk, butter, cheese, eggs, and various fatty materials has been carried out on a commercial scale with Dry-Ice with the great satisfaction to the users. Exposure of cut beef to high concentrations of carbon dioxide is an almost sure test for its age. Fresh, chilled beef remains unchanged by the gas, but if it has been held some time in storage before exposure, a brown color develops to replace the healthy red of the fresh cut. Beef that has been discolored in this way is still perfectly edible and its keeping qualities have not been disturbed in the least, the only change being in the color. The explanation of this peculiarity of old beef, and it appears to be solely confined to beef, is not clear, but it seems probable that oxygen is required to keep the hemoglobin of this meat oxidized to its customary bright red.

Vegetable materials present a different problem, because they continue to respire long after they are removed from the parent plant. On the supposition that oxidation is the principal, if not the sole, process of decay, various recommendations have been made from time to time that fruit be preserved by placing it in an atmosphere of carbon dioxide or other inert gas. The fallacy in such suggestions lies in the



Specially Constructed Refrigerator Cars for Supplying Dry-Ice to Distant Markets in Solid Carloads

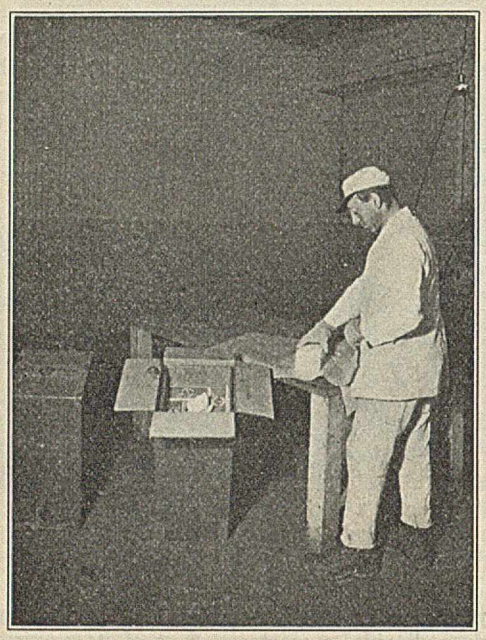
necessity of supplying oxygen to the fruit and in supposing that carbon dioxide, a waste product of its respiration, is indeed inert. While the complete plant in normal growth actually consumes carbon dioxide and produces oxygen, the fruit or other part of it performs the reverse operation when normal metabolism is disturbed. Under such circumstances it is remarkable that such materials will tolerate considerable percentages of this gas. No particular difficulty is experienced in handling even so perishable fruits as strawberries in properly designed containers arranged to maintain minimum concentrations in contact with the berries themselves. Results of a careful study of the tolerance to carbon dioxide of many of the usual commercial fruits and vegetables will shortly be published (*6*). Suffice it to state here that refrigerated equipment has been designed to provide satisfactorily low percentages of the gas to prevent hazard to fruits and vegetables from this source, and this is done without serious loss of refrigeration efficiency.

Flowers have characteristics different from those of most other vegetable products. Indeed, it has been shown that the effective life of rosebuds in particular is prolonged several days by proper dosage of carbon dioxide (*5*). Concentrations effective for this purpose are not higher than 25 to 30 per cent and alternate dosages with carbon dioxide and air yield better results than either alone. Fortuitously the conditions met in the florists' refrigerators are almost ideal for this purpose. During the night, when the refrigerator is closed, the concentration is built up to the optimum point and during the day the continual opening necessary to serve purchasers provides the air dosage needed.

Problems of Manufacture

The problems of manufacture and distribution created by the rapid growth of demand for solid carbon dioxide have

been manifold and many of them have required exercise of the highest type of engineering skill. To grasp some conception of what they are the background of the industry must be studied. Liquid carbon dioxide has been made and marketed for several decades. In producing it the peak demand for soft drinks in the summer has been a governing factor. Production has had to be elastic and plants have been located for economic reasons near centers of demand. Relatively small plants at many points have operated generally well below capacity except during seasons of pronounced demand. Now if upon this industry of small scattered plants



Shipping Ice Cream by Express in Paper Cartons with Dry-Ice as Refrigerant

running at capacity a small part of the time, one superposes another demand, already grown to much larger proportions than its own, for its product to form the raw material for another industry whose product is highly perishable and whose season of greatest demand coincides with an existing peak, some idea of the magnitude of the problems involved can be gained.

It early became necessary to supplement existing sources of liquid carbon dioxide by building independent plants and by utilizing by-product gas from sources not profitably available to the liquid carbon dioxide industry. By-product gas from fermentation was a possible raw material early in the development of solid carbon dioxide and other similar sources are being developed as need for them arises. The selection of a particular by-product source necessarily depends upon economic factors, such as location, power cost, purity, and above all continuity. In an industry growing so rapidly as this one is, the relative weights of various factors in the situation change rapidly and didacticism is distinctly out of place. Many of the factors involved have already been discussed (*2*), but a few points bearing on the general situation may be of interest here.

Carbon dioxide in low concentrations containing various kinds of impurities is the most common and cheapest industrial waste. In order to have value the gas must be in relatively high concentrations and must be easily freed from contamination. The coke process for producing liquid carbon dioxide (*1*, *3*) furnishes its own power and operates upon its own flue gas, and it is only on account of this self-sufficiency of this process that it is possible to utilize flue gas at all as a source. The removal of inerts, nitrogen, etc., is a serious problem from a power standpoint, and hence the availability of sources depends on extremely high concentrations of carbon dioxide, their value diminishing rapidly as concentration decreases below 100 per cent. Impurities other than inerts (sulfur, odors, etc.) frequently offer problems quite as serious, especially since every trace of odor and taste must be removed from a product which is to be used in connection with food.

Power costs loom large in the manufacture of solid carbon dioxide, for in the final analysis calorific value makes the product salable. Hence low power rates are practically imperative at the source of by-product gas if operations are to be continuously profitable.

The continuity of supply must be sure and the quantity great enough to warrant investment in plant to utilize it. In general, a minimum of 20 tons of pure carbon dioxide continuously available will barely justify its use.

The impression seems to have gained wide currency that practically no equipment is necessary to manufacture solid carbon dioxide on a practicable scale and indeed that the operation can be carried on in the back of the family garage. Nothing could be further from the fact. Momentary consideration of the fact that the liquid, a necessary intermediate raw material, has a vapor pressure of about 1000 pounds at ordinary temperatures and that the gas must be compressed to this pressure in order to obtain liquid from it, will convince anyone with even elementary engineering training of the impracticability of doing things that way.

The manufacturing operation consists essentially of compressing the gas to a liquid, cooling this liquid and converting it into solid form and finally compressing it into compact blocks for use. Early methods of manufacture are described in considerable detail in previous papers (*1*, *3*). Great modifications have been made in the process. Improvements have been made, not only by conducting the entire operation of solidification and pressing in a single vessel, but also in producing an entirely new form of solid carbon dioxide. The avoidance of transfer and of the hand operation of tamping the snow into a mold preparatory to pressing have increased the economy of the operation, making standardization of the density and the size of the product possible. The preparation of pure liquid carbon dioxide from coke has been fully described (*1*, *3*) and the removal of the various impurities met in utilizing by-product gas from the fermentation process follows regular commercial practice. New problems in purifying gas from other sources have also been solved.

Storage and Distribution Problems

The vagaries of demand and the economy of continuous manufacture on a relatively large scale have forced this new industry to provide methods of storage for its product to smooth off peaks of demand and methods of transportation with minimum waste in transit. The proposition of storing several thousand tons of so highly perishable a material as solid carbon dioxide at a temperature more than 100 degrees below zero Fahrenheit over a period of months presents no mean problem in engineering and design. However this has been accomplished with the greatest satisfaction to all. During the past winter more than 5 million pounds of solid carbon dioxide were manufactured during the idle period and stored for use during the peak demand period of July and August. The resemblance of this to the old practice of holding ice from winter to summer ceases with the statement, for the problems involved are of an entirely different order.

Realizing the handicap of depending solely on scattered small scale production and the value of utilizing huge sources

of by-product gas at sources of cheap power, the problem of conserving the solid on long rail journeys to market was seriously attacked. While it is practice to ship small amounts by mail or express in paper cartons, large-scale demand required the development of more economical shipping methods. Shipping cases have been designed which in large sizes allow a loss in transit of as little as 1 per cent a day. An efficient railroad transport car has been devised and now a fleet of forty such cars is devoted solely to the transportation of Dry-Ice to remote points. The transit loss in these cars even on a journey of several days is much less than that in loading and unloading them. By utilizing this low-loss method of rail transportation it has been easily possible to supply peak demands in Chicago, Baltimore, and Washington from Niagara Falls and to equalize supply and demand throughout the entire United States. Obviously, to be profitable such shipments must get the product to market cheaper than it can be had from competitive sources.

These things sound simple in the telling, but as short a time as two years ago they were far away in the realm of impossibilities even in an industry based on doing the impossible.

Freedom from Hazard

Especial interest attaches to the fact that the introduction on so wide a scale of so totally novel a material has brought with it no serious industrial hazard. The extremely low temperature of solid carbon dioxide can cause serious frost bite, but the use of even thin gloves to protect the hands effectively prevents injury. A few cases of "burns" have occurred, but their prevention is so simple and so effective and their occurrence so rare that each one attracts unwarranted attention. In our own plants, where new employees have had to be broken in in groups to care for rapidly expanding production, in four and a half years of operation only two cases of frost bite have occurred that were considered serious enough to require a physician. No time was lost on account of either. The treatment of frost bite of this kind is identical with that for burns. Unguentine, picric acid gauze, carron oil, bicarbonate of soda, and other burn treatments are quite effective.

In the early days it was freely prophesied that many workmen would be overcome by the gas itself when it was used in refrigerating large spaces. Practice has demonstrated the inconsequence of this possible hazard. Human lungs are so delicately balanced to carbon dioxide that even the slightest variation in concentration of the gas above a tolerated minimum brings about an immediate reaction and any who have been exposed to carbon dioxide realize that a person will not permit himself to be exposed to dangerous concentrations. No case of collapse or near collapse from this cause has occurred in the wide general use of Dry-Ice.

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Studies in Diffusion

I—Estimation of Diffusivities in Gaseous Systems[1]

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Methods are presented for the calculation of diffusion constants in gaseous systems at any temperature, using as a basis the Stefan-Maxwell-Sutherland expression from the kinetic theory of gases. It is shown that the molecular diameters required for the evaluation of this expression are calculable in terms of the liquid molecular volume at the boiling point, found by Kopp's law. A method of calculating the Sutherland constant for diffusion from the boiling points and molecular volumes of the constituent substances is described. The basic equation is applied to the existing data on the diffusion of gases and vapors, and found to be in good agreement. The methods of estimation are believed valid for all gaseous systems, and are of especial value for engineering purposes in that they require a knowledge of only the molecular formulas and the boiling temperatures of the substances involved.

In the study of the mechanism of the industrially important processes of absorption, extraction, and distillation, the two-film theory proposed by Whitman (*23*) has proved of great value in the evaluation of the rate of material interchange between a gaseous and a liquid phase. This theory postulates that the principal resistance to material transfer is due to the existence of relatively quiet and convectionless layers of gas and liquid on either side of the interface, through which films material transfer occurs by the slow process of diffusion. At any point within the film the diffusion rate is given by Fick's law,

$$dN/d\theta = DAdc/dx$$

This equation is valid for both gaseous and liquid films, N being the number of mols transferred and c the concentration in mols per cubic centimeter; if N is desired in grams, c must be expressed in grams per cubic centimeter. The integration of this expression throughout the film gives the rate of transfer through the film as a whole; this integration has been carried out by Lewis and Chang (*10*) and by McAdams and Hanks (*13*). The application of the integrated expressions so obtained to problems of engineering design requires a knowledge of the diffusivity, or diffusion coefficient, D. Experimental values of D are available for a number of systems composed of the ordinary fixed gases, as well as for the diffusion of some vapors through air, hydrogen, and carbon dioxide. However, for the interdiffusion of vapors, highly important in distillation, no experimental results whatever have been published; consequently, the engineer is handicapped in any effort effectively to utilize the theoretical methods just outlined. It is accordingly the purpose of this paper to review the existing theories and data on diffusion in gaseous systems in order to develop therefrom a reliable method for the estimation of D from a knowledge of the nature of the substances involved.

[1] Received July 31, 1930.

Theories of Diffusion Based on Kinetic Theory of Gases

The kinetic theory of gases has provided two basically different theories of diffusion—that of Stefan, also put forward by Maxwell, and that of Meyer, as modified by Jeans (*6*). These differ principally in the predicted variation of D with the composition of the gas mixture, the Stefan-Maxwell formula predicting no variation, and the Meyer-Jeans expression allowing a maximum variation of 33 per cent. The recent more rigorous theory of Chapman and Enskog predicts a variation of only a few per cent, which is supported by the experimental data of Schmidt, Jackmann, Deutsch, and Lonius. The formula given by Enskog (Jeans, p. 319) indicates a maximum variation in D (from 0 per cent of one component to 100 per cent of that component in the diffusion mixture) of 8.33 per cent when the mass ratio of the diffusing molecules is infinite, 8.2 per cent for an 80:1 ratio, and 6.1 per cent for a 5:1 ratio. From these facts we conclude (1) that the Stefan-Maxwell formula gives a more nearly accurate representation of the facts; and (2) that the influence of composition of the value of D is small enough to be disregarded for engineering purposes, especially in view of the fact that the experimental errors are of the same order of magnitude. In addition, the Stefan-Maxwell formula is simpler and better adapted to rapid computations.

With the exception of minor variations in the value of B, the same formula has been deduced by Stefan, Maxwell, Langevin, and Chapman, and modified by Sutherland to allow for the effect of intermolecular forces in increasing the resistance to diffusion:

$$D = \frac{B\sqrt{\frac{1}{M_1} + \frac{1}{M_2}}\,T^{5/2}}{S^2(T + C)}$$

The factor $T/(T + C)$ is due to Sutherland (*19*), who has developed the theory of diffusion along the same lines as his well-known theory of viscosity; in view of the marked success of his viscosity theory, we may suppose with confidence that the similar diffusion theory is valid. Of the quantities in the formula, T and M are known; B is given by kinetic theory, or may be obtained empirically from known values of D. For the estimation of D we must obtain suitable values of S and C, S representing the distance between centers of two molecules of different sorts at contact, while C is the Sutherland constant for the system.

Calculation of Sutherland Constant

Sutherland has given an expression for the value of C in terms of the corresponding constants for the viscosity of the individual gases composing the system:

$$C = \sqrt{C_1C_2}\left[\frac{2\sqrt{V_1 \cdot V_2}}{V_1 + V_2}\right]^3 = F\sqrt{C_1C_2}$$

The factor F is generally quite close to unity, decreasing slowly from unity as the molecular volumes differ more and more. For several values of the volume ratio, F has the values:

V_2/V_1	1	2	3	4	5	6	8	10
F	1.00	0.980	0.953	0.920	0.894	0.875	0.838	0.805

The constants C_1 and C_2 are to be obtained from experimental measurement of the variation of viscosity with temperature, using the Sutherland equation

$$Z/Z_0 = (T/T_0)^{3/2}\left(\frac{T_0 + C}{T + C}\right)$$

It will be noted that this equation contains the constant C in such a manner that its value is extremely sensitive to small errors in either T or Z; when C is zero, Z varies as the square root of T, while for C infinite, the variation follows a $^3/_2$-power law. Thus, while the exponent of T changes by unity, C varies from zero to infinity; accordingly, several accurately determined values of Z are necessary to give a reliable value of C. Unfortunately, for most gases values of Z are available at only two temperatures, and an error of 0.5 per cent in one of these values is reflected to C as an error of about 10 per cent.

The calculation of Sutherland constants from theory in a rigorously accurate manner has not yet been accomplished; Enskog (*4*) has given a relation between C and the law of force of intermolecular attraction; Debye (*3*) and Keyes (*7*) have related C to the dielectric constant. The most generally useful relation for the present purpose is one originally due to Sutherland (*18*), later put forward more clearly by Vogel (*22*); Vogel's equation is

$$C = 1.47T_B$$

where T_B is the absolute boiling temperature. Since C is a measure of the intermolecular potential energy, which in turn determines the ease of vaporization, such a relation appears quite logical.

Table I contains values of C calculated from the Vogel relation, together with observed values taken from the Landolt-Börnstein Tabellen, the International Critical Tables, and Jeans' "Dynamical Theory of Gases" (p. 285). The recently determined values of Titani (*21*) for a number of organic vapors, mainly hydrocarbons, are also given. The values 123.6 for air and 533 for bromine are due to Braune, Basch, and Wentzel (*1*); the 650 for water is from Smith (*16*), and is of doubtful accuracy.

A study of this table indicates that the agreement is as good as may be expected, considering the difficulty of obtaining accurate values of C experimentally. For the common fixed gases for which several values of C are available, the calculated C appears to be accurate to within the experimental error; hydrogen and helium are anomalous, obeying the Sutherland equation at high temperatures only and having a C larger than calculated. The fairly large deviations shown in some instances are not to be considered serious in view of the large experimental errors to which the vapor-viscosity determinations are subject, especially for high-boiling vapors. We shall therefore make use of calculated values of C in the remainder of this paper; as will be shown, this procedure does not reduce the accuracy of the formulas presented. For hydrogen and helium we retain the experimental values of 72 and 78.

Calculation of S

The most logical method of calculating values of S for use in the diffusion equation is the use of molecular diameters calculated from the closely related phenomenon of viscosity. This procedure requires a knowledge of both the Sutherland constant and the viscosity of the gas or vapor. As noted above, C is not easily found from experiment with accuracy, and in the case of organic vapors accurate values of Z are usually not available. It is therefore necessary to develop and test an alternative method for finding S. This is provided by the equation

$$S = V_1^{1/3} + V_2^{1/3}$$

where V is the volume of one mol of liquid at the boiling point. To avoid the necessity for experimental data we make use of Kopp's law of additive volumes, which states that the value of V is an additive function of the atomic volumes. In doing this, the boiling points are assumed to be van der Waal's corresponding temperatures, the actual volume of the molecules in any liquid then being proportional to the space occupied, so that the cube root of V is a measure of the molecular

diameter. We shall use the system of computation developed by Le Bas (*5*, *8*), assigning values to the several elements as follows: carbon 14.8, hydrogen 3.7, chlorine 24.6, bromine 27.0, iodine 37.0, sulfur 25.6, nitrogen 15.6; in primary amines, 10.5; in secondary amines 12.0. Oxygen, 7.4; in methyl esters, 9.1; in higher esters, 11.0; in acids, 12.0; in methyl ethers, 9.9; in higher ethers, 11.0. For benzene-ring formation deduct 15; for naphthalene, 30. (Numerous minor constitutive effects are noted, for the evaluation of which Le Bas' book should be consulted, if accuracy is desired.)

Table I—Sutherland Constants (*C*)

Gas	t_b	Calcd.	Obsd.	Ratio Calcd./Obsd.
Hydrogen	−252.7	30	72.2, 71.7, 79, 83	...
Nitrogen	−195.7	114	110.6, 113, 118	...
Air	−192	119	123.6, 113, 111.3, 119.4	...
Oxygen	−183	132	138, 127	...
Carbon monoxide	−190	122	118, 100	...
Carbon dioxide	− 78.5	286	240, 277 274 ...	...
Methane	−164	160	144, 198	1.11, 0.81
Ethane	− 88.3	272	287	0.95
Propane	− 44.5	336	341	0.99
n-Butane	0.6	402	377	1.07
Isobutane	− 10.2	386	336	1.15
Isopentane	28	336	500	0.67
Ethylene	−103.9	248	259	0.96
Propylene	− 47	332	322	1.03
Butylene (1:2)	− 18	364	329	1.11
Butylene (2:3)	1.4	403	362	1.11
Isobutylene	− 6	392	339	1.16
Isoamylene	20.1	430	368	1.17
Cyclopropane	− 35	350	372	0.94
Acetylene	− 83.6	278	198	1.40
Allylene	− 32	354	277	1.28
Carbonyl sulfide	− 48	330	330	1.00
Nitric oxide	−151.5	180	195	0.92
Nitrous oxide	− 89.5	270	260	1.04
Sulfur dioxide	− 10.1	386	396	0.98
Ammonia	− 33.5	352	370	0.95
Water	100	548	650	0.84
Hydrogen sulfide	− 61	312	331	0.94
Chlorine	− 33.6	352	325	1.08
Bromine	58.6	487	460, 533	1.06, 0.91
Iodine	184.4	672	590	1.14

Calculation of Molecular Volumes

On adding together the proper values selected from the table, we obtain a value of V which Le Bas has shown to correspond closely to that measured at the boiling point; we have now to investigate the relationship between this value of V and the value calculated from gas-viscosity data. Jeans (*6*, p. 276) gives the relation

$$Z = \frac{0.499m\bar{c}}{\sqrt{2}\pi\sigma^2}$$

The molecular velocity $\bar{c}$ is to be evaluated from the relations

$$p = {}^1/_3\rho(1.086\bar{c})^2 \quad \text{(p. 118)}$$
$$M = 22{,}400\rho = mN = 6.06 \times 10^{23}m$$

with the result that

$$m\bar{c} = 3.96 \times 10^{-19}\sqrt{M}$$

since p, the atmospheric pressure, is 1,013,230 dynes per sq. cm. Insertion of this result in the equation for Z gives, after the introduction of the Sutherland temperature factor,

$$Z = 2.70 \times 10^{-21}\frac{\sqrt{M}}{\sigma z}\left(\frac{T^{3/2}}{T + C}\right)$$

Solving this equation for the cube of the molecular diameter,

$$\sigma^3 = (1.40 \times 10^{-31})\left[\frac{\sqrt{M}}{Z}\left(\frac{T^{3/2}}{T + C}\right)\right]^{3/2}$$

Since the molecular volume V_k found from Kopp's law is to be shown proportional to σ^3, we have to test the validity of the equation

$$V_z = A\left[\frac{\sqrt{M}}{Z}\left(\frac{T^{3/2}}{T + C}\right)\right]^{3/2}$$

where V_z is to be shown equal to V_k.

Table II shows values of V_z calculated from the data of Titani, with the aid of the equation above, using the calculated values of C from Table I; the best agreement between V_z and V_k is obtained with A set equal to 1.40 times 10^{-7} (determined graphically). The values of V_z/V_k tabulated in the last column are as near unity as may be expected, considering the rather large probable errors in C. It may be noted in passing, however, that the use of the observed values does not decrease the average deviation appreciably, and in some cases—e. g., acetylene—gives much greater deviations.

Table II—Molecular Volumes Using Data of Titani

Substance	Z_0	V_z	V_k	V_z/V_k
Ethane	863	53.2	51.8	1.028
Propane	751	74.0	74.0	1.000
n-Butane	682	88.1	96.2	0.916
Isobutane	689	91.6	96.2	0.953
Ethylene	907	49.9	44.4	1.123
Propylene	783	67.5	66.8	1.010
Butylene (1:2)	708	91.0	88.8	1.025
Butylene (2:3)	694	85.5	88.8	0.963
Isobutylene	732	80.5	88.8	0.907
Isoamylene	665	100.9	111.1	0.907
Acetylene	954	40.5	37.0	1.094
Allylene	808	58.8	59.2	0.992
Cyclopropane	807	61.5	60.4	1.020

In Table III a similar comparison is made for a number of gases, using data from the International Critical Tables, together with calculated values of C from Table I and the value of A just found. In calculating V_k for those gases which contain oxygen or nitrogen, the atomic volumes were used which gave the best agreement. It is of interest to note that the atomic volumes of hydrogen, oxygen, and carbon stand in the ratio 1:2:4—that is, in the same ratio as the valences (Le Bas). In the case of carbon monoxide the best agreement is obtained by assigning an atomic volume of 4 × 3.7 or 14.8 to the oxygen, assuming it to be fully quadrivalent.

Table III—Molecular Volumes Using Data from International Critical Tables

Substance	Z	V_z	V_k	V_z/V_k
Hydrogen	842	14.3	7.4	...
Oxygen	1926	25.6	24.0	1.067
Nitrogen	1675	31.2	31.2	1.000
Air	1724	29.9	29.7	1.006
Carbon monoxide	1660	30.7	29.6	...
Carbon dioxide	1370	34.0	34.0	1.000
Sulfur dioxide	1170	44.8	45.4	0.986
Nitric oxide	1780	23.6	24.0	0.983
Nitrous oxide	1350	36.4	36.0	1.010
Ammonia	918	25.8	26.7	0.966
Water	882	18.9	18.4	1.027
Hydrogen sulfide	1175	32.9	33.0	0.996
Carbonyl sulfide	1126	51.5	51.4	1.002
Chlorine	1230	48.4	49.2	0.984
Bromine	1428	53.2	54.0	0.985
Iodine	1190	71.5	74.0	0.965

Evaluation of *B*

Returning to the original formula for D, we shall now evaluate the constant B, both from theory and from experiment. Chapman (*2*) found a relation which in our notation is

$$\frac{BT_0^{3/2}(\sigma/2)^2}{V^{2/3}} = \frac{3}{16}\sqrt{\frac{2}{\pi} \times 22{,}400p}\ (22{,}400/N)$$

where p = 1,013,230 dynes per sq. cm.
$N = 6.06 \times 10^{23}$
$T_0 = 273$

From the comparison of V_z and V_k we find the relation

$$\sigma^3/V = 1.40 \times 10^{-31}/1.40 \times 10^{-7} = 10^{-24}$$

showing that the molecular diameter in Ångström units is numerically equal to the cube root of the molecular volume of the liquid at the boiling point, as noted by Titani. On making the substitutions indicated and solving for B, we have

$$B = 0.00740 \quad \text{(Chapman)}$$

Jeans and Maxwell have given slightly different values for the numerical multiplier, leading to

$$B = 0.00740\ (32/9\pi) = 0.00837 \text{ (Jeans, p. 316)}$$
$$B = 0.00740\ (4/3) = 0.00985 \text{ (Maxwell)}$$

Calculation of Diffusivities

As a matter of interest, we may calculate the fraction of the liquid volume at the boiling point actually occupied by the molecules; this is, agreeing with Titani's value,

$$\pi/6\, N\sigma^3/V = \pi/6\,(6.06 \times 10^{23})\,(10^{-24}) = 0.318$$

Table IV contains values of $D/BT^{3/2}$ calculated from the equation for D; S has been found from the values of V_s in Tables II and III, while C is obtained from the C's for the individual gases given in Table I as C calculated, using the relation given above,

$$C = F\sqrt{C_1 \cdot C_2}$$

As B and T are the same for all systems, these values should be proportional to the observed diffusivities. Figure 1 shows $D_{obsd.}$ plotted against $D_{calcd.}/BT^{3/2}$. The values of $D_{obsd.}$

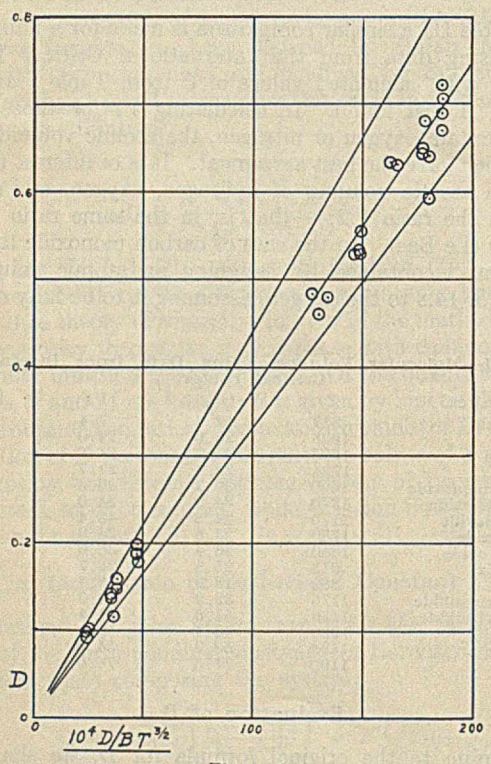

Figure 1

are taken from the Landolt-Börnstein Tabellen, except for the system ammonia-air recently investigated by Wintergerst (*25*); all values are at 0° C. and 760 mm. Those in the first column under $D_{obsd.}$ are due to Obermayer, and in the second, to Loschmidt. Figure 1 also contains three lines representing the three values of B due to Maxwell, Jeans, and Chapman; it is seen that the value 0.00837 given by Jeans agrees best with experiment, while those of Maxwell and Chapman represent upper and lower limits, almost all the data falling between these two lines. We may therefore write as the final equation

$$D = \frac{0.00837\sqrt{\dfrac{1}{M_1} + \dfrac{1}{M_2}}}{(V_1^{1/3} + V_2^{1/3})^2}\left(\frac{T^{5/2}}{T + C}\right) \text{ sq. cm. per second}$$

Application of Diffusivity Equation to Existing Data

The diffusion of vapors through fixed gases has been investigated by a number of workers, all employing the evaporative method devised by Stefan (*17*). The most extensive research was that of Winkelmann (*24*), who determined the diffusivities of about forty substances, mainly aliphatic acids, alcohols, and esters, through hydrogen, air, and carbon dioxide. His work was continued and extended by Pochettino (*15*), who worked only with air, and found results in good agreement with those of Winkelmann, with an exactly similar apparatus. Le Blanc and Wuppermann (*9*), however, have shown Winkelmann's technic to be faulty in that it took no account of evaporative cooling of the liquid surface, which at times amounted to nearly 2 degrees, and caused considerable error in the diffusivities obtained. Mack (*12*) has recently used a modification of the Stefan method for the diffusion of several vapors through air; his experiments with iodine vapor were repeated by Topley and Gray (*20*), who found his result too high and the method difficult of application.

Table IV—Calculation of Diffusivities

System	S^2	$\sqrt{\frac{1}{M_1}+\frac{1}{M_2}}$	C	$D \times 10^4/BT^{3/2}$	$D_{calcd.}$	$D_{obsd.}$	cm.²/sec.	
H_2–O_2	29.0	0.730	96	186	0.700	0.67	0.722	0.690
								0.706
H_2–air	30.5	0.730	90	180	0.679	0.64	...	0.593
H_2–CO	31.0	0.731	91	177	0.667	0.65	0.642	...
H_2–CO_2	32.1	0.723	139	149	0.561	0.53	0.556	0.533
H_2–N_2O	33.0	0.723	135	146	0.550	0.53	...	...
H_2–SO_2	35.8	0.718	158	127	0.479	...	0.483	...
H_2–CH_4	32.8	0.750	103	166	0.625	0.63	...	...
H_2–C_2H_4	37.4	0.731	127	134	0.505	0.48	...	...
H_2–C_2H_6	38.3	0.730	130	130	0.490	0.46	...	...
H_2–N_2	31.1	0.731	88	178	0.670	...	...	0.681
CO_2–O_2	38.2	0.232	194	35.5	0.134	0.136	0.141	...
CO_2–air	40.1	0.239	184	35.6	0.134	0.135	0.142	0.136
CO_2–CO	40.5	0.242	187	35.4	0.133	0.131	0.141	...
CO_2–N_2O	43.0	0.213	278	24.5	0.093	0.092	0.098	...
CO_2–CH_4	42.6	0.292	214	38.4	0.145	0.147	0.159	...
CO_2–C_2H_4	48.0	0.242	266	25.5	0.096	0.101	...	...
CO–O_2	37.0	0.258	127	47.5	0.179	0.187	0.180	...
CO–C_2H_4	46.5	0.267	174	36.7	0.132	0.117	...	...
O_2–air	36.5	0.256	125	48.1	0.181	0.178	...	...
O_2–N_2	37.2	0.258	123	47.8	0.180	0.179	...	0.186
A–He	24.3	0.525	92	162	0.610	...	...	0.634
NH_3–air	36.8	0.305	204	47.4	0.179	...	...	0.198

Table V—Diffusion of Vapors in Air

Vapor	t	V	C	$D_{calcd.}$	$D_{obsd.}$
		MACK			
Iodine	25	74	272	0.0828	0.108
Toluene	25	118.2	237	0.0797	0.0844
Napthalene	25	147.7	261	0.0675	0.0611
Anthracene	99.2	199	284	0.0850	0.0782
Octane	25	185	228	0.0655	0.0602
Aniline	25	110.2	260	0.0785	0.0726
Diphenyl	25	184.6	263	0.0600	0.0727
Benzidine	99	213	291	0.0810	0.0555
		LE BLANC AND WUPPERMANN			
Benzene	42	96	234	0.0994	0.102
Propyl acetate	42	129.4	230	0.0860	0.092
Chlorobenzene	42	116.9	244	0.0863	0.094
Ethyl alcohol	42	59.2	242	0.1285	0.145
Water	42	18.4	250	0.238	0.288
		WINKELMANN			
Ethyl formate	0	85.0	232	0.0793	0.0852
Ethyl acetate	0	107.2	238	0.0698	0.0709
Ethyl propionate	0	129.4	244	0.0630	0.0631
Ethyl butyrate	0	151.6	250	0.0576	0.0574
Ethyl valerate	0	174.8	257	0.0526	0.0505
Ethyl ether	0	107.2	223	0.0735	0.0775
Carbon disulfide	0	66.0	229	0.0876	0.0883
Benzene	0	96.0	234	0.0740	0.0751
Water	0	18.4	250	0.180	0.198

Table V shows the data of Mack, Le Blanc, and Wuppermann, and Winkelmann for diffusion through air; only a portion of Winkelmann's data is given. Study of this table indicates that the agreement in many cases is excellent; in others, much of the error is probably experimental. It is of interest to note that Mack's value of 0.108 for iodine is much too high, while Topley and Gray, by a sphere-evaporation method as well as by Mack's method, obtained 0.0824 (graphically smoothed), almost identical with the calculated 0.0828. Table VI contains additional data by Winkelmann for diffusion through hydrogen and carbon dioxide; the large deviations in the case of hydrogen are probably due mainly

to the high diffusion rate and consequent large cooling effect at the liquid surface. It is evident, as Loeb (*11*) has pointed out, that the evaporative method requires further development of certain correction factors before it may be regarded as trustworthy.

The validity of the Vogel rule as a method seems substantiated by the agreement of calculated and observed diffusivities; little accurate work has been done on the variation of diffusivities with temperature. From the data of Obermayer (*14*), Sutherland (*19*) has calculated values of C shown in Table VII for comparison with the estimated values; as these are based on two temperatures only, the probable error is large, and the agreement with the estimated values is as good as may be expected. That the constants for the last two systems should be larger than either C_1 or C_2 is very unlikely.

Table VI—Diffusion in Hydrogen and Carbon Dioxide

	In Hydrogen			In Carbon Dioxide		
Vapor	C	$D_{calcd.}$	$D_{obsd.}$	C	$D_{calcd.}$	$D_{obsd.}$
Ethyl formate	163	0.360	0.336	360	0.0532	0.1572
Ethyl acetate	162	0.327	0.273	364	0.0470	0.0487
Ethyl propionate	162	0.300	0.237	366	0.0423	0.0450
Ethyl butyrate	161	0.279	0.224	370	0.0384	0.0407
Ethyl valerate	162	0.261	0.205	374	0.0357	0.0366
Ethyl ether	153	0.334	0.296	340	0.0500	0.0552
Carbon disulfide	167	0.398	0.364	359	0.0584	0.0630
Water	198	0.633	0.687	384	0.1270	0.1320
Benzene	166	0.338	0.294	368	0.0495	0.0527

Table VII—Sutherland Constants for Gaseous Systems

System	Obsd.	Calcd.
Hydrogen-oxygen	100	96
Hydrogen–carbon dioxide	106	139
Carbon monoxide–oxygen	124	127
Nitrogen-oxygen	136	123
Carbon dioxide–air	250	184
Carbon dioxide–nitrous oxide	380	278

It may be shown that, provided the molecular volumes are calculated from viscosity data, errors in C_1 and C_2 have a negligibly small effect on the estimated D. When V_1 and V_2 are not far different, we may use a geometric mean value of S instead of the arithmetic,

$$S = V_1^{1/3} + V_2^{1/3} = 2(V_1^{1/3} \cdot V_2^{1/3})^{1/2}$$

and, since $V^{1/3}$ varies inversely as $(T + C)^{1/2}$, write the equation for D as

$$D \propto \frac{(T + C_1)^{1/2}(T + C_2)^{1/2}}{T + (C_1C_2)^{1/2}} = \left[\frac{T^2 + T(C_1 + C_2) + C_1C_2}{T^2 + 2T(C_1C_2)^{1/2} + C_1C_2}\right]^{1/2}$$

It may be seen from this that D is affected only by the difference in the middle terms of numerator and denominator—that is, the difference between the geometric and arithmetic means of C_1 and C_2, which is usually small. If both Sutherland constants are set equal to zero (forceless sphere theory), good correlation will still be obtained, the error in the molecular volumes offsetting the error introduced by omitting the Sutherland factor in the equation for D. This has, in the past, been the usual procedure (v. 4, 16), and accounts for the lack of application of Sutherland's formula. Sutherland's own failure to obtain the correlation found in the present paper is traceable to his use of molecular volumes calculated from his equation of state for liquids. These, probably fortuitously, agree closely with the values found from viscosity on the forceless sphere theory; hence the omission of the Sutherland factor from the equation for D is required for good agreement. Also, if the estimated values of C are used to calculate V_z, and V_z is found to agree with the Kopp law, V_k, use of the estimated C and the V_k must produce good agreement in the equation for D, regardless of the agreement of the estimated and observed C's; this, in fact, is the basis of the present system of correlation.

Conclusion

For ready reference the equations necessary for estimating D may be summarized:

$$D = \frac{0.00837\sqrt{\frac{1}{M_1} + \frac{1}{M_2}}}{(V_1^{1/3} + V_2^{1/3})^2}\left(\frac{T^{5/2}}{T + C}\right) \text{ sq. cm. per sec.}$$

$$V = \text{molecular volume} = \Sigma \text{ (atomic volumes)}$$

$$C = F\sqrt{C_1C_2} = 1.47F\sqrt{T_{B_1}T_{B_2}}$$

F depends on the ratio V_2/V_1.

It is believed that the methods of estimation herein presented are of fundamental soundness, and, in the absence of experimental data, provide the best available means of obtaining values of diffusivities at any given temperature for any system. The agreement obtained with gas-gas and vapor-gas systems indicates that the equations may safely be used for extrapolation to vapor-vapor systems of engineering importance. The most serious source of error is in the estimation of C from the boiling temperature. It is hoped in a subsequent communication to present more accurate methods of calculating this quantity.

Acknowledgment

The writer is indebted to Professors W. K. Lewis and W. H. McAdams for their interest and assistance in the work above described.

Table of Nomenclature

A, B—Proportionality constants
A—Area of interfacial contact
C—Sutherland constant
c—Concentration, in mols per cubic centimeter
D—Diffusion coefficient (diffusivity), in sq. cm. per second
d—Differential operator
F—Factor in equation for C
M—Molecular weight
N—Avogadro's number; number of mols transferred
S—Sum of diameters of unlike molecules
T—Absolute temperature, degrees Kelvin
T_b, t_b—Boiling point, degrees Kelvin or Centigrade
V—Molecular volume at boiling point
x—Distance, measured in direction of diffusion
Z—Viscosity, in poises $\times 10^{-7}$
θ—Time, in seconds
σ—Molecular diameter
1, *2*—Subscripts referring (interchangeably) to the two gases composing the system

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Special Equipment for Protection against Toxics in the Chemical Industry[1]

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THE manufacture and handling of chemicals present many special hazards in addition to the more usual possibilities of accident, which must be carefully studied and for which adequate protective equipment must be provided. Whether a particular plant is engaged in the manufacture of lacquer solvents, acids, steel rails, or automobiles, the possibility of injury to men employed in that industry by falls, falling objects, improper lighting, the handling of material, and many other similar hazards is, with slight variations, common to them all. The chemical industry, however, presents many unique problems to which much thought, time, and attention are being given both by manufacturers and laboratories actively engaged in the chemical industry and by manufacturers and laboratories specifically interested in the development of protective equipment.

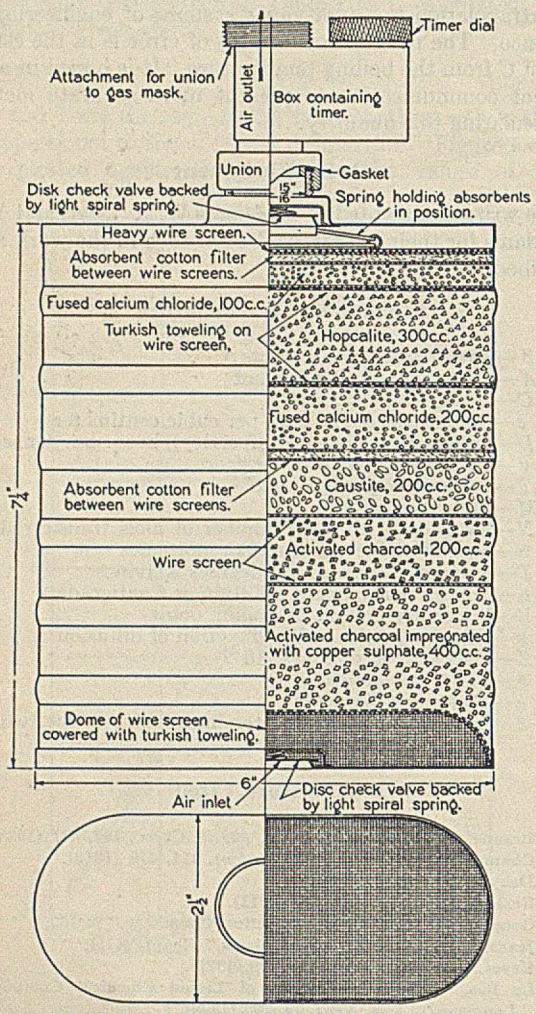

Figure 1—Sectional, Diagrammatic View of Burrell All-Service Gas Mask Canister

Protective Equipment

A few years ago in many branches of the chemical industry gas masks were rarely used in daily work. Coincident with the development of new chemical processes, especially during the war and since, the necessity for proper and adequate respiratory protective equipment became very apparent, with the result that today there are gas masks available providing respiratory protection against practically all known poisonous gases.

The gas mask itself has been improved in many ways. The resistance to breathing has been considerably reduced—to the point where, if it is necessary to wear masks continuously in certain operations, no discomfort is experienced by the operator. Mouthpieces and noseclips have been eliminated; rubber facepieces with an extremely long life and which are readily cleaned are now obtainable. A great deal of thought has been given to the development of a facepiece which will assure maximum comfort. Modern facepieces fit all types and sizes of faces, so that in case of emergency they may be quickly and safely applied by any person.

The heart of the gas mask is the canister, which purifies the air reaching the lungs of the wearer. The canister, in addition to providing absolute protection against all gases for which it is designed, must permit free breathing so that the wearer may at all times obtain a sufficient volume of air without undue exertion. Canisters in modern gas masks protect against specific gases, either singly or in combination. Protection is afforded for practically every known gas, including the deadly carbon monoxide. Protection against carbon monoxide alone or in combination with other gases has until recently been unimportant in the chemical industry, but with the development of synthetic processes employing carbon monoxide the need for such masks has become necessary. For this purpose a special catalyst has been provided which when placed in the canister in combination with certain other absorbents renders protection against practically all emergency conditions.

Figure 2—Workman Wearing Burrell All-Service Gas Mask

For use in operations where men must enter confined spaces where high concentrations of gas exist and where there may be a deficiency of oxygen, hose masks are now available. They are obtainable in several models. The simplest form consists of a suitable body harness, a facepiece equipped with the necessary exhalation valves, and a 25-foot length of hose, through which the worker may draw fresh air from an area outside the gaseous zone. When greater lengths of hose are necessary, these hose masks are equipped with manually or electrically operated blowers for overcoming the resistance of breathing through the hose line. Hose masks equipped with blowers assure the wearer of a continuous supply of fresh air.

[1] Received July 7, 1930.

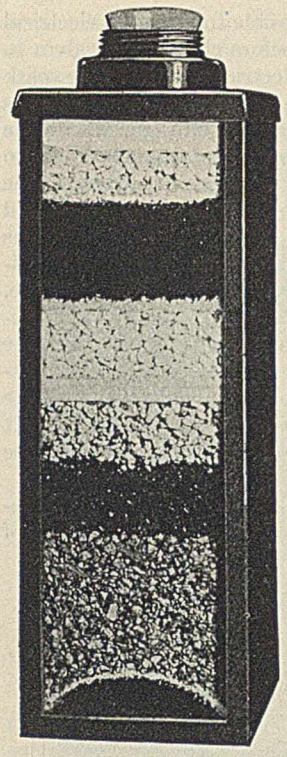

Figure 3—Sectional View of the Burrell All-Service Gas Mask Canister, Showing Layers of Chemicals, Filter Pads, Etc.

They are equipped with specially designed safety belts to which rope life lines may be readily attached. Masks of this type are particularly adapted for use in tanks or vats, or wherever it may be necessary for a man to enter a gas-laden atmosphere through a manhole, and in rooms where high concentrations of gas exist at a relatively short distance from fresh air.

In atmospheres which may be low in oxygen, or where large quantities of lethal gas exist, and where for certain reasons the use of a hose mask is not practicable, there are available oxygen self-contained breathing apparatus. Such apparatus are valuable in times of emergency, particularly when in the case of fire it is necessary to enter buildings heavily charged with gas. In the last few years great progress has been made in the perfection of this type of apparatus and its maintenance and operation have been considerably simplified. It requires, nevertheless, familiarity with the apparatus by the wearer. It is seldom worn except in times of great emergency and when surrounding conditions are extremely dangerous. It is therefore imperative that where these apparatus are installed proper training and inspection be carried on, so that in time of need the apparatus will be ready for operation and men will be thoroughly familiar with its application.

Various types of gas masks, hose masks, and oxygen self-contained breathing apparatus have been tested and labeled as "approved" apparatus by the U. S. Bureau of Mines for certain specific work. All types of apparatus bearing the approval of the Bureau of Mines have been carefully studied, actually tried out under working conditions, and are considered adequate by the bureau for the work intended.

Detective Equipment

The detection of dangerous conditions, particularly in the handling of explosive gases, has lately been given serious consideration by many agencies. One of the outstanding developments is that of the F-M flammable vapor indicator, a device developed in the Factory Mutual Laboratories for the indication of the percentage of flammability. The F-M indicator is unique in that it will indicate without special calibration the percentage of lower explosive concentration of any gas containing hydrogen and oxygen or hydrogen and carbon in combination with oxygen. It will satisfactorily indicate the percentage of flammability of any of these gases, either singly or in combination. Therefore, in processes where various hydrocarbons may be used and where the mixtures of solvents may be changed, it will continually indicate the exact condition existing in the atmosphere irrespective of any change which may be made in mixtures.

Figure 5—Workman Wearing McCaa Half-Hour Self-Contained Oxygen Breathing Apparatus

The F-M indicator is based upon the law recently confirmed by N. J. Thompson, of the Factory Mutual Laboratories, that practically all gases containing hydrogen and carbon or hydrogen, carbon, and oxygen, when burned at the lower explosive limit, produce the same number of calories of heat per unit burned. Thus, when we burn 100 cc. of alcohol, benzine, gasoline, propane, etc., at the lower explosive limit, approximately 50 calories of heat are produced. The F-M indicator makes use of this law by continuously drawing a sample through the device by means of an electrically driven impeller. The sample, in passing through the detection unit, is first exposed to a high-temperature chamber containing a hot filament and the cold junction of a thermocouple. The temperature of this chamber is not sufficiently high to cause combustion of the gas. On leaving this chamber the sample passes into a similar chamber containing a hot filament maintained at exactly the same temperature. This filament, however, is surrounded by a catalyst and combustion takes place. The hot junction of the thermocouple is also located in this chamber. The percentage of lower explosive limit concentration is indicated by a sensitive meter, calibrated in percentage of flammability, located in the thermocouple circuit.

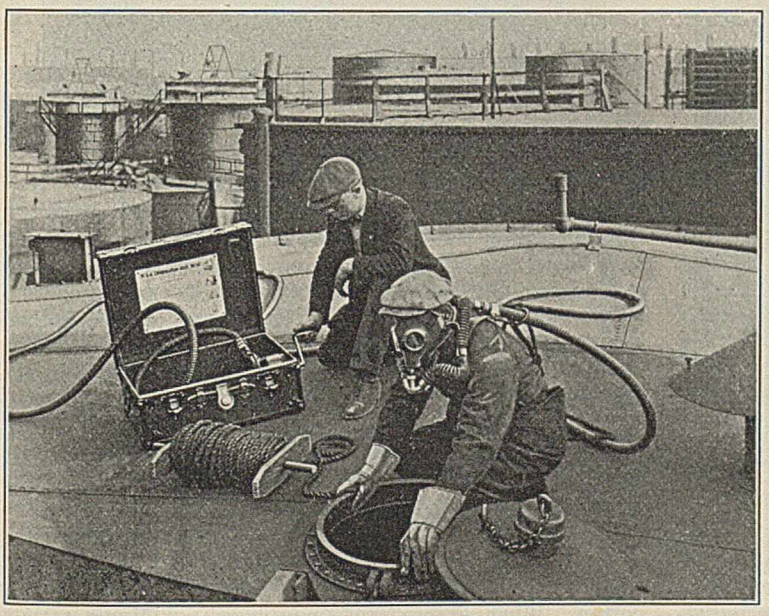

Figure 4—M-S-A Combination Hose Mask Being Used at a Refinery

The F-M indicator is particularly useful in detecting the percentage of flammability in various compartments, in exhaust systems, ovens, and around can-filling machines. It is also useful in indicating the completeness of recovery in solvent-recovery operations. In this use it is installed behind

Figure 6—Jones Gas Detector in Practical Field Use

the absorbent chamber and will indicate the percentage of solvent in the effluent air from the absorber. The F-M indicator is supplied in several models and may be equipped with recording devices, contacts for operating external electrical circuits, alarm gongs, lights, and so forth.

For the rapid determination of approximate explosive contents, where permanent installations are not desired, a gas detector has recently been developed by G. W. Jones of

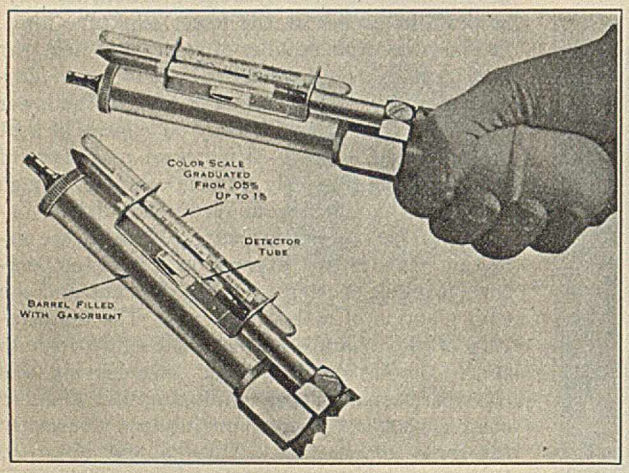

Figure 7—M-S-A Carbon Monoxide Detector

the U. S. Bureau of Mines. It consists essentially of an explosion chamber fitted with a spark plug and the necessary batteries and spark coil, into which a sample of suspected atmosphere is drawn by means of an aspirator bulb. The device is so arranged that it is impossible to close the electrical circuit to the explosion chamber before closing the valves to the sampling tube. If, when the electrical circuit to the spark plug in the explosion chamber is closed, an explosion takes place, it is indicated by a deflection of the dragneedle on the pressure gage connected to the explosion chamber. If no explosion occurs and it is desired to determine whether the sample is below the lower explosive limit, this is accomplished by adding a measured increment of a known explosive gas from the cylinder attached to the detector. This will indicate the relative percentage of flammability in the sample. It is also possible, by adding fresh air to the apparatus, to determine whether the sample is above the upper explosive limit or an inert gas. The Jones gas detector is readily portable and is an excellent device for rapidly determining the relative explosibility of the atmosphere at any point. It is very useful in sampling the contents of tanks, vats, pipe lines, etc.

For rapid determination of small quantities of carbon monoxide, the Hoolamite detector is recommended. In the use of

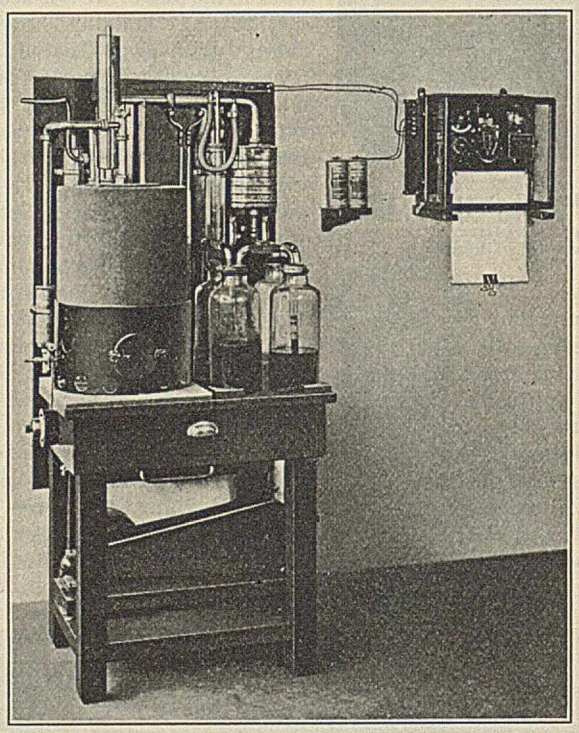

Figure 8—M-S-A Continuous Carbon Monoxide Recorder

this device, samples of the suspected atmosphere are drawn through a filter chamber by means of an aspirator bulb and then forced through a tube containing Hoolamite, which turns to a characteristic green when affected by varying concentrations of carbon monoxide. The Hoolamite tube is then compared with a standard color tube mounted on the detector, giving an accurate determination of the gas present in the samples.

A more recent development in the detection of carbon monoxide is the palladium chloride ampoule as developed by the Bell Telephone Laboratories. This detector consists essentially of a small ampoule of a solution of palladium chloride which is surrounded by a sack of absorbent cotton. In use the glass ampoule is broken by crushing, which permits the palladium chloride solution to saturate the absorbent cotton. When exposed to atmospheres containing carbon monoxide for a definite time, a characteristic color ranging

from canary yellow to deep gray is produced and the amount of carbon monoxide present may be determined by comparison with a standard color card.

For the continuous indication and recording of the amount of carbon monoxide present in any atmosphere, there is available the continuous carbon monoxide recorder. These are in use for the control of ventilation in the great vehicular tunnels and in recording the completeness of combustion in some industries. This monoxide recorder is of the permanent installation type, although some models have been developed which are more or less portable. Continuous samples are drawn through the instrument by means of an electrical pump; gases other than carbon monoxide are completely removed, the humidity being definitely controlled, and finally, the measured sample is run through a combustion unit where, in the presence of a catalyst, complete combustion takes place. The heat of combustion is recorded by means of a thermocouple and recording potentiometer which is calibrated in percentage of carbon monoxide.

Figure 9—H-H Inhalator Being Used in Connection with the Schaefer Prone-Pressure Method of Artificial Respiration

Resuscitation Equipment

Industrial plants employing chemical processes are by their very nature interested in gas protecting, detecting, and recording devices in an effort to eliminate accidents. Yet, in spite of all the splendid efforts put forth by the safety departments, accidents will occasionally happen. In case of gas asphyxia or partial gassing from most of the gases commonly encountered in the chemical industry, resuscitation can often be effected by the use of an inhalator, which administers Carbogen (93 per cent oxygen and 7 per cent carbon dioxide) in accordance with the treatment perfected by Yandell Henderson and Howard W. Haggard, of Yale University, in coöperation with the Accident Prevention Committee of the American Gas Association. Inhalators of this type are used in conjunction with the Schaefer prone-pressure method of artificial respiration with outstanding success.

Conclusion

The development of protective, detective, and resuscitation equipment for the chemical industry is being given serious consideration at all times by the development laboratories of the Mine Safety Appliances Company, which invites the coöperation of the industry itself in presenting to it its problems as they may relate to accident prevention.

A Western Nitrogen Fixation Plant[1]

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OF THE natural resources necessary to the agriculturist and the manufacturer but not found in the United States, fixed nitrogen is one of the most important. Among these fixed-nitrogen products are the nitrites, which are used in the dye industries, in the manufacture of explosives, and in agriculture. One practical process for the manufacture of nitrites is the arc process, but its use has never attained commercial proportions generally in this country. However, for almost ten years the American Nitrogen Products Company, using this process, manufactured high-grade sodium nitrite assaying in accordance with market demands between 96.5 and 99.0 per cent $NaNO_2$. At the end of this period the plant had sufficient installed capacity to furnish the entire American market with nitrite, but after the destruction of the plant by fire in May, 1927, and owing to uncertainty as to its future power supply, the company dissolved. It is believed, however, that a description of this somewhat unique plant and its operation and product might be of some technical as well as historical interest.

The factory was located at La Grande, Wash., on the Mount Ranier branch of the Chicago, Milwaukee & St. Paul Railroad and within half a mile of the Nisqually hydroelectric station of the city of Tacoma.

The plant consisted of arc or electric furnaces, heat interchangers, an absorption-tower section, evaporators, crystallization floor, drying section, packing department, storage arrangements, and all necessary mechanical and electrical equipment for these departments. In general, the plant comprised units which grew from the first of the experimental structures, expanding as experience pointed the way. In the beginning the furnace design was in an embryonic stage and the capacity quite uncertain. The conditions governing the formation of sodium nitrite under the new controlling circumstances were not well known and the proportionate adjustment of each department of the plant to any other had to be made in the light of experiment. With the solution of the major problems there resulted ultimately an arrangement of parts which might have impressed the visiting engineer as planless and built without the formality of blueprints. However, during the course of years gradual changes evolved a plant which was peculiarly adapted to the product that was to be manufactured, with costs which made possible profitable competition with other chemical works producing the compound. Necessarily, cheap electric power was the foundation on which the whole enterprise rested.

The apparatus used and the procedure followed in the manufacture of sodium nitrite by the La Grande process might conveniently be summarized as follows:

[1] Received July 16, 1930.

(1) Fixation of nitrogen and oxygen of the air by means of the electric arc.
(2) Rapid cooling of heated gases and utilization of heat interchangers.
(3) Absorption of nitrose gases and production of sodium nitrite.
(4) Evaporation of nitrite liquors.
(5) Crystallization of sodium nitrite.
(6) Drying nitrite crystals.
(7) Packing the product.

Fixation of Gases in Arc Furnace

The arcing furnace used in the fixation of nitrogen and oxygen with the formation of nitrose gases was a development of the Wielgolaski furnace. This furnace is a modification of the Schonherr, which has been used so successfully in Scandinavian nitrogen fixation plants. Unlike Schonherr, the La Grande furnace was set horizontally and built so that the furnace as a whole was composed of two symmetrical parts made up of standard iron pipe. The total length of the furnace was about 40 feet, but the length of the arc varied between 20 and 30 feet. Figure 1 is a photograph of the plant after the fire, showing the furnaces in the foreground.

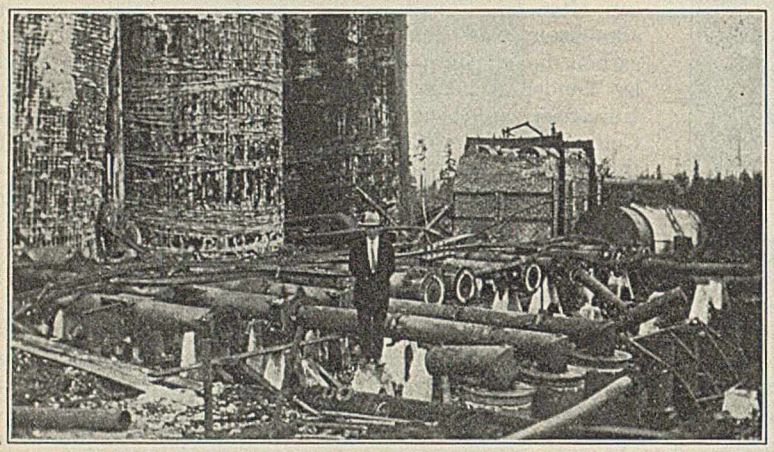

Figure 1—Arcing Furnaces, Absorption Towers, Etc., after Fire

The arc was struck between the points of iron kindling horns which projected through a cylindrical slotted soapstone sleeve, and was swept inward by a regulated air current. As the air volume split inside the soapstone cylinder, the arc was carried through the twin sections of the furnace to elbows at each end near where the arc terminated. The air volume carrying the arc was given a spiral or whirling motion by passage through tangential slots in the soapstone sleeve. The current of spiraling air tended to hold the arc in the axis of the furnace and incidentally protected to a limited extent the interior surface of the furnace. The air before admission to the soapstone ports was preheated as it cooled pipe sections on each end of the soapstone sleeve, thus effecting an increase in furnace efficiency.

Cooling and Utilization of Heat Interchangers

The end sections of the furnace were water-cooled, as were the downtake elbows located at the extreme ends. The passage of the furnace gases through these sections completed the primary cooling effect initiated by the injections of the comparatively cold air into the central wind box of the furnace. The cooled gases, approximately at a temperature of 800° C., passed down soapstone-insulated elbows at each end of the furnace to gas mains leading to the main conduit receiving gas discharges from all the furnaces in operation, and then were drawn through the tubes of a heat interchanger to the absorption system, entering the system at a temperature near 200° C.

The air was driven into and through the furnaces by means of two pressure blowers having a total capacity of 10,000 cubic feet of air per minute under standard conditions. The static pressure at the blowers ranged between 13 and 16 ounces per square inch, but the friction of the entire system, including furnaces, mains, heat interchanger, and the absorption towers, necessitated the use of a supplementary or booster fan, which was located at the downtake of the first tower of the series and acted both as an exhaust and pressure fan.

Construction Features of Furnaces

An important factor bearing on the economics of production was the general design and construction features of the furnaces. These were so built that a defective or burnt section could be removed and a replacement introduced 15 minutes after the power was thrown off.

Excepting for the wind box at the center of the furnace length, the apparatus was made up of sections of jacketed, standard, wrought-iron pipe, and each section was of a size and length which could be easily handled by two men with the aid of a chain block attached to trolley wheels on a track suspended above the furnaces. In the design the length of section was also dependent on the relative corrosive action of the electric flame on different parts of the furnaces, so that the part most subject to the destructive action of the arc could be most quickly and cheaply replaced.

The most actively attacked parts of the furnace were the so-called arcing tubes, which were exposed to the intense radiant heat of the flaming arc, and although they were cooled on the exterior surface by the blast of cold air entering, the iron during the operation of the furnace was at a dull red heat. The arcing tubes were about 7 feet long and extended along the axis of the furnace on each side of the wind box containing the median insulating sleeve; these parts of the furnace section consisted of a central 6-inch wrought-iron flanged pipe forming the arcing tube, encased within a 9-inch pipe which in turn was enclosed in an outside 12-inch shell attached to the wind box. The jacketing was so arranged that air forced into the casing near the wind box was driven by plenary pressure over the jacketed 9-inch pipe and returned to the wind box as a cooling stream flowing over the exterior surface of the arcing tube. The flanged-arcing tube was removable by loosening three wing nuts and then turning slightly in the horizontal plane the furnace half being worked on, using the downtake elbow as a center; the burnt or punctured tube could then be withdrawn and replaced by a new or repaired tube.

The water-cooled sections extending beyond the arcing-tube flanges to the jacketed downtakes were interconnected by heavy rubber hose attached to nipples welded into the outer casing. The end joints of the sections were closed by hinged iron clamps, which were lined with wire-inserted graphited asbestos cloth.

The downtakes below the elbows at the furnace ends were simply short vertical flues made of No. 18 black sheet iron rolled to form 22-inch cylinders; these were lined with a tamped refractory 3 inches thick. The top connection to the live furnace was made through a soapstone ring 4 inches thick which ordinarily served as an effective electric insulator. The soapstone was set on a flange welded to the top edge

of the downtake. The long leg of the water-cooled elbow of the furnace passed through an iron ring closely fitted to the ell and resting on top of the soapstone ring. The downtakes joined gas-main ells set about 5½ feet below the axis of the furnace; these were provided with apertures for cleaning purposes.

The gas mains were of No. 12 sheet-iron pipe lined with a refractory made from water glass, fire clay, and ganister or, in the case of the newer furnaces, by No. 1 fire brick. Gas, water, and air mains were placed in concrete channels cutting the floor level parallel with and directly under the furnaces. The gas mains were made up of sections about 10 feet in length which were connected by means of bolts in slotted flanges and were removable for relining, patching, or replacement, if required.

The electric capacity of the nine furnaces in operation during the later history of the plant approximated a total of 9000 kilowatts with an impressed voltage across each furnace of about 2150 and a power factor of about 70; they were operated star-connected from a 3-phase, 60-cycle, 6600-volt supply and individual furnaces were accordingly grouped into banks of three. The banks were controlled from switchboards which permitted the use of overloads when additional power was available. On the switchboard were the usual measuring instruments and switch gear controls. The general electrical arrangement is shown diagrammatically in Figure 2.

The air supply was controlled from the switchboard by means of a wheel and ratcheting device actuating a slide valve. When about 1000 kilowatts were put through the furnace, about 800 cubic feet of air per minute were required under standard conditions.

Production and Operating Efficiency of Plant

Furnace sheets registering the climax of production and operating efficiency of the plant were those recorded a few days before the fire. On days during which there were no interruptions to the flow of electric energy through the furnaces, a consumption of nearly 180,000 kilowatt-hours was shown on the instrument boards. At a furnace efficiency of 550 kg. of nitric acid per kilowatt-year, a possible production of 12.42 tons per 24 hours is indicated with the energy given.

About 30 per cent of the heat developed in the furnace operation was available for the production of steam and its utilization in the evaporation of nitrite solutions. The steam was generated by means of a heat interchanger in the form of a horizontal multitube boiler which was set in the furnace room and which operated between 60 and 80 pounds steam pressure. A door at the rear of the boiler facilitated cleaning, a process which became necessary after about 30 days' continuous operation, owing to clogging of the tubes with finely divided iron oxide from the action of the arcs on the iron interior of the furnaces.

An idea of the quantity of heat available for steam generation may be had by considering the fact that 30 per cent of 180,000 kilowatt-hours, which has been mentioned as a possible furnace input, would be equivalent to the theoretical heat derived from the combustion of 6.5 tons of coal (14,000 B. t. u. per pound) per 24 hours.

Absorption of Gases

The nitrose gases reduced to a temperature between 200° and 250° C. discharged from the heat interchanger and passed through 25 feet of 16-inch sheet-iron pipe to the first of a series of three absorption towers, where they were brought in countercurrent in tower No. 1 of the series with a partially saturated soda-ash solution. The gases were exhausted from the top of tower No. 1, drawn through a sheet-steel fan, and then driven through the two other towers of the series, finally discharging into the atmosphere from a pipe on the third absorption tower.

The towers were each about 60 feet in height and 18 feet in outside diameter, and were constructed of redwood staves, bound with iron rods and lined with concrete and chemical-resistant brick. The closed tops of the towers were formed of reënforced concrete 8 inches thick, and the structures were built on stone piers sufficiently high to allow the circulating liquors to discharge by gravity to sump tanks set below the floor of the towers.

The solutions circulated through the towers over the surfaces of earthenware filters which presented about 30 square feet of scrubbing surface per cubic foot of packed space. Distribution of the liquor at the top of the tower was effected by sprays attached to radial arms of pipe of varying length inset on central mains passing through the center of the tower top. The spray consisted of a nozzle through which the liquor impinged on an inverted conical plate, thus causing a spume of liquor to be ejected around the circumference of the plate.

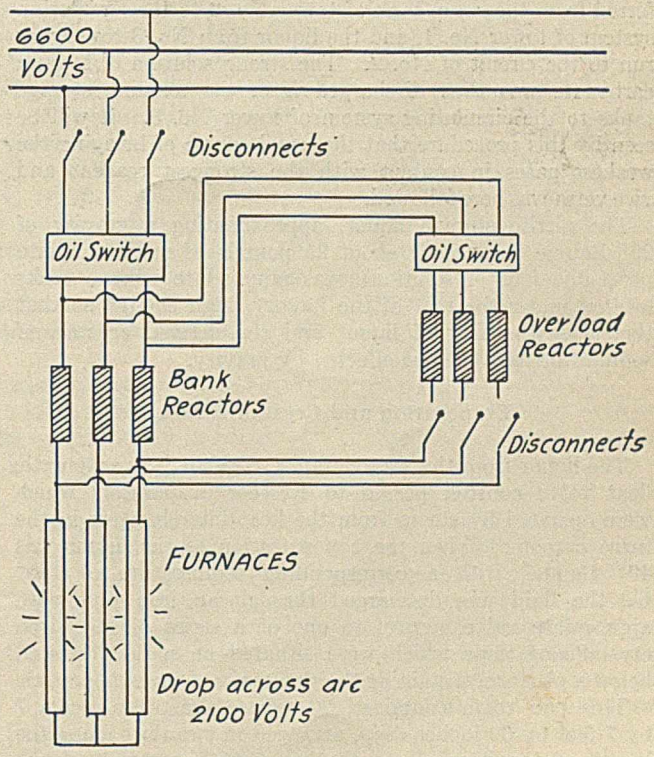

Figure 2—Electrical Arrangement of Furnaces

The sump tanks receiving the liquors discharged from the towers were connected to motor-driven, direct-connected centrifugal pumps mounted on low piers set in a sunken concrete slop floor. The function of the pumps was to keep the liquor in circulation through the tower systems, although they were occasionally used in the intertransfer of solution between tanks when the alkalinity of the solution circulating in tower No. 1 had become neutralized and converted to a solution of sodium nitrite.

The alkaline liquor used in the tower system was derived from a solution of soda ash in water at a concentration approximating 15 pounds per cubic foot of liquor. The soda ash was dissolved in warm water using an agitating device in an iron vat placed below the floor level, and then was pumped to storage tanks near the absorption towers.

The liquor was kept hot until required for tower circulation by steam from the heat interchanger, the tanks being somewhat insulated by a coating of crystals deposited on the interior surface of the storage tanks.

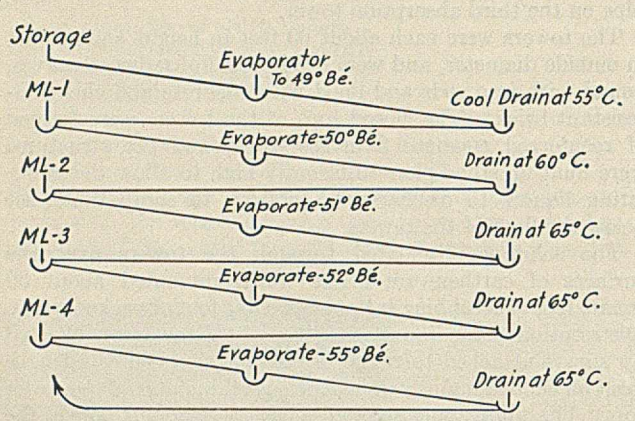

Figure 3—Flow Sheet of Evaporator and Pan System

When the nitrite-charged liquor was pumped to storage from tower No. 1, partially neutralized solution was transferred from the sump tank of tower No. 2 to the circulation system of tower No. 1, and the liquor from No. 3 tower was run to the circuit of No. 2. The strong solution of sodium carbonate was then discharged from the alkaline storage tanks to the circulating system of tower No. 3. It will be seen by this procedure that the usual course of bringing the weakest gases in contact with the strongest reagent and vice versa was here followed.

The nitrite storage liquor, approximating a gravity of 26° Baumé (containing about 25 pounds of sodium nitrite per cubic foot of solution), was pumped to reserve tanks located under the roof of the factory, high enough so that thereafter the flow of liquor and the derived crystals of sodium nitrite would be effected by gravity.

Evaporation and Crystallization

The liquor from the reserve tanks, regulated by automatic float valve control, passed to Kestner evaporators which were operated by steam from the heat interchangers in the furnace room. When the concentration of the liquor was 49° Baumé, with a corresponding temperature of 120° C., the fluid was discharged through an iron pipe with appropriate valve control to one of a series of sheet-iron crystallizing pans which were situated on a floor located below a platform sustaining the slop tanks of the evaporators.

This pan room contained 20 square sheet-iron tanks 7 by 7 feet by 30 inches deep, arranged in two lines along the length of the floor on which they were supported. Light rails extended between the two rows of tanks, forming a track for a 1-ton rocker-type dump car. Over the pans were steam, air, and evaporator discharge pipe lines, and over some a chain-hoist mechanism for handling the crystals.

The sodium nitrite crystallized from the lye as the liquor cooled by the radiation and convection of heat from the exterior surfaces of the pan. An air jet forced through a small iron pipe into the liquor accelerated the cooling effect, principally by causing rapid currents of liquor to wash the comparatively cold interior surfaces of the tanks.

When the pan contents had cooled to approximately 50° C., a cylindrical screen about 12 inches in diameter by 20 inches high was placed over a plugged aperture in the bottom of the pan, the stopper of the aperture removed, and the mother liquor drained from the crystals. Usually about 4000 pounds of crystals were deposited in each batch.

The mother liquor drained from the crystals was discharged to mother liquor (ML) tanks and later successively retreated by evaporation and subsequent crystallization, with the recovery of more nitrite crystals until about one-half of the salt content consisted of sodium nitrate; this residuum was ultimately recovered as a by-product and sold as fertilizer. However, there was very little of the material formed and during the last year of the company's operation less than 2 tons were barreled. The general course of the treatment of the liquor is shown in Figure 3.

Ordinarily the crystals of the sodium nitrite, after draining, were transferred into the dump car from the crystallizing pan. The crystals in the filled car were then discharged to a centrifuge hopper which was set beneath the pan floor adjacent to the dump car track. The nitrite crystals were intermittently drawn from the hopper and centrifuge until the moisture content was reduced to about 1.5 per cent. The crystalline material was then dropped to a second bin, located so that its funnel was directly connected with the worm of a spiral conveyor which was used as a drier feed.

Drying

The drier was a steam-jacketed cylinder through which the material was transferred by means of a cut flight conveyor mounted on a shaft supported on bearings at the drier cylinder ends. A spout at the discharge end of the apparatus conveyed the dried crystals to paper-lined barrels in which the nitrite was generally packed.

Packing

A shaker on which the barrel was placed served to pack the crystals very compactly. Usually the packed standard barrel weighed about 450 pounds. After filling, the barrel was headed, labeled, weighed, numbered, and transferred to the storage floor, ready for shipment.

Economics of Process

The equipment and methods described were not the most modern, and the handicaps of a thirty-three mile haul to Tacoma and of the uncertainties of the power situation were serious, but the product of the plant was very good. There was generally a satisfactory market for the nitrite and during the later years of the history of the plant the costs were such that a good margin of profit was indicated.

The measure of the efficiency of a plant is not necessarily the cost sheet, but known items, when taken into consideration with the limiting conditions, are illuminative and suggestive. The following list will give some idea of relative costs when the plant was operating under fair conditions of cost and availability of power and an assumed production of 200 tons of sodium nitrite per month.

	Cost per Month	Per Cent of Total Cost
Alkali (sodium carbonate)	$7200	39.4
Labor	$2000	11.0
Power	$4104	22.4
Supplies	$1040	5.7
Packing	$ 800	4.4
Taxes	$ 166	0.9
Depreciation	$1458	8.0
Overhead and incidentals	$1500	8.2

Total per month.....$18,268
Cost per pound of nitrite.....4.55 cents

The lowest price quoted for sodium nitrite in a number of years is 6 cents per pound; but the normal price range is between 7 and 9 cents per pound.

In the past nearly all the sodium nitrite produced in the United States was used in the manufacture of azo dyes, but there is now a relatively large market developing in meat-packing industries, as a result of the discovery that this

salt is superior in some respects to sodium nitrate for use in meat preservation.

The American Nitrogen Products Company was nearing financial stability with an expanding market before it; but the plant had reached a point of growth where further improvisation was impracticable. Further progress called for reconstruction of the factory; new buildings were almost essential for continued operation and a removal of the plant to Tacoma or Seattle was eminently desirable. A department for the manufacture of the alkali used in neutralization of the nitrous acid was needed and in general a modernization of all the equipment.

Ordinarily with input of normal power there was little disturbance of continuous furnace operation, and the La Grande furnaces were a remarkably practicable electrical apparatus for the specific purpose for which they were intended, but important improvements were possible in new design and reconstruction.

The Condensation of Vapors[1,2]

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Several important theoretical contributions have been made to the subject of vapor condensation that have not been generally recognized. The contributions of Nusselt in particular show the quantitative effects of physical properties of the vapor and liquid, impurity, superheat and velocity of the vapor, and the size and shape of the surface on the transmission of heat from condensing vapors. This theory is briefly reviewed.

Application of the Nusselt theory to data on vapor condensation on the outside of horizontal tubes shows that the theory is valid for this case.

Application of the theory to data on vertical tubes shows that on long tubes, or at high temperature differences, the theory does not hold, probably owing to turbulence and drop formation. An equation for determining the start of turbulence in a film of condensate is derived, and it is shown that turbulence accounts for most of the observed deviations from the Nusselt theory.

The effects of superheat, vapor velocity, and impurities are pointed out. Several corrections to the Nusselt theory are made, especially on the effect of vapor velocity.

A CRITICAL survey of the literature on heat transfer from condensing vapors to solid surfaces shows that this subject is extremely complicated theoretically, and that experimental results to date seem to be rather inconsistent and incomplete.

A large amount of work has been done on the transfer of heat from steam to water through a metal wall, but very few investigators have measured the temperature of the metal. Therefore, in most cases only over-all coefficients of heat transfer have been obtained, which could be changed by varying conditions on either side of the metal boundary. A rough calculation of the meta' surface temperature could be made if the coefficient of heat transfer for the water side were known, but such calculations are never accurate and may lead to erroneous conclusions.

The subject of heat transfer from condensing vapors to solid surfaces has not received so much attention as that from a solid surface to a non-boiling liquid because of the experimental and theoretical difficulties. Moreover, until very recently it was not necessary to know very much about this subject, because the resistance to heat flow of the condensing vapor has been much less than the other resistances involved and often could be neglected. The application of dimensional analysis to the problem is extremely difficult because of the large number of variables and because there is a change of state from vapor to liquid.

Very recently, however, liquor velocities in evaporators and condensers have been increased to such a point that the vapor resistance is becoming of greater importance. In fact, in the experiments by Badger, Monrad, and Diamond (*4*) on the evaporation of caustic soda with diphenyl vapor, the major resistance to heat flow was on the vapor side, and the liquor resistance could be almost neglected in calculating the heat flowing. This means that any appreciable increase in the amount of heat transferred must be made by changing conditions on the vapor side.

Nomenclature

The writers have thought it advisable throughout this paper to use the symbols found most generally in American practice and at the same time not to use the same symbol for more than one property. In general the properties of the liquid are used without subscript and those of the vapor symbolized with the subscript v.

For the most part all physicists and other scientists use the c. g. s. system for the units involved, but no such agreement is found in technical practice. The European or technical metric system was for a long time based on the meter, kilogram, large calorie, second, etc., and conformed in general to the c. g. s. system except that the units of force were defined in kilograms, corresponding to grams instead of dynes in the c. g. s. system. This had a marked effect on the units of various other properties such as viscosity. More recently a mixed set of units has been used in which the hour replaced the second for many of the properties. This has led to considerable confusion.

The English system of units is in even worse condition. Very few workers use the same units, and in general all use a mixed system. Thus a very familiar example is the common Reynolds' criterion, which is supposedly a dimensionless group.

In the English system this is usually

$$\frac{Du\rho}{z} = \text{inch} \times \frac{\text{foot}}{\text{second}} \times \frac{\text{pound}}{\text{cubic foot}} \times \frac{\text{second-centimeters}}{\text{gram}}$$

If the correct units were used, the numerical value of the criterion would be independent of the particular system used. It so happens that in the technical system Reynolds' criterion must be $Du\rho/zg$ in order to be dimensionless.

A large part of this paper deals with the theoretical work of Nusselt, who used the older technical units throughout.

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In order to use Nusselt's derivations in the most simple manner, it is necessary to adopt a technical English system that is comparable with the system used by him, and, most important of all, a system in which the fundamental units are consistent.

Throughout this discussion the old technical metric system is used for fundamental calculations. The final results of heat-transfer coefficients, etc., are calculated on the hour basis by multiplying by the factor 3600. To convert to the English system, it is merely necessary to divide the value thus obtained by 4.88.

Symbol	Value	Units (Technical Metric)
a	$\frac{L\rho^2}{4\,kz(t_v - t_w)}$	....
A	$\frac{L\rho^2k^3}{z}$	....
b	$\frac{C_3w^2\rho_v}{3\rho}$	....
B	Width	m.
C	Constant	....
D	Diameter of tube	m.
E	$\frac{C_3\rho_v}{3\,\rho k}$	....
f	Friction factor	....
g	Acceleration of gravity	$\frac{\text{m.}}{\text{sec.}^2} = 9.81$
G	Weight of condensate	kg.
H	Height of wall	m.
k	Thermal conductivity	$\frac{\text{Cal.}}{\text{m.}^\circ\text{ C. sec.}}$
l	Tube length	m.
L	Latent heat	$\frac{\text{Cal.}}{\text{kg.}}$
m	Hydraulic radius	m.
P	Pressure	$\frac{\text{kg.}}{\text{m.}^2}$
Q	Heat flowing	$\frac{\text{Cal.}}{\text{m.}^2\text{ hr.}}$
r	Radius	m.
S, s_1, s_2	Friction force	$\frac{\text{kg.}}{\text{m.}^2}$
t, T	Temperature	° C., ° A.
u	Velocity, x direction	$\frac{\text{m.}}{\text{sec.}}$
U	Coefficient of heat transfer	$\frac{\text{Cal.}}{\text{m.}^2\text{ ° C. sec.}}$
v	Velocity, y direction	$\frac{\text{m.}}{\text{sec.}}$
w	Relative vapor velocity	$\frac{\text{m.}}{\text{sec.}}$
y_0	Condensate thickness	m.
z	Viscosity	$\frac{\text{kg. sec.}}{\text{m.}^2}$
θ	Temperature difference	° C.
ϕ	Angle	radians
ρ	Density	$\frac{\text{kg.}}{\text{m.}^3}$

Experimental and Theoretical Results to Date

Probably Joule (*27*) was the first one to understand clearly the fact that the major resistance to heat flow from a fluid to a solid surface is a film of nearly stagnant fluid at the interface. Both he and Lord Kelvin realized that the thickness of this film was indeterminate, since in general heat flows both by conduction and convection through the film. Kelvin suggested that, instead of "thermal conductivity," the term "heat-transfer coefficient" be used for such cases. This coefficient was defined as the amount of heat passing through unit surface in unit time with unit temperature difference.

In 1873 Reynolds (*48*) studied the effect of air on the over-all coefficients of heat transfer from steam to water. He concluded that there is no limit to the rate at which heat will flow from pure condensing steam to a metal surface except the power of the surface to carry away the heat. He found that a small amount of air in the steam has a very marked effect in decreasing the flow of heat.

From the time of Reynolds until about 1910 no significant experiments were made. A large number of investigators worked on the over-all coefficients of heat transfer from steam to water in condensers and evaporators, but these were largely tests on specific apparatus.

Since 1910 rather a large number of experiments have been made measuring the actual metal temperatures when steam was condensed on tubes. In this way the heat-transfer coefficients of the condensing vapor could be determined.

Webster (*54*), Clement and Garland (*8*), McAdams and Frost (*33*), Morris and Whitman (*37*), and Othmer (*40*) have investigated the condensation of steam on the outside of a horizontal tube. McAdams and Frost also reported experiments on benzene and carbon tetrachloride. Jakob, Erk, and Eck (*24*) have studied steam condensation inside a horizontal tube.

Jordan (*25*), Callendar and Nicolson (*6*), Philipp (*42*), and Jakob and Erk (*22*) have studied steam condensation on vertical tubes. Badger, Monrad, and Diamond (*4*) have reported results obtained with diphenyl vapor condensing at high temperature differences on a long vertical tube.

Othmer (*40*), Merkel (*35*), Josse (*26*), Arzoomanian and Alpert (*1*), Kerr (*29*) and Robinson (*49*), Chambers and Eskew (*7*) and very recently Colburn and Hougen (*9*) have studied the effect of air on the condensation of steam.

The effects of vapor velocity have been studied experimentally by several of the above investigators, but no very definite conclusions were reached. The effect of superheat of the vapor has been studied by Jakob and Erk (*22*) and shown to have a very small effect on the transfer of heat.

In 1916 Nusselt (*38*) in an excellent mathematical paper, studied the effects of vapor and liquid properties, shape of the surface, and the purity and superheat of the vapor on the condensation of any vapor on a solid surface. This paper has not received the attention it merits, possibly because it has not been abstracted in this country.

Note—The authors have found that a large amount of foreign literature on such subjects as heat transfer, fluid motion, diffusion, etc., has not been abstracted in English. Considerable advances in these fields have been made in Germany during the past twenty years that have never been noticed by the abstracting journals. It is especially to be noted that only very recently *Chemical Abstracts* has been covering these fields to any extent and thus should not be relied upon solely. Some additional information may be obtained in the *Engineering Index* and the *Industrial Arts Index*, but these subjects are covered most completely in the *Technische Zeitschriftenschau*.

This theory will be reviewed in some detail as it is of fundamental importance. Application of this theory to experimental work of the authors and others will be shown.

In 1925 Stender (*52*) applied Nusselt's theory to superheated steam and calculated several formulas for this case. Merkel (*34*), Gröber (*15*) and ten Bosch (*5*) give excellent summaries of Nusselt's work on the condensation of vapors.

In 1920 Parr (*41*) calculated steam-film coefficients on somewhat different assumptions than Nusselt but using the same general idea. His assumptions did not hold for conditions actually found in practice as well as those of Nusselt; and the treatment was not nearly so thorough. A brief comparison of the two theories is given by Jakob (*21*).

Nusselt's Theory of Condensation of Vapors

CASES CONSIDERED AND FUNDAMENTAL ASSUMPTIONS—Nusselt considered the following five fundamental cases:

(1) Vapor condensing on a smooth, plane surface making the angle ϕ with the horizontal, assuming that the vapor is pure and saturated and relatively stationary with respect to the condensate.
(2) Vapor condensing on the outside of a horizontal tube under the above conditions.
(3) Vapor condensing on surface as in (1) but with appreciable vapor velocity.
(4) Superheated vapor condensing on any surface.
(5) Vapor condensing on any surface, vapor impure.

Nusselt first pointed out that surface tension of the condensate can have no effect on the thickness of film formed, and this thickness may be calculated from hydrodynamical considerations.

In order to simplify the mathematical treatment, Nusselt made several assumptions, some of which he was later able to prove. These assumptions should be clearly borne in mind throughout the discussion and are essentially as follows:

(1) The film of condensate is so thin that the temperature gradient through it is a straight line.
(2) The heat is all carried to the metal surface by pure conduction in the direction perpendicular to the surface.
(3) Physical properties of the condensate may be taken at the mean film temperature.
(4) The surface is relatively smooth and clean.
(5) The film of condensate always moves in viscous motion.
(6) The curvature of the film may be neglected.
(7) The temperature of the solid surface is constant.

CASE 1. VAPOR CONDENSING ON INCLINED TUBE OR WALL—Consider a wall making the angle ϕ with the horizontal and kept at a uniform temperature t_w. Saturated pure vapor at a temperature t_v is condensing on this surface. Let x be the direction parallel to the wall and y the direction perpendicular to it—i. e., through the condensate film.

At any point in the condensed film a shear stress, S, is set up owing to the viscosity of the condensate and the variation of velocity of the condensate with distance from the wall.

$$S = z\frac{du}{dy}$$

and

$$dS = z\frac{d^2u}{dy^2}\,dy$$

If ρ is the density of the condensate, the differential shear stress set up as above must be counterbalanced by the differential weight of the condensate tending to pull the condensate downward, or

$$dS + \rho \sin\phi\, dy = 0$$

and

$$\frac{d^2u}{dy^2} = -\frac{\rho}{z}\sin\phi$$

This integrates at once to

$$u = -\frac{\rho \sin\phi y^2}{2z} + C_1 y + C_2$$

Since at $y = 0$, $u = 0$; therefore $C_2 = 0$, and if the vapor is stationary there is no force tending to shear the condensate at the surface and

$$z\frac{du}{dy} = 0, \text{ at } y = y_0$$

Thus

$$\frac{du}{dy} = 0$$

and

$$C_1 = \frac{\rho \sin\phi y_0}{z}$$

Therefore

$$u = \frac{\rho \sin\phi}{2z}(2y\,y_0 - y^2)$$

The mean condensate velocity, u_m, at any point down the wall x is given by the following equation:

$$u_m = \frac{1}{y_0}\int_0^{y_0} u\,dy = \frac{\rho}{3z}y^2_0 \sin\phi$$

If k is the thermal conductivity of the condensate, then the heat passing through unit surface in unit time at the point x is

$$Q = \frac{k}{y_0}(t_v - t_w)$$

If L is the latent heat and G the weight of vapor condensed, then

$$G = \frac{k}{Ly_0}(t_v - t_w)$$

represents the amount of vapor condensed on unit surface in unit time.

For simplicity consider a vertical wall of width B and height H. In a unit time the amount of condensate flowing past a point x down the wall is

$$\rho\, u_m\, y_0\, B = \frac{\rho^2 B y^3_0}{3z}$$

At dx lower

$$\rho\, Bd\,(u_m y_0) = \frac{\rho^2\, B\, y^2_0\, dy_0}{z}$$

more condensate flows downward. This differential amount of condensate must be due to the vapor condensed in the strip $B\,dx$, or

$$dG = \frac{k(t_v - t_w)B\,dx}{Ly_0}$$

or

$$\frac{k(t_v - t_w)dx}{Ly_0} = \frac{\rho^2\, y^2_0\, dy_0}{z}$$

Therefore

$$x = \frac{L\rho^2\, y^4_0}{4\,kz(t_v - t_w)} + C$$

Since at $x = 0$, no liquid runs down from above, $C = 0$, and

$$y_0 = \sqrt[4]{\frac{4\,kz(t_v - t_w)x}{L\rho^2}}$$

Thus Q at the point x =

$$Q_x = \sqrt[4]{\frac{L\rho^2k^3(t_v - t_w)^3}{4zx}}$$

If the heat-transfer coefficient, U_v, is defined by the equation

$$Q_x = U_v(t_v - t_w)$$

then

$$U_v = \sqrt[4]{\frac{L\rho^2k^3}{4\,zx(t_v - t_w)}} \text{ at the point } x$$

To obtain a mean coefficient it is necessary to integrate Q_x over the length H and the width B.

$$\text{Therefore } BQH = B\int_0^H Q_x dx = \frac{4}{3}B\sqrt[4]{\frac{L\rho^2k^3H^3(t_v - t_w)^3}{4\,z}}$$

$$\text{or}\quad U'_{m_v} = \frac{4}{3}\sqrt[4]{\frac{L\rho^2k^3}{4\,zH(t_v - t_w)}} = \frac{0.943\sqrt[4]{A}}{\sqrt[4]{H(t_v - t_w)}} \qquad (1)$$

where $A = L\rho^2k^3/z$ and is a function of the condensate

properties alone. It may be plotted versus temperature for any fluid.

If the wall is at the angle ϕ with the horizontal

$$U'_{m_v} = 0.943 \sqrt[4]{\frac{L\rho^2 k^3 \sin\phi}{z\,H\,(t_v - t_w)}} \qquad (1a)$$

Nusselt showed that from the equation of continuity there is a component of condensate velocity toward the wall, and therefore some heat is carried by convection to a point nearer the wall. This velocity may be calculated and the heat carried in this manner is found to be negligible. The error caused by neglecting this effect is doubtless no greater than that due to the assumption of a straight-line temperature gradient through the film.

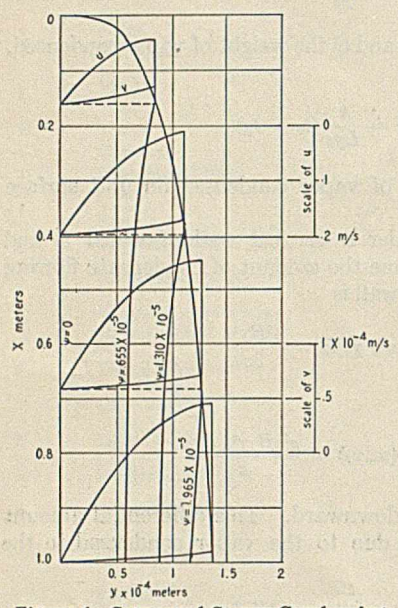

Figure 1—Saturated Steam Condensing on Wall 1 Meter High (Nusselt)

Figure 1 shows Nusselt's theory applied to saturated steam condensing on a vertical wall 1 meter high. The vapor temperature is 100° C., and the wall 90° C. The condensate thickness at any point is shown by the curve starting at $x = 0$. At four points on the wall the velocity components of the condensate in the x and y direction are given by the curves labeled u and v, the scales of which are indicated at the right. Four stream lines are shown labeled as ψ = constant, and these indicate the path of the condensate as it moves down the tube. It is apparent that condensation is very rapid at the top of the wall and gradually becomes less.

Nusselt pointed out that, since there is a temperature gradient in the film, some sensible heat is given up by the condensate and the above calculation is somewhat in error. The error is never more than 1 to 3 per cent even at very high temperature differences. He has developed a more exact formula which is of very little practical significance.

Case 2. Vapor Condensing on Horizontal Tube—For horizontal tubes the same assumptions are made as above, but it is necessary to consider the force of gravity acting in the direction tangential to the tube surface. Nusselt found that the average coefficient over the whole tube may be given as

$$U_{m_v} = 0.8024 \sqrt[4]{\frac{2L\rho^2 k^3}{3zD(t_v - t_w)}} = \frac{0.725\sqrt[4]{A}}{\sqrt[4]{D(t_v - t_w)}} \qquad (2)$$

where D is the diameter of the tube.

Note—Colburn and Hougen (*9*) have mentioned this equation and calculated the constant to be 0.61 instead of 0.725. This was apparently due to the omission of the fourth root of 2.

$$\left(0.8024\sqrt[4]{\frac{1}{3}} = 0.61, \text{ but } 0.8024\sqrt[4]{\frac{2}{3}} = 0.725\right)$$

The upper half of the tube condenses 59.4 per cent of the vapor if no condensate flows from tubes above. If tubes are in banks and the condensate from one drips on the one below, the coefficient is decreased. For the case of a tube directly below a single tube the constant in Equation 2 becomes 0.545, and becomes still less for tubes lower in the bank.

Nusselt applied Equation 2 to the experiments of English and Donkin (*13*) and found fair agreement in the case of smooth tubes, although these experiments were made on very crude apparatus and could not be expected to give very accurate results. The agreement between theory and experiment was of the order of magnitude of ±20 per cent.

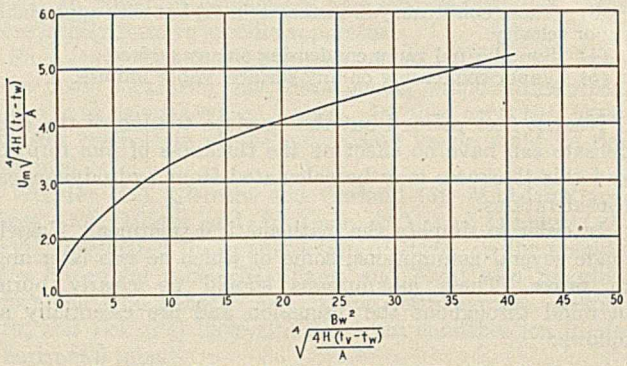

Figure 2—Effect of Vapor Velocity (Ten Bosch)

Case 3. Effect of Vapor Velocity—If vapor is moving with a velocity w with respect to the outside of the condensate film on a vertical wall or tube, the constant C_1 can no longer be determined from the condition that there is no shearing force at the surface, since the vapor exerts a force S per unit area on the condensate surface.

For the case of steam flowing through a tube or pipe Nusselt was able to calculate the constant C_1 by considering the pressure drop through the tube. The experiments of Eberle (*11*) showed that

$$\frac{dP}{dl} = \frac{C_3 u_v^2 \rho_v}{D}$$

where $C_3 = 10.5 \times 10^{-4}$ sec./m.

The subscript v refers to the vapor.

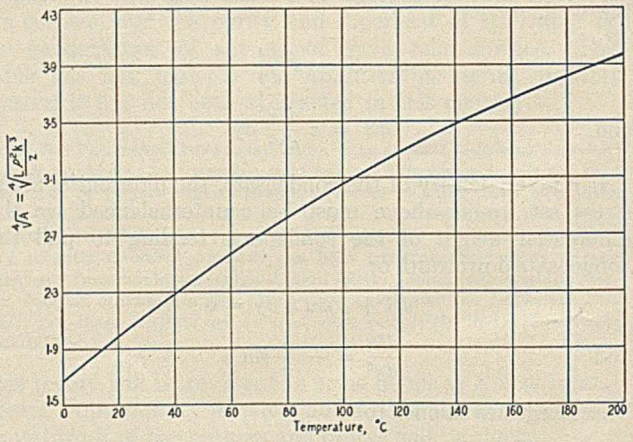

Figure 3—$\sqrt[4]{\frac{L\rho^2k^3}{z}}$ for Water (Old Technical Metric Units)

Since the friction forces on the tube circumference must equal the pressure forces on the tube cross section,

$$S\pi D = \frac{\pi D^2}{4}\frac{dP}{dl}$$

and

$$S = \frac{C_3 w^2 \rho_v}{4} \text{ if } w = u_v$$

Therefore

$$S = \frac{\pm C_3 w^2 \rho_v}{4} = z\frac{du}{dy} = -\rho y_0 \sin\phi + C_1 z$$

or $$C_1 = \frac{\pm C_3 w^2 \rho_v}{4z} + \frac{\rho y_0}{z} \sin \phi$$

If the steam velocity is in the direction of the condensate drainage the positive sign is used, and the negative if the flows are countercurrent.

Proceeding in general as with stationary vapor, Nusselt was able to show that

$$\frac{U_{m_v}}{k} \sqrt[4]{\frac{H}{a}} = \text{function of } \sqrt[4]{\frac{b}{a}}$$

where $$a = \frac{L\rho^2}{4\,kz(t_v - t_w)}$$

and $$b = \frac{C_3 w^2 \rho_v}{3\rho}$$

Ten Bosch (*5*) has pointed out that if the above relationship is true, then

$$U_{m_v} \sqrt[4]{\frac{4H}{A}(t_v - t_w)} = \text{function of } \sqrt[4]{\frac{Ew^2}{\frac{4H}{A}(t_v - t_w)}}$$

where $$A = \frac{L\rho^2 k^3}{z}$$

and $$E = \frac{b}{kw^2} = \frac{C_3 \rho_v}{3\rho k}$$

This function is shown in Figure 2 for concurrent flow of vapor and condensate. The value of $\sqrt[4]{A}$ is shown for water in Figure 3 in metric units. (L may be taken at mean film temperature for small temperature differences.)

Nusselt discussed several very interesting cases for the flow of vapor countercurrent to condensate drainage and showed that sometimes all or part of the condensate is carried to the top of the wall. It is necessary to use very high vapor velocities in order to do this, and such cases would seldom be found in commercial practice.

Nusselt did not attempt to apply the theory described above to any other vapor than steam and only then in the case of steam condensing inside of a tube since the constant C_3 was unknown in all other cases. This is discussed later, and a method shown by means of which the effect of velocity of any vapor in any cross section may be calculated.

Case 4. Effect of Superheat—There are two subcases to the case of heat transfer from superheated vapor. When the wall temperature is above that of saturated vapor at the given pressure, no vapor will condense and the heat transfer will be the usual one from a gas or vapor to a solid surface. When the wall temperature is less than that of saturated vapor, condensation will take place, but the phenomenon is not the same as in the case of saturated vapor. There is a temperature difference between the vapor and the surface of the condensate corresponding to the degrees of superheat. Heat is carried to this interface by the usual gas-solid method. Thus if U_s is the heat-transfer coefficient from vapor to interface,

$$U_s(t_s - t_v)dx + \frac{L\rho^2 y^2_0 dy_0}{z} = \frac{k}{y_0}(t_v - t_w)dx$$

or $$\frac{dy_0}{dx} = \frac{kz(t_v - t_w)}{L\rho^2 y^3_0}\left[1 - U_s \frac{(t_s - t_v)y_0}{k(t_v - t_w)}\right]$$

If $$h = \frac{U_s(t_s - t_v)}{k(t_v - t_w)}$$

then $$x = \frac{L\rho^2}{kz(t_v - t_w)}\left[\frac{1}{h^4}\log\frac{1}{1 - hy_0} - \frac{y^3_0}{3h} - \frac{y^2_0}{2h^2} - \frac{y_0}{h^3}\right]$$

Since $hy_0 < 1$, the logarithm may be expanded into a power series,

or $$x = \frac{L\rho^2}{kz(t_v - t_w)}\left[\frac{y^4_0}{4} + \frac{hy^5_0}{5} + \frac{h^2y^6_0}{6} + \frac{h^3y^7_0}{7} + \dots\right]$$

Note—In the original article Nusselt had $-y^3_0/h^3$ and y^4_0/h instead of $-y_0/h^3$ and $y^4_0/4$. This was probably due to a typographical error. Obviously if h becomes zero (no superheat), the equations should degenerate into the one previously calculated for saturated steam.

This complicated power series is not satisfactory to use in practice. Recently Stender (*52*) and Merkel (*34*) have shown that a very good approximation may be made, since the amount of heat flowing is proportional to the condensate thickness and to the cube root of the amount of condensate if t_v and t_w are the same. Therefore

$$\frac{Q_s}{Q} = \frac{y_0}{y_{0_s}} = \sqrt[3]{\frac{G}{G_s}} = \beta$$

where the values with the subscript s refer to the condensation of superheated vapor and those without subscript to the saturated vapor. β has been shown by Merkel to be a function of $\frac{U_s(t_s - t_v)}{U(t_v - t_w)}$ alone and may be plotted as in Figure 4. U_s must be calculated as the usual heat-transfer coefficient from a superheated vapor or gas to a wall, and depends on the velocity, temperature, etc.

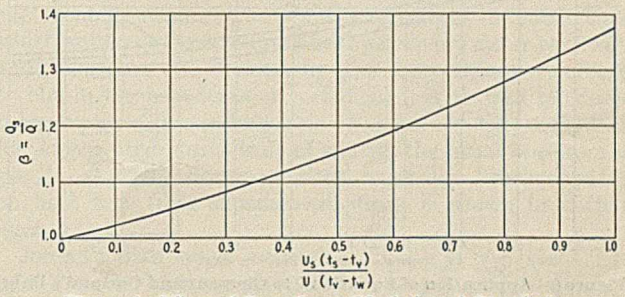

Figure 4—Effect of Superheat (Merkel and Stender)

For an example, consider the condensation of saturated steam on a vertical wall 0.5 meter high; vapor at 100° C.; temperature difference to wall, 5° C. The mean film temperature = 97.5° C., and therefore from Figure 3

$$U = \frac{0.943}{\sqrt[4]{0.5 \times 5}} \times 3.03 \times 3600 = 8190 \text{ Cal./m}^2\text{/hr./°C.}$$

Let the vapor be superheated to 200° C. Then $t_s - t_v$ = 100° C., and $t_v - t_w$ = 5° C. Assume that U_s = 50. Then

$$\frac{U_s(t_s - t_w)}{U(t_v - t_w)} = 0.1220$$

and from Figure 4 the ratio of the amount of heat flowing to that with saturated steam is 1.032. Thus, there is only a 3 per cent increase in the amount of heat, which is nearly negligible. If the steam velocity is increased, the value of U_s is increased and the effect of superheat is greater.

Case 5. Effect of Non-Condensable Gases—The effect of non-condensable gases on the heat-transfer coefficient is very important technically. However, exact calculation of the effect is very difficult and Nusselt merely indicated a general method. Colburn and Hougen have recently attacked this problem theoretically and experimentally with some definite results.

Applications of Nusselt's Theory

Case 2. Vapor Condensing on Horizontal Tube—The condensation of pure saturated vapors on the outside of a horizontal tube has been studied experimentally by McAdams and Frost (*35*), Morris and Whitman (*37*), Clement and Garland (*8*), Othmer (*40*), Webster (*54*) and several others.

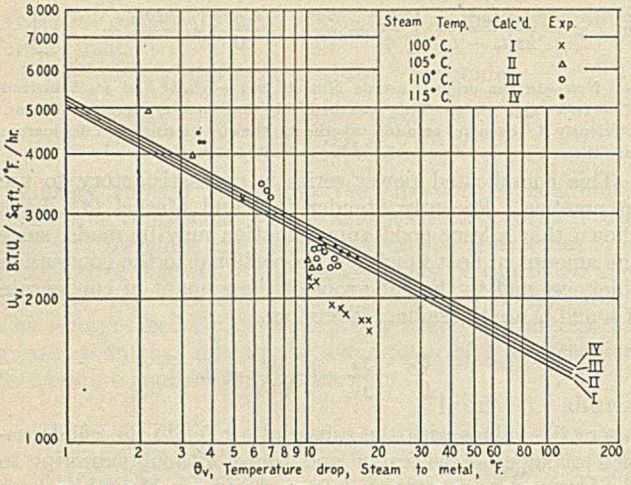

Figure 5—Application of Equation 2 to Othmer's Data

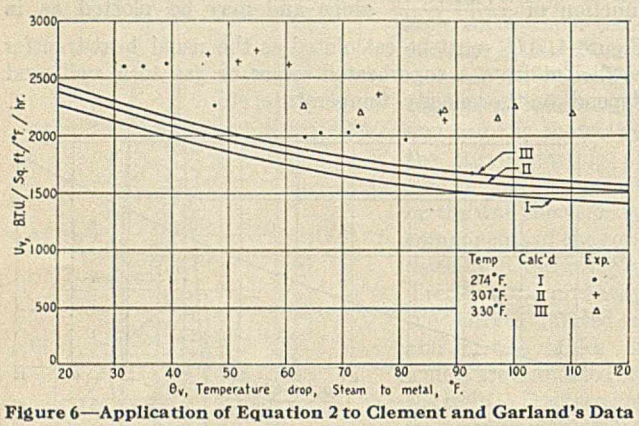

Figure 6—Application of Equation 2 to Clement and Garland's Data

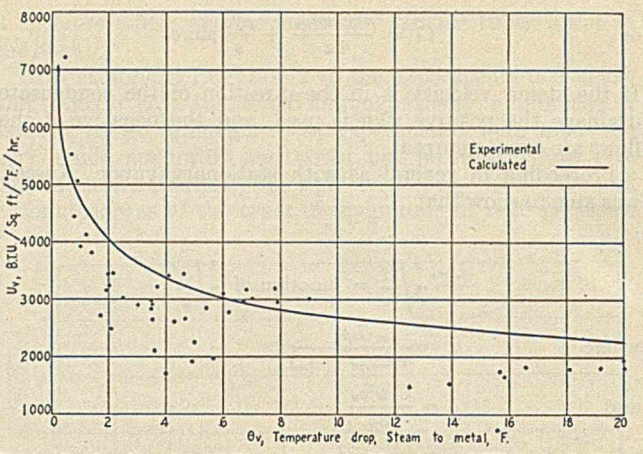

Figure 7—Application of Equation 2 to Morris and Whitman's Data

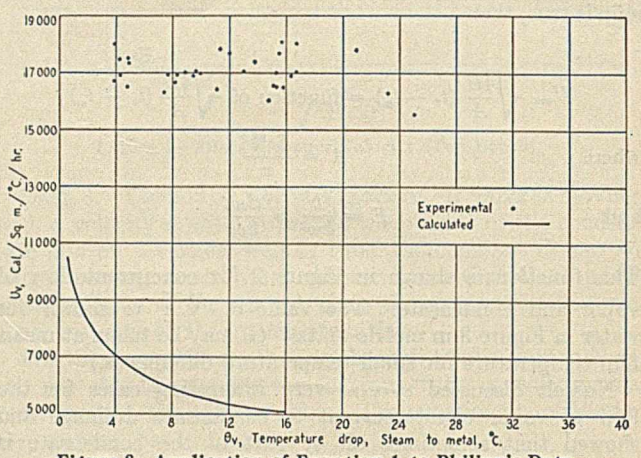

Figure 8—Application of Equation 1 to Philipp's Data

Figure 5 shows Nusselt's Equation 2 applied to Othmer's data for approximately pure steam. The vapor velocity was in all cases very small and its effect should be negligible in all of Othmer's work. This is apparently true, as the experimental data check the theory almost within the experimental error. For high temperature differences Othmer's data spread for different steam temperatures and do not follow the theoretical curves very well. It seems scarcely plausible that a change of only 15° C. in the temperature of the steam could have as great an effect on the coefficient as that indicated by the data. The experimental difficulties in obtaining pure steam probably account for most of the discrepancy between theory and experiment.

Of even greater interest, perhaps, is the application of the theory to the data of McAdams and Frost on steam, benzene, and carbon tetrachloride, as shown in Table I. The experimental data on steam check the theoretical values more closely than those of Othmer's except for one point, which is probably too high. The checks on carbon tetrachloride and benzene are especially interesting, as no satisfactory explanation of the data has appeared previously. McAdams and Frost atempted a rough correlation by assuming that the coefficient increased with the first power of the thermal conductivity and fluidity of the condensate. This was admittedly empirical and very unsatisfactory for the prediction of coefficients of even the same vapors under different conditions. Actually the coefficient varies as the three-quarter power of the thermal conductivity and as the fourth root of the fluidity. In addition many other important factors, such as density and latent heat of the liquid and the size and shape of the tube, have a great effect.

Clement and Garland had an indefinite amount of steam blowing out continuously in their experiments. This probably accounts for the fact that their coefficients are about 30 per cent above those calculated by Nusselt's equation. (Figure 6)

Table I—Nusselt's Theory Applied to Data of McAdams and Frost
(Tube 0.675 inch o. d. = 0.01715 meter)

Run	Av. Vapor Temp. °C.	Av. Temp. Diff. °C.	Approx. Film Temp. °C.	U_v Expt. B. t. u./sq. ft./° F./hr.	U_v Calcd. B. t. u./sq. ft./° F./hr.
H_2O	99.3	19.3	89	2190	2075
H_2O	102.3	20.6	90	2110	2045
H_2O	105.1	23.7	93	2060	1990
H_2O	100.5	22.1	89	2150	1995
H_2O	116.0	12.0	110	3360	2535
H_2O	99.7	13.4	94	2310	2319
H_2O	99.1	12.4	93	2475	2360
CCl_4[a]	75.1	14.8	67	283	303
Benzene[a]	78.4	15.5	69	306	375
Benzene[a]	78.9	12.6	72	366	396

[a] It was found impossible to obtain accurate values for the thermal conductivities of carbon tetrachloride and benzene, as no two investigators agree within 20 per cent. The values used by McAdams and Frost were used here as they appeared to be the average values in the literature.

The effect of vapor velocity outside a tube and at right angles to the condensate drainage was not calculated by Nusselt. It is apparent that the calculation would be extremely tedious in such a complicated case and the results would be doubtful.

Webster's data afford a good experimental basis on which to calculate the effect of vapor flow at right angles to the condensate flow. His data are somewhat higher than those calculated from Equation 2, because of the high velocities used. Very few practical applications will be found in which such high velocities are used.

Morris and Whitman heated oils with steam and it was possible to calculate the steam-film coefficient from their data. Since in most cases their temperature differences between steam and tube surface were low, the coefficients

obtained from their data are probably not very accurate. In general their data were about 20 per cent lower than the theoretical. (Figure 7)

For the case of vapors condensing on the outside of horizontal tubes, therefore, it appears that the assumptions made by Nusselt are quite well fulfilled in practice under ordinary conditions if proper venting of non-condensable gases is insured. However, the vapor must be relatively stationary and the tube surface smooth and clean. Under these conditions the coefficient of heat transfer may be calculated for any vapor within a probable accuracy of 10 per cent, if the physical properties of the vapor are known.

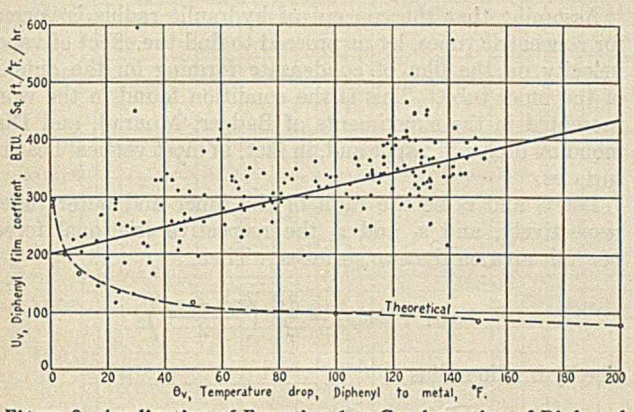

Figure 9—Application of Equation 1 to Condensation of Diphenyl

For vapors condensing inside horizontal tubes no theoretical equation has been developed. Removal of the condensate is by means of a slight inclination of the tube and the use of high vapor velocities. The work of Jakob, Erk, and Eck gives experimental data for this case that may be used with proper caution for the prediction of coefficients.

Cases 1 and 3. Stationary or Moving Vapor Condensing on Inclined Wall—Not many data are available to check the theory for the case of vapors condensing on a tube or a vertical or inclined wall. The data of Philipp (*42*), Callendar and Nicolson (*6*), Jordan (*25*), Jakob and Erk (*22*) on steam, and of Badger, Monrad, and Diamond (*4*) on diphenyl vapor are the only ones that the authors have found that may be relied upon.

Philipp's data were rather erratic, and in only one series of runs was it possible to obtain consistent results. The coefficient obtained by him for steam at 99° C. condensing on a 4-foot tube was about 3480 in English units. The 6- and 8-foot sections gave him about the same value independent of temperature difference. The steam velocities used by him were very low (less than 30 feet per second), and according to Nusselt's theory should have had a negligible effect. In several series of runs he found an increase in coefficient with temperature difference. Figure 8 shows his experimental results at 99° C. and Nusselt's theoretical curve (Equation 1) for his 4-foot length. It is apparent from the curve that Nusselt's theory does not hold and gives values that are much too low at high temperature differences.

Callendar and Nicolson's experiments on a 2-foot vertical thick-walled tube gave coefficients roughly about 2700 when a temperature difference of about 30° F. was used. According to Nusselt the coefficient should be

$$U_v = \frac{0.943\sqrt[4]{A}}{\sqrt[4]{H(t_v - t_w)}} = \frac{0.943 \times 2.97 \times 3600}{\sqrt[4]{0.609 \times 16.7}} = 5270 \text{ (new metric) or } = 1169 \text{ (English)}$$

Thus the experimental values are more than twice the theoretical based on zero steam velocity. No data were given concerning the velocities, but they were probably not very high.

Results were obtained in a 1/4-inch diameter platinum tube that were at least twice the theoretical, even when the flow of steam was countercurrent to condensate drainage; in fact, even higher results were obtained in the latter case. It appeared to Callendar and Nicolson that when steam is condensing on the outside of very small tubes moving drops of water are formed which aid rather than retard the flow of heat, owing possibly to the increased surface.

In the experiments on diphenyl by Badger, Monrad, and Diamond (*4*) the vapor coefficient was found to increase markedly with temperature difference and to be independent of temperature, whereas the theory gave a curve that showed a rapid decrease in coefficient with temperature difference. From Figure 9 it is obvious that the vapor velocity is not sufficient to explain the fivefold increase in coefficient. This will be shown later.

Jakob and Erk found that for their short tube (0.466 meter) Nusselt's theory gave rather fair results, but not by any means exact. In all cases the theoretical results were high, whereas in other work on longer vertical tubes the theory gives low results. Figures 10 and 11 show the results obtained by Jakob and Erk with saturated and superheated steam. The data are shown in solid lines which represent the amount of heat per square meter per hour, and thus must be divided by the temperature difference to obtain the heat-transfer coefficient. With wall temperatures above the condensation temperature the coefficient for superheated steam was, of course, the usual one from a gas to a solid. Some previous work by Poensgen (*43*) on heat flow from superheated steam is shown in dotted lines.

Jordan's data on a vertical tube 1 meter long are given in Figure 12 and Nusselt's theoretical curves are also plotted. It is apparent that the data check the theory qualitatively at low vapor velocities, but not at high. At extremely low velocities the theoretical results are high. This agrees to some extent with the conclusions of Jakob and Erk.

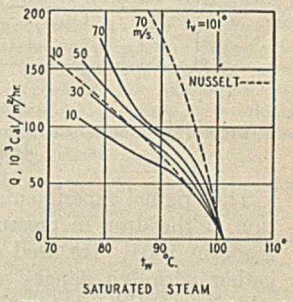

Figure 10—Condensation of Saturated Steam from Data of Jakob and Erk

Apparently, therefore, one or more of the assumptions made by Nusselt does not hold for rather long vertical tubes when temperature differences of any magnitude are used. According to Nusselt the use of a horizontal tube is preferable, especially when the tubes are long and high temperature differences are used, but experiment tends to show that vertical tubes are to be preferred under these conditions.

Limitations and Corrections of Nusselt's Theory

Whether it is permissible to use the mean film temperature for fluid properties is not clear at present. At high temperature differences and with fluids whose properties change very markedly with temperature, it may be better to recalculate Nusselt's equations using these properties as variables. However, the assumption of a linear temperature gradient in the film as well as that of a smooth surface probably leads to as much as, if not more error than, that of mean fluid temperature.

Effect of Vapor Velocity inside Circular Tube—One point in Nusselt's derivation was found to be obviously in error. In calculating the pressure drop due to steam flowing through a circular tube, the use of some equation

such as the following has been shown to be exact for all fluids:

$$\frac{dP}{dl} = \frac{2f\rho u^2}{g\ D}$$

where f = friction factor
ρ = fluid density
u = fluid velocity
g = acceleration of gravity
D = tube diameter
P = pressure
l = tube length

The friction factor, f, has been shown to be a function of Reynolds' criterion, which is the dimensionless group $Du\rho/zg$. f is the same for the same values of this criterion, and may be obtained quite exactly from Jakob and Erk's (*20*) equation

$$f = 0.00714 + 0.610\ Re^{-0.35}$$

where Re is the Reynolds' criterion calculated on the diameter of the tube. It is obvious that Nusselt's constant C_3 is equal to $f/2g$, and is, accordingly, not a constant, but a function of Reynolds' criterion. Moreover, this calculation of C_3 is valid, not only for steam, but for all fluids.

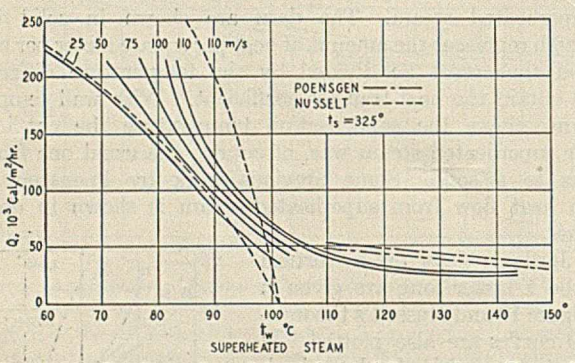

Figure 11—Condensation of Superheated Steam from Data of Jakob and Erk

The original experiments by Eberle (*11*) on the determination of the drop in pressure of steam through a tube were made in 1908. He used a combination of pipes joined together with ten flanges and three right-angled bends. In addition to this, every time a high velocity was used the corresponding pressure of the steam was low, and the value of Reynolds' criterion was approximately constant, since the viscosity of the vapor is fairly constant. Naturally, the friction factor was found to be even more constant, as it varies approximately with the fourth root of Re. Eberle stated that previous work had shown the constant to be as high as 15×10^{-4} second per meter, but that his experiments showed conclusively that the value was about 10.5×10^{-4}. In all probability both experimenters were correct since C_3 is not a constant.

It is apparent that the so-called effect of vapor velocity on the heat-transfer coefficient is really the effect of frictional forces on the surface of the condensate. The factor "'velocity" is rather a poor one, since with the same velocity the frictional forces may be quite different. Thus a certain velocity inside a tube has a much different effect from the same velocity outside a tube, or in fact in a different tube.

Effect of Vapor Velocity in Cross Sections Other Than Circular—For vapor condensing inside a circular tube the above method of the calculation of the effect of velocity is valid, provided all the assumptions made are true. With the vapor condensing outside a circular tube, or in fact in any other cross section, the problem is quite different. It has been shown (*2, 20, 50, 14, 18*) that for a first approximation the pressure drop through any cross section may be calculated from the following equation if the fluid is in turbulent motion:

$$\frac{dP}{dl} = \frac{f\rho u^2}{2gm}$$

where m is the so-called hydraulic radius which is defined as the ratio of the free cross-sectional area divided by the wetted perimeter. Thus in a circular tube the value of m is $^1/_4\ D$. Many cross sections have been used—circular, annular, star, rectangular, open channels, etc.—and the results have been fairly consistent. (Figure 13)

Assuming that the concept of hydraulic radius is correct for concentric tubes, let us proceed to find the effect of vapor velocity on the film of condensate forming on the outside of the inner tube. This is the condition found in the work presented in the experiments of Badger, Monrad, and Diamond on diphenyl vapor and, in fact, in most vertical heating surfaces.

Let r_1 and r_2 be the radii of the inner and outer tubes, respectively, and s_1 and s_2 the respective frictional forces per unit area on the two surfaces. Then,

$$2\pi s_1 r_1 + 2\pi s_2 r_2 = \frac{dP}{dl}\left(\frac{r_1^2 - r_2^2}{2}\right)\pi$$

The hydraulic radius

$$m = \frac{(r_1^2 - r_2^2)\pi}{2\pi(r_1 + r_2)} = \frac{r_1 - r_2}{2}$$

and $$S = \frac{dP}{dl} \times m, \text{ if } s_1 = s_2 \text{ and } S = \frac{f\rho_v u_v^2}{2g}$$

If s_1 and s_2 are the same, it is easy to calculate the force on the outer part of the condensate. There is nothing to show that they should be alike, but it is very probable that they are if the concept of hydraulic radius holds. Doubtless they are of the same order of magnitude, at least, and some idea of the effect of vapor velocity may be obtained.

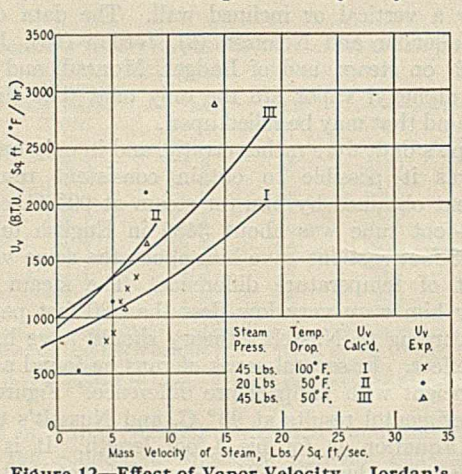

Figure 12—Effect of Vapor Velocity. Jordan's Data

The effect of vapor velocity on the coefficients reported on diphenyl were calculated on the above assumption. In the case showing the greatest effect, the coefficient was raised about 9 per cent, whereas the actual difference to be accounted for was about 400 per cent. Thus it is apparent that the effect of vapor velocity alone is not enough to account for the discrepancy between theory and experiment.

Effect of Turbulence in Film—Of much greater importance than the effect of vapor velocity is the effect of turbulence in the fluid film of condensate. Apparently no one has considered the possibility of turbulence except

at the end of very long tubes. The authors have derived an approximate equation for the calculation of the point at which turbulence commences, and have shown that the observed deviations from Nusselt's theory may be explained by the phenomenon of turbulence.

A large number of attempts have been made to determine theoretically the start of turbulence between two parallel infinite planes when a fluid is placed between them of thickness d and the planes move with a velocity u, with respect to one another. Reynolds (*47*), Lorentz (*30*), Rayleigh (*45*, *46*), Kelvin (*28*), Orr (*39*), Sommerfeld (*51*), von Mises

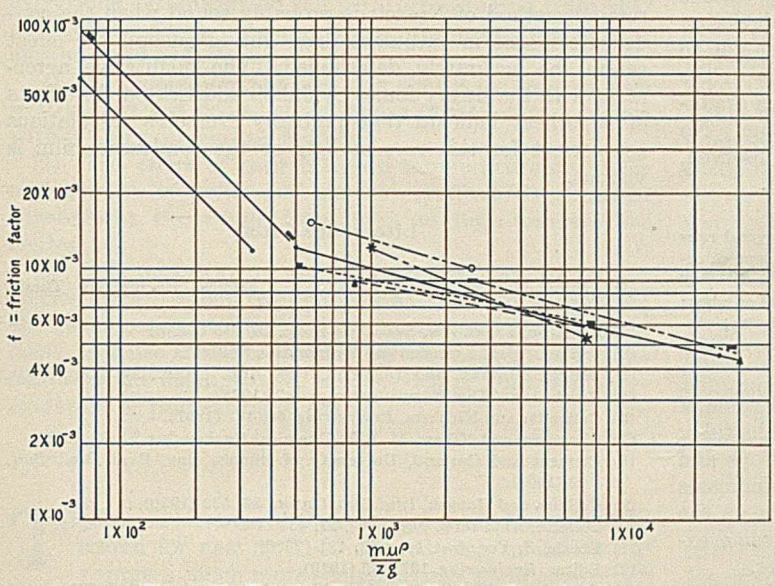

Figure 13—Friction Factor in Various Cross Sections

(*36*), Hopf (*19*), and more recently Heisenberg (*17*) and Lorenz (*31*) have studied this question mathematically. It is obviously impossible to make an experimental study of this case except very approximately owing to edge effects.

Nearly all investigators agree that turbulence should start at some value of Reynolds' criterion. Very little agreement is found in the value of the critical criterion except in the case of the work of Lorenz and Heisenberg. These two men give the value $du\rho/zg$ = 1560 (approximately), and determined it by two different methods; although Lorenz states that he cannot follow the reasoning of Heisenberg. Other workers in the field give values of the criterion from 250 to 2000, but recent work has shown that the low results are in error. Probably the value of 1560 is about correct.

Couette (*10*), Mallock (*32*), Taylor (*53*), and Harrison (*16*) have studied experimentally and theoretically the critical velocity when liquid is placed between two concentric cylinders, one or both of which are rotating. It was found in all cases that instability begins at some definite value of Reynolds' criterion.

Hopf (*20*) points out that turbulence begins for all shapes of conduits at about the same value of Reynolds' criterion when the so-called hydraulic radius is substituted in place of D (or d). The criterion becomes $mu_m\rho/zg$, in which u_m is the mean velocity. In most cases the critical criterion is between 300 and 400. Thus for parallel plates it is 390, for open channels 300, for rectangular channels 300 to 500, and for circular tubes 500. Since the flow of fluid down a wall is similar to that between two plates and in an open channel, the value of the critical Reynolds' criterion was assumed to be 350.

Nusselt's equation for the velocity at any point for the flow of condensate down a vertical tube is given by the equation

$$u = \frac{\rho}{z}\left(y_0 y - \frac{y^2}{2}\right)$$

At $$y = y_0,\ u = \frac{\rho}{z} \times \frac{y^2_0}{2},\ \text{and}\ u_m = 2/3\ u$$

Therefore in technical units

$$\frac{y_0 u_m \rho}{gz} = 350 = y_0 \frac{\rho y^2_0 \rho}{3\ zgz} = \frac{\rho^2}{3\ gz^2}\left[\frac{4kzx_c(t_v - t_w)}{L\rho^2}\right]^{3/4}$$

Therefore $$x_c = \frac{2668\ Lz^{5/3}g^{4/3}}{\rho^{2/3}k(t_v - t_w)}$$

x_c is the distance down the tube or wall at which turbulence may be expected to begin if the vapor is relatively stationary.

For water at 1 atmosphere and 10° C. temperature drop,

$$x_c = \frac{2668 \times 9.81^{4/3} \times 540(31 \times 10^{-6})^{5/3}}{1.7 \times 10^{-4} \times 10 \times 962^{2/3}} = 5.8 \text{ meters}$$

For diphenyl under the same conditions,

$$x_c = \frac{2668 \times 9.81^{4/3} \times 140(27.4 \times 10^{-6})^{5/3}}{1.8 \times 2.72 \times 10^{-5} \times 10 \times 840^{2/3}} = 4.4 \text{ meters}$$

For the tube used by Jakob and Erk (0.466 meter) the temperature difference necessary to start turbulence for atmospheric steam is $\frac{5.8 \times 10}{0.466} = 124°$ C.

Note—Colburn and Hougen (*9*) attempted to define the point at which turbulence would start and decided that if the coefficient for condensing steam became less than 700 in English units, turbulence would commence. Since values below 700 are not found in practice, they concluded that a turbulent condition rarely exists. This conclusion is scarcely compatible with the generally observed fact that when turbulence does appear the coefficient increases markedly. An observed coefficient greater than 700 does not, therefore, necessarily indicate a non-turbulent condition.

From the preceding discussion one would expect that for stationary steam condensing on short tubes at low temperature differences Nusselt's theory would give correct results. However, if the tube length, temperature difference, or vapor velocity is increased, a point is reached at which turbulence begins, and one would expect deviations from the theory. For the usual commercial tube lengths of 2 to 4 meters and for temperature drops of over 10° to 20° C. an effect due to turbulence may be anticipated. In the case of the experiments of Badger, Monrad, and Diamond, on diphenyl vapor, turbulence may be expected to have an effect over the entire range of temperature difference covered. Nusselt's equations can no longer be expected to be accurate and in fact may lead to very erroneous results.

Although moderate steam velocity has rather a small effect on the coefficient as given by Nusselt's theory, it may be shown that it has a marked effect on the start of turbulence, and even in the case of very short tubes turbulence may be expected to begin with as low a temperature drop as 5° C. Thus in the tube used by Jakob and Erk, increasing the vapor velocity from 0 to 70 meters per second changed the start of turbulence from 125° to 4.4° C. temperature drop.

Just what happens when turbulence begins is of great importance both theoretically and practically, but this question offers many serious difficulties. A laminar layer of fluid must still be next to the wall, and outside of this a turbulent region. The temperature drop through this thin turbulent layer may be considered negligible and the entire drop must be through the viscous film. The thickness

of this film depends to some extent on the properties of the fluid, the thickness and velocity of the turbulent layer, and also on the velocity of the vapor past the outside of the condensate, though this latter effect is probably not of such great importance as when only a viscous film is present.

At the start of turbulence at the bottom of the tube most of the surface may be treated as following Nusselt's theory. However, as the turbulent layer moves upward with increasing temperature drop, more and more heat goes through the turbulent region; and one would expect that there would be more and more deviation from the theory, until the amount of heat going through the region covered by a purely viscous film is nearly negligible. From this point on, the deviation might be expected to be about constant, or at least not to change as quickly. Apparently this is what occurs in the case of diphenyl. The coefficient increases and then gradually seems to be approaching an asymptotic value. No indication of a falling off in the coefficient was observed, even at very high temperature differences (300° F.).

Note—In addition to the coefficients shown in Figure 9, several runs were made heating water with diphenyl. The heat transferred was calculated from the rise in temperature of the water as well as from the diphenyl condensed, and the coefficient was found to be from 400 to 450 at about 300° F. temperature difference, thus showing that the curve does not continue to be a straight line as given in Figure 9, but is apparently approaching an asymptotic value.

In addition to turbulence it may be possible that some of the liquid drops off before it reaches the bottom of the tube; and also that some of the condensate may form drops and run down the outside of the film. The continued increases in coefficient is, however, rather difficult to explain on the basis of these phenomena alone, though there is some experimental evidence for their occurrence in some cases.

The apparent inconsistency obtained by most observers in experimental work with long tubes and with high temperature differences is, no doubt, due to the fact that there is no definite boundary between the viscous and turbulent layers, but that there is a gradual change from one régime to another. This has been shown to be true with turbulent flow through pipes, and one might expect that the effect would be more marked in the case of a film of condensate. Apparently there is a sort of weaving of the interface of the two types of flow, allowing more or less heat to flow at a particular point on the tube. Average results may be obtained only by a relatively large amount of experimental work.

Jakob and Erk found that at high temperature differences the tube temperature first decreased, then increased at some point down the tube, and finally decreased slightly. This may be understood quite easily if the film is in turbulent motion. For a short distance down the tube the film is entirely viscous and therefore the wall temperature decreases as the film becomes thicker. At some point turbulence begins and the viscous layer is much thinner, allowing more heat to pass, and the wall temperature increases. As the turbulent layer increases in thickness it probably has some effect on the viscous film and the wall temperature varies slightly. The fact that this phenomenon was only observed at high temperature differences or at high vapor velocities is an added confirmation of the turbulent theory.

Jakob and Erk found also that at constant vapor velocity a point was reached when the effect of temperature difference on the coefficient increased greatly. This break was quite definite and apparently occurred at lower temperature drops as the velocity of the vapor increased, and was not apparent in the runs at very low velocities. This break was approximately at the point where turbulence would be expected to start.

Conclusion

At present all that may be said is that the fundamental theory of Nusselt is doubtless sound as is proved in the excellent correlation with the condensation of vapors on the outside of horizontal tubes, where the critical velocity is probably never reached in ordinary practice. The formulas developed for the case of vertical tubes are probably accurate for short tubes and low temperature differences; but are in general inaccurate for industrial operations, owing probably to the effect of turbulence and possibly to the formation of drops. The effect of vapor velocity as calculated by the revised method of Nusselt is probably sound when the condensate is not in turbulent flow, but in general the effect cannot be accurately determined. The qualitative agreement with the theory found by Jakob and Erk on the effects of superheat indicate that probably Nusselt's calculations are correct for this case as long as the condensate film is viscous.

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Gas-, Coke-, and By-Product-Making Properties of American Coals and Their Determination[1]

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An apparatus and method are described for determining the gas-, coke-, and by-product-making properties of coal at various carbonization temperatures ranging from 500° to 1100° C. The advantages of this new procedure may be summarized as follows:

(1) The yields (except NH_3), as shown by tests on two well-known gas coals, check those obtained in practice without any correlating factors.

(2) The effect of carbonization temperature on yields and quality of coke, gas, and by-products is obtained throughout the range from low- to high-temperature coking.

(3) The temperature and other coking conditions can be closely controlled, thus affording a means of comparing the carbonizing properties of various coals on a uniform basis, and also a means of studying the influence of various factors such as moisture, inerts, size of coal, and preoxidation or preheating of coal.

(4) The autogenously welded sheet-iron retort is gas-tight and permits uniform heating from all sides.

(5) The 75-pound charge of coal is large enough to yield sufficient coke and by-products for analysis and physical tests and yet small enough for convenient laboratory manipulation and accurate control.

(6) It is possible with this uniform method of carbonizing at various temperatures to study and correlate carbonizing properties with the constitution of coal as shown by microscopic examination, extraction with solvents, and various methods of analysis.

(7) The agglutinating value, softening temperature, plastic range, and other physical tests of coal can be correlated with coking value.

(8) The value of laboratory distillation assay tests using only a few grams of coal can be determined by comparing their results with those obtained in this new test which uses 75 to 90 pounds of coal, and which gives actual plant yields.

THE rapid advance of the coke and gas industry and the search for new methods of producing smokeless fuel require a much more comprehensive knowledge of the physical and chemical properties of the many varieties of American coals than is now available in the published coal analyses of the U. S. Bureau of Mines (*5*). Analyses and B. t. u. determinations may be sufficient for evaluating coal for ordinary fuel purposes, but they are inadequate for selecting coal for the production of gas, coke, and by-products. The coal-processing industries need to know the yields and quality of these products, and the effect of different temperatures and methods of carbonization. Obviously, such a study should be comprehensive and broadly fundamental. The chemical and physical properties of the coal and the method of heat treatment should be correlated with the yields and nature of the products obtained; furthermore, the results of the laboratory investigation should be correlated as far as possible with commercial results obtained in the gas and coking industries.

Interest in this problem was crystallized by the Carbonization Committee of the American Gas Association, which, in a report at the 1927 convention of the association (*2*), recommended coöperation with the Bureau of Mines in a preliminary study of laboratory and small-scale testing methods for determining the carbonizing properties of coals. The association accepted this recommendation, and appointed a subcommittee on Survey of Gas- and Coke-Making Properties of American Coals to represent the association in a coöperative study of present-day knowledge on the subject of testing coal for gas- and coke-making properties.

In carrying out this study a review was made of various present and past methods of testing, ranging from the small-scale laboratory tests using only a few grams of coal, such as the well-known U. S. Steel Corporation test, to full-scale commercial oven tests. Also, the leading gas and coke technologists in America and Europe were consulted and questionnaires on (1) optimum scale of test, (2) best design of apparatus, and (3) data to be obtained were sent to chemists and engineers experienced in coal-carbonization testing.

The results of this preliminary investigation, which were reported to the association at the 1928 convention (*3*), indicated, first, that fundamental information on the mechanism of carbonization throughout the entire range from low- to high-temperature coking is desired; and, second, that a uniform basis on which to compare the carbonizing properties of different coals should be developed. Since fundamental information on mechanism is fragmentary at present, the comparison method developed must needs be largely empirical; nevertheless the aim should be so to conduct the comparative testing that it will furnish data fundamental to any carbonizing process. These considerations indicate use of an experimental retort or oven small enough for definite temperature control and accurate measurement of yields, yet large enough to obtain coke in sufficient quantity and of sufficient size for the usual physical and chemical tests.

Seventy-five pounds of coal is probably the minimum amount that will yield sufficient coke and by-products for examination; 300 pounds is about the upper limit beyond which the cost of apparatus and operation becomes rather high and accurate control of conditions becomes more difficult. The other important requirements in the proposed carbonization investigation may be summarized briefly as follows:

(1) Carbonization tests should be made at 100-degree intervals in the range from 500° to 1100° C.

(2) The retort should be of metal to avoid leakage.

(3) The shape of retort should be either cylindrical, heated on all sides, or rectangular, heated on the two opposite sides only.

(4) The temperature of the outside of the retort should be kept constant and uniform during the entire test.

(5) The coals for test should be subject to all possible analyses and tests that may have any bearing on their carbonizing properties.

[1] Received August 2, 1930. Coöperative investigation, U. S. Bureau of Mines and American Gas Association. Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

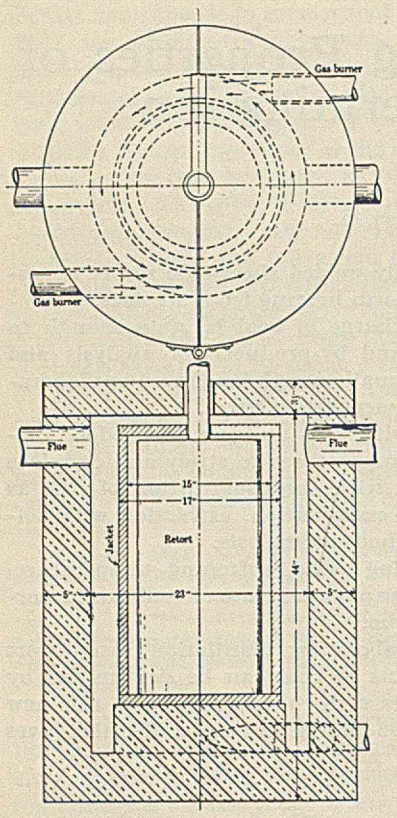

Figure 1—Retort, Jacket, and Setting

(6) The yields and quality of all products should be determined.

(7) The first series of coals to be tested should be selected from well-known gas and coking coals, on which commercial oven and retort test data are available so that correlation with commercial yields may be obtained.

Development of Apparatus

RETORT—To minimize operating expense it was decided to design the experimental carbonizing apparatus for the minimum acceptable charge of coal—i. e., 75 to 100 pounds. The most difficult problem was the retort material. Silica and other refractories are difficult to keep gas-tight under testing conditions that involve frequent heating and cooling. High-temperature resisting alloys, such as iron-chromium or nickel-chromium, are expensive and of questionable durability under the proposed test conditions. It was desired to have a retort that could be charged with the coal, made gas-tight, and then placed in a furnace at the desired carbonization temperature in a manner similar to making a volatile-matter determination with an electrically heated vertical tube furnace. After some preliminary experimentation it was found that a gas-heated pot furnace and an autogenously welded cylindrical canister of ordinary $^1/_{16}$-inch sheet steel answered these requirements. The steel canister served as a retort in a similar manner as the platinum crucible in the volatile-matter determination. It was expected that a single retort would serve for only one test at the highest temperatures, but it was found that two or three tests could be made before oxidation penetrated the metal. At the lower temperatures the same retort served for a number of tests.

As shown in Figure 1, the retort is simply a steel can 26 inches high and 13 inches in diameter. The cylinder is rolled from $^1/_{16}$-inch steel sheet and the ends are cut from $^1/_8$-inch material. All seams are welded autogenously with an oxy-acetylene torch, the bottom being left open for welding after charging with coal. The standpipe is a $1^1/_2$-inch iron pipe 12 inches high and is welded to the center of the retort top. For heat-flow experiments five $^1/_8$-inch iron pipes, which served as thermocouple wells, were let through the head as shown in Figure 2, and welded into place. The spacing of the wells was as follows: Well No. 1, 1 inch, No. 2, 2 inches, No. 3, 3 inches, No. 4, 4 inches, and No. 5, 5 inches, respectively, from the retort wall. Since the retort is 13 inches in diameter, well No. 5 was $1^1/_2$ inches from its center. These wells were placed on concentric circles on the retort top so that no two of them fell on a vertical principle plane. With this arrangement it was believed that the pipes would least affect horizontal heat flow through the charge. The flow of heat in a coking charge, as illustrated in Figure 4, is based on a continuous record from couples so spaced. Some of these wells were removed after the flow of heat through the charge had been investigated, and the method of heating had been adjusted to secure uniform flow. In subsequent routine tests, thermocouples were maintained at the following points: three couples, *A*, *B*, and *C*, in the space between jacket and retort; three couples in well 2: No. 1, 5 inches from bottom of retort; No. 2, in the middle of retort; and No. 3, 5 inches from the top of retort. Three couples, Nos. 4, 5, and 6, were similarly placed in well No. 5, making six couples inside the retort and three couples just outside the retort in the space between the retort and the wall. The outside couples *A*, *B*, and *C* determine the carbonization temperatures of the tests.

FURNACE—The retort is protected from direct contact with flame by a jacket (Figure 1), consisting of a high-chrome steel cast cylinder (with top and bottom plates) of internal diameter 1 inch larger than the external diameter of the retort and $26^1/_2$ inches high. The jacket wall 1 inch thick equalizes the temperature around the retort and serves as a muffle in the pot furnace. The flames from two Maxon-Premix burners entering tangentially at the bottom of the furnace whirl around in the 3-inch annular space between the jacket and the furnace wall. The combustion gases leave the furnace through two 4-inch flues at opposite sides of the top. These are fitted with dampers and are connected to a stack.

The furnace (Figure 1) consists of a cylindrical steel casing 39 inches in diameter and 46 inches high, lined with firebrick to a thickness of $4^1/_2$ inches, and provided with a hinged, divided cover.

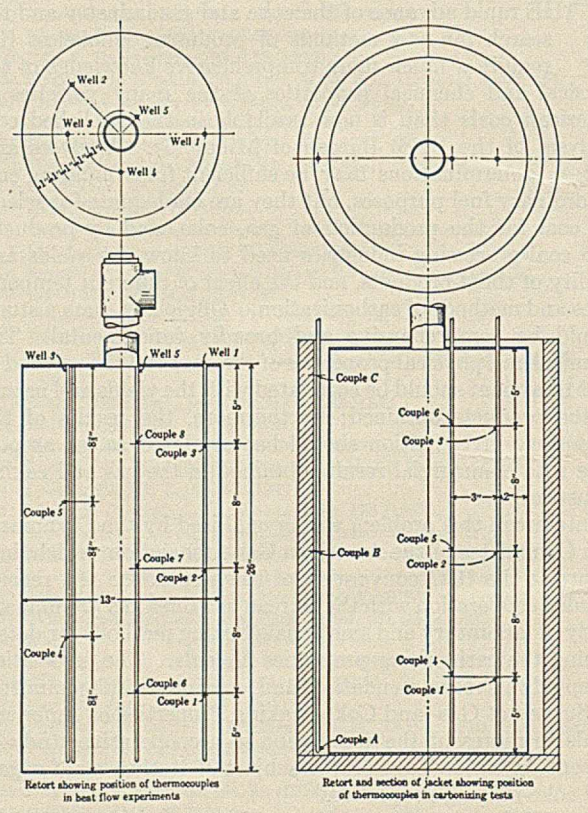

Figure 2—Position of Thermocouples in Retort and Jacket

CONDENSING, TAR-PRECIPITATING, AND SCRUBBING TRAIN—The condensing and scrubbing train for the recovery of the by-products is shown diagrammatically in Figure 3. Figure 5 is a photograph of the entire apparatus, showing the charged retort being lowered into the furnace. The distillation products pass from the retort offtake first to a dry

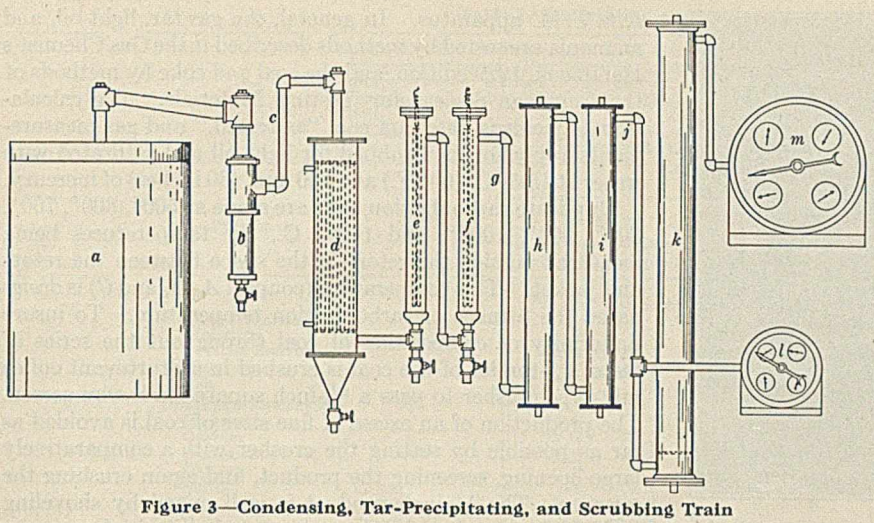

Figure 3—Condensing, Tar-Precipitating, and Scrubbing Train

trap, *b* (Figure 3), and then to a tubular water-cooled condenser, *d*, of large capacity. This is an 8-inch vertical pipe, 39 inches in length, with welded heads into which twelve $^3/_4$-inch seamless copper pipes are brazed. These are the gas passages. Two Cottrell precipitators, *e* and *f*, follow in series. Each is a 3-inch standard pipe, 36 inches in length, with a standard flange at the top. To this is bolted a cover disk of fiber, 1 inch in thickness, through which passes the stem of a squirrel-cage electrode. The electrode is suspended vertically in the pipe extending to within 3 inches of the bottom. The gases enter centrally at the bottom and are discharged through a 1-inch pipe welded to the side of the 3-inch pipe, 4 inches from the top. The suspended electrode consists of a $^1/_4$-inch brass rod passing through two $1^1/_8$-inch brass disks at the top and bottom. Eight No. 22 steel wires are soldered to the peripheries of the disks at equal intervals. A 1-kilowatt transformer supplies the power at about 20,000 volts. The output of the transformer is rectified by highly insulated commutator of the disk type driven by a $^1/_4$-horsepower synchronous motor.

The trap, condenser, and precipitator are provided with drip cocks and with steam connections for removing adhering tar after a run is completed. The detarred gas then passes upward through a 5-inch lead tower, *h*, 57 inches high, supplied with 2 *N* sulfuric acid for removing ammonia. It then passes through a similar iron tower, *i*, supplied with caustic liquor for removing hydrogen sulfide. The circulating liquor in both towers passes through perforated distributors in the tower tops. It then descends through the tower packing (Knight $^5/_8$-inch hollow cylinders form packing) countercurrent to the gas stream. The liquor leaves the tower base through a trap and is caught in a 5-gallon bottle.

The scrubbed gas is now metered by two standard American Meter Company's wet-test meters in parallel. A large meter, *m*, takes $^{49}/_{50}$ of the make gas and a small one, *l*, takes $^1/_{50}$ of it, which is collected in a 10-cubic foot holder for analysis. The remainder of the gas is burned. The spindles of the two meters are geared together so that the small meter continuously takes $^1/_{50}$ of the make gas, regardless of what the gasification rate may be. A pressure equalizer insures accurate proportioning of the sample. Just before entering the make-meter the gas passes through the light-oil scrubber, *k*, which consists of a 7-foot piece of standard 6-inch pipe fitted with standard flanges and caps at top and bottom, and packed with Knight standard $^5/_8$-inch cylindrical stoneware tower packing. The gas enters at the bottom into a 5-inch space between the bottom cap and the packing support, which consists of a $^1/_8$-inch steel plate drilled with $^3/_8$-inch holes. Wash oil is admitted from a reservoir at the tower top, passing to a cup-type distributor and thence through the packing countercurrent to the gas. The wash oil is not recirculated; it is admitted at such a rate that approximately $4^1/_2$ gallons will have passed the tower during a run. This quantity of wash oil is, of course, a large excess for the low-temperature runs where the gas make is small, but is required for the high-temperature runs since here the gas make is high. This scrubber was installed after the runs on coal No. 1 had been completed; accordingly only the gas from coal No. 2 was scrubbed before passing to the recording calorimeter.

Before passing to the small meter this portion of the gas ($2^1/_2$ to 12 cubic feet, depending on the carbonization temperature) is scrubbed for light oil by passage through a tube of active charcoal. This oil is recovered from the charcoal by steaming at the end of each run.

Measuring Apparatus—Retort temperatures (couples 1 to 6, inclusive) are recorded by an 8-point Leeds & Northrup potentiometer. The thermocouples are made from B. & S. No. 18 chromel-alumel[2] wire of a grade especially selected for uniformity and for reproducibility of electromotive force. The couple leads are insulated from each other, and from the iron wells, by the usual clay insulators, 2- or 4-hole insulators being used depending on the number of wires. The three couples in each well are formed by welding with oxyacetylene flame three different alumel leads to one chromel lead at the points shown in Figure 2. That part of each lead which extends from the top of the well to the potentiometer distribut-

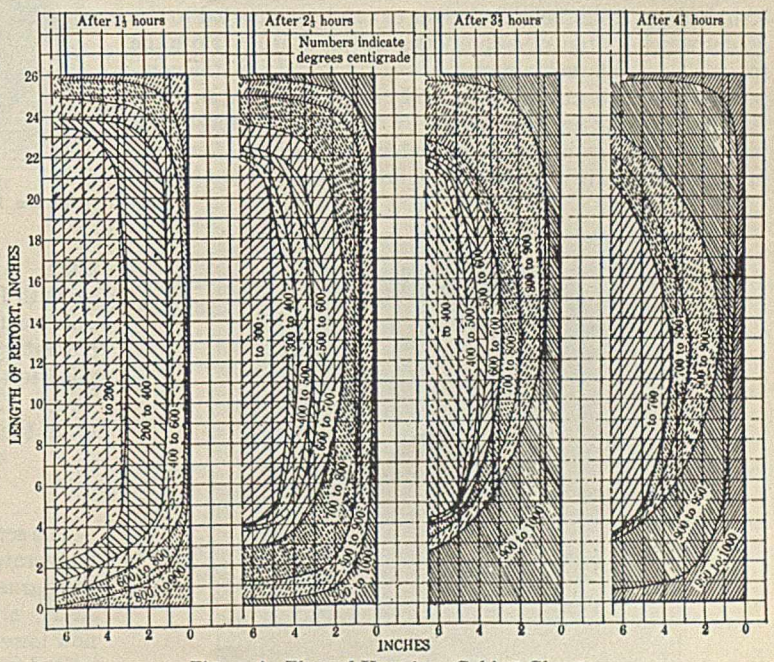

Figure 4—Flow of Heat in a Coking Charge

[2] At temperatures above a red heat alumel wire must be protected from gases containing carbon monoxide; otherwise it rapidly disintegrates.

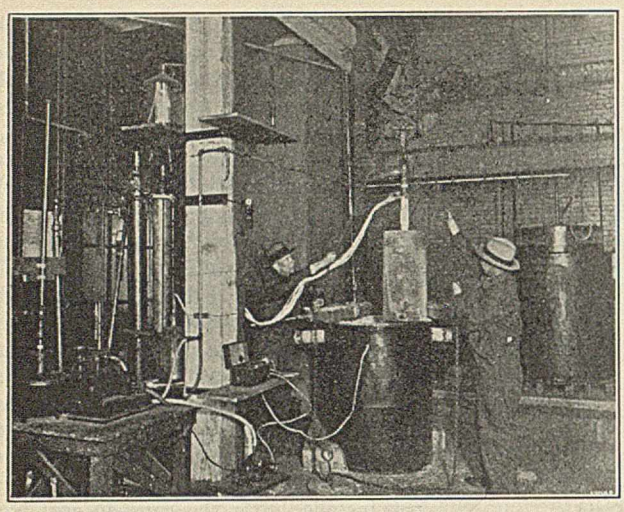

Figure 5—Charged Retort Being Lowered into Furnace

ing panel is insulated with asbestos loom. Carbonization or furnace temperatures (couples *A*, *B*, and *C*) are measured at 15-minute intervals with a Leeds & Northrup portable potentiometer.

The gases are analyzed by a Burrell gas apparatus. A standard Thomas recording gas calorimeter is connected to the gas line at the outlet of the make-meter, so that the heating value of the scrubbed gas as made is recorded continuously. At the end of a test the calorimeter is connected to the holder which contains the scrubbed composite sample, and the heating value of this gas is determined. A Ranarex standard specific gravity recorder is connected in parallel with the calorimeter. This can be used to record the gravity of the scrubbed gas from the make-meter or can be connected to the holder which contains the composite sample at will. Both the recorded calorific value and the specific gravity of the composite gas sample are checked, the former by calculation from the gas analysis and the latter by the effusiometer. Gas-pressure readings in inches of water are read at 15-minute intervals at points *c*, *g*, and *j*. (Figure 3)

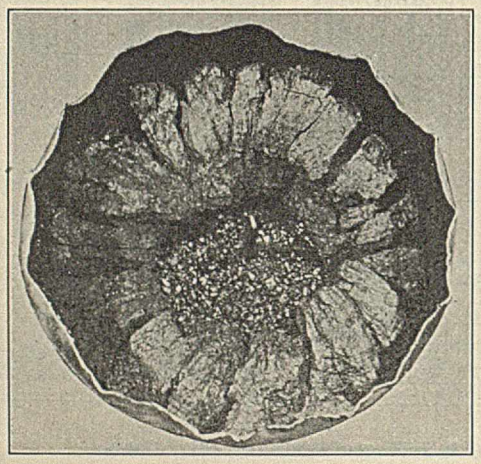

Figure 6—Coal No. 2, Elkhorn, Run at 1000° C. Carbonization Temperature and Topped at End of 2 Hours

Weighings of coal, coke, and tower liquors are made to the nearest 10 grams. Weighings of tar and gas liquor are made on a standard 10-kg. laboratory balance. Tars are fractionated in the U. S. Bureau of Mines standard apparatus for analysis of crude petroleum. Cokes are tested on standard A. S. T. M. apparatus. In general, the gas tar, light oil, and ammonia are tested by methods described in the Gas Chemist's Handbook, 1929 edition, and the coal and coke by methods of the American Society for Testing Materials. The calculation of yields is based on coal "as tested," and gas measurements apply to gas scrubbed for light oil and saturated with water at 15.5° C. (60° F.) and 760 mm. (30 inches) of mercury.

Duplicate carbonization tests are made at 500°, 600°, 700°, 800°, 900°, 1000°, and 1100° C., the temperatures being measured outside the retort in the space between the retort and jacket. This temperature (couples *A*, *B*, and *C*) is designated the furnace or carbonization temperature. To insure uniformity of composition of coal throughout the series of tests, a 1-ton lot of the coal is crushed in a Sturtevant coffee mill-type crusher to pass a $^1/_4$-inch square-mesh wire screen. The production of an excess of fine sizes of coal is avoided as far as possible by setting the crusher with a comparatively large opening, screening the product, and again crushing the oversize. The $^1/_4$-inch product is well mixed by shoveling and is then spread out in a long, rectangular pile in the manner recommended by the American Society for Testing Materials. Twenty galvanized-iron garbage cans, of about 100 pounds capacity each, are filled from this pile. Uniformity of sampling is insured by placing the cans in a semicircle and putting one shovelful of coal in each can successively until all are

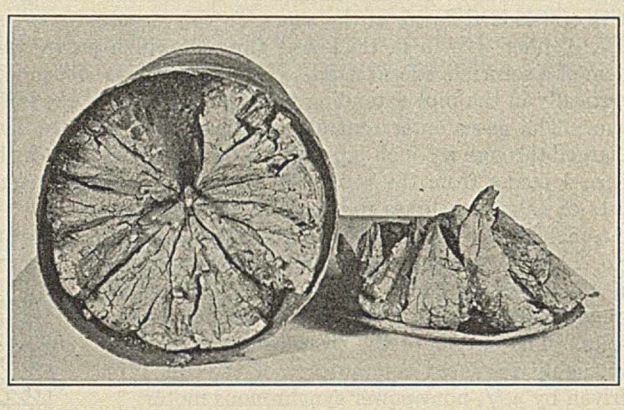

Figure 7—Coke from Coal No. 1, Pittsburgh Bed, at End of 900° C. Test

filled. All cans were completely filled and the cover sealed on with friction tape. The cans were stored in a cool place until required for test. One of the cans was taken for the laboratory sample for analysis and the various tests that applied to the coal. One can is more than enough for a retort charge. About 80 pounds of minus $^1/_4$-inch coal are required to fill the retort.

Test Procedure

The setting is first heated to a predetermined carbonization temperature, indicated by thermocouples *A*, *B*, and *C*, and the burners are adjusted until this temperature becomes constant; about $1^1/_2$ hours are required. The charged retort is now lowered into place by means of a crane and quickly connected to the purification train, all thermocouples having been previously connected; fresh solutions are provided for the towers and the meters set at zero. The towers are flushed with an excess of the solutions before gas evolution starts and the precipitator is started after 1 cubic foot of gas has passed. This is sufficient to displace air and prevent ignition in the precipitator.

Observations taken are gas pressures at three points in the train (*c*, *g*, and *j*, Figure 3) of rate of gas make, temperatures and pressures at the meters, temperatures (three points,

Table I—Description and Properties of Coals

COAL No. 1—Pittsburgh Bed, Ocean No. 2 Mine, near Sutersville, Allegheny County, Pa. Sample 1, unwashed forked lump. Sample 2, minus 3/8-inch, washed. Top half of coal bed, mainly anthraxylous coal; bottom half, anthraxylon with considerable attritus. No splint in either half.

COAL No. 2—Elkhorn Bed, Mine 204, near Jenkins, Letcher County, Ky. Anthraxylous coal with considerable proportion of splint.

Property	Coal No. 1						Coal No. 2		
	As tested		Moisture-free		Moisture- and ash-free		As tested	Moisture-free	Moisture- and ash-free
	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2			
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
PROXIMATE ANALYSIS:									
Moisture	1.6	2.4	..	..	..	..	2.2	..	..
Volatile matter	34.2	34.5	34.7	35.4	37.6	37.6	36.6	37.4	38.3
Fixed carbon	56.7	57.2	57.7	58.5	62.4	62.4	59.0	60.4	61.7
Ash	7.5	5.9	7.6	6.1	..	..	2.2	2.2	..
ULTIMATE ANALYSIS:									
Hydrogen	5.4	5.7	5.3	5.6	5.7	5.9	6.1	6.0	6.1
Carbon	77.8	78.3	79.1	80.3	85.6	85.4	80.9	82.7	84.6
Nitrogen	1.6	1.6	1.6	1.6	1.8	1.7	1.5	1.6	1.6
Oxygen	6.6	7.5	5.3	5.4	5.7	5.9	8.7	6.9	7.1
Sulfur	1.1	1.0	1.1	1.0	1.2	1.1	0.6	0.6	0.6
Ash	7.5	5.9	7.6	6.1	..	..	2.2	2.2	..
B. t. u.	13,810	13,910	14,030	14,250	15,200	15,170	14,410	14,730	15,070
Softening temperature of ash	Sample 1, 1399° C. (2550° F.); Sample 2, 1421° C. (2590° F.)						1310° C. (2390° F.)		
Agglutinating value of coal (Bird-Marshall test)	6700 grams						4300 grams		
Softening temperature of coal (Damm)	320° C.						340° C.		
Initial temperature of active decomposition (Damm)	390° C.						390° C.		
Plastic range (Layng-Hawthorne):									
Pressure rises	395° C.						415° C.		
Pressure drops	580° to 625° C.						454° C.		
Maximum pressure	1700 to 2300 mm. H_2O						440 mm. H_2O		
Low-temperature assay at 510° C. (Fischer aluminum retort), yields:	*Per cent*						*Per cent*		
Coke	78.0						71.3		
Tar	13.0 or 31.2 gal. per ton						15.7 or 37.6 gal. per ton		
Gas	3.5[a] or 1830 cu. ft. per ton						7.9[a] or 2690 cu. ft. per ton[b]		
Liquor	5.5						5.1		
Sum	100.0						100.0		
Extraction with benzene at 285° C. (Fischer)—yield of bitumens on moisture- and ash-free basis:									
Oily	3.88						2.77		
Solid	7.97						7.23		
Total	11.85						10.00		

[a] By difference. [b] 15.5° C., 760 mm. H_2O pressure.

Table II—Average and Maximum Differences in Results of Duplicate Tests at Same Carbonization Temperatures

Yields	Difference Av.	Difference Max.	Gas Data	Difference Av.	Difference Max.
Coke, per cent	1.1	2.6	Specific gravity	0.02	0.05
Gas, cu. ft. per ton	345	987	B. t. u. per cu. ft.	22	61
Tar, gal. per ton	1.3	2.9	H_2S, gr. per 100 cu. ft.:		
Light oil, gal. per ton	0.68	1.40	Coal No. 1	95	176
$(NH_4)_2SO_4$, lbs. per ton	1.7	3.6	Coal No. 2	22	56
Total yields, per cent	98.0	101.5[a]	CH_4, per cent	2.6	7.3[b]
Coke Data			**Tar Data**		
Volatile matter, per cent	0.5	1.2	Specific gravity	0.012	0.030
Ash, per cent:			Per cent distilled between 170° and 230° C.	1.43	4.10
Coal No. 1	1.1	2.9	Tar acids, per cent	3.6	13.4
Coal No. 2	0.1	0.2	Tar bases, per cent	1.4	7.1
True specific gravity	0.028	0.040	Neutral oils, per cent	4.3	15.1
Apparent specific gravity	0.025	0.050	Free carbon, per cent	1.64	4.00
Shatter on 1½ inch, per cent	3.5	9.6	B. t. u.	66	170
Tumbler on 1½ inch, per cent	4.6	13.3			
Tumbler through ¼ inch, per cent	1.5	8.5			

[a] Minimum 95.5 per cent.
[b] Low-temperature tests.

A, *B*, *C*, Figure 2) of the retort jacket, and rate of flow of tower solutions. These data are recorded at 15-minute intervals.

In a 900° C. test, for example, the gas flow rises immediately to about 2 cubic feet per minute, then gradually falls off to a fraction of a cubic foot at the end of the run. Finally a drop in the rate indicates that the charge is coked. This is checked by recorded temperatures at the retort center. The carbonization is considered complete when couples 4, 5, and 6, near the center of the retort, show a temperature within 30° C. of the average of couples *A*, *B*, and *C* outside the retort. The retort is allowed to cool overnight. It is then opened by cutting out its bottom with a cold chisel, and the coke is carefully removed and weighed. Meanwhile the tower solutions have been weighed, sampled, and analyzed for ammonia, hydrogen sulfide, and carbon dioxide absorbed. The tar and liquor have also been recovered and weighed; live steam is used to drive out the tar adhering to condensers and tar-trap surfaces. The tar is collected, dehydrated, and fractionated, and the ammonia liquor is weighed and analyzed. The coke from duplicate runs is combined, analyzed, and tested by A. S. T. M. methods. The gas as sampled is analyzed for gaseous constituents by the Burrell method and light-oil vapors for the total sample are collected in active char, from which they are steamed and condensed.

Flow of Heat in Retort

The first carbonizing experiments in this cylindrical retort were undertaken to observe the flow of heat and temperature gradient in the charge and then so to adjust the burners that the heat should penetrate the charge uniformly from all sides. With the retort resting solidly on a 1-inch plate of chrome-iron, which in turn was in contact with the refractory bottom of the furnace and with a 4½-inch fire-clay cover resting on the chrome-iron top plate, fairly symmetrical penetration of heat took place from all sides and from the top and bottom,

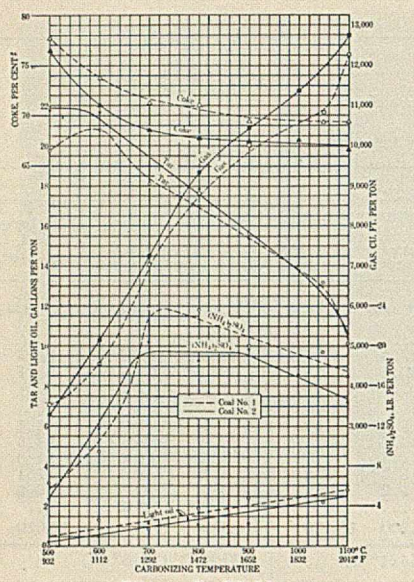

Figure 8—Yields

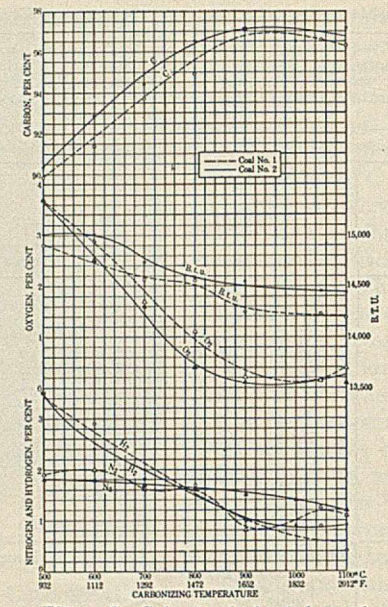

Figure 9—Coke Analysis, Ash- and Moisture-Free

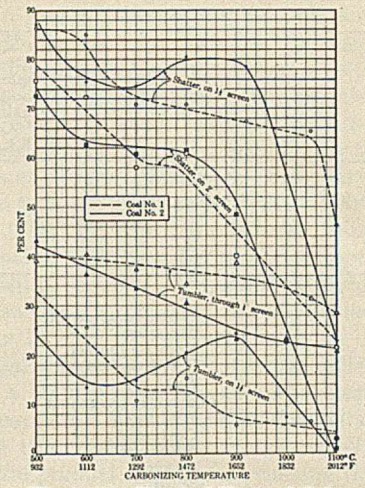

Figure 10—Physical Tests of Coke

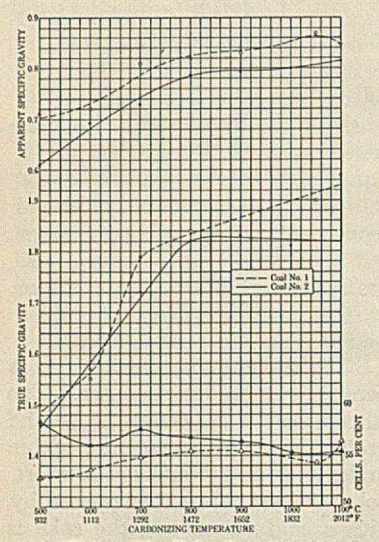

Figure 11—Coke Structure

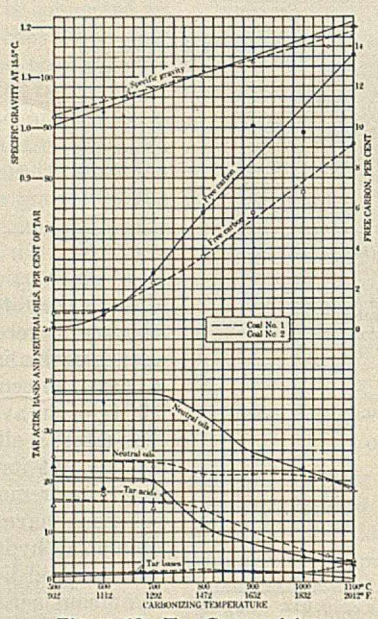

Figure 12—Tar Composition

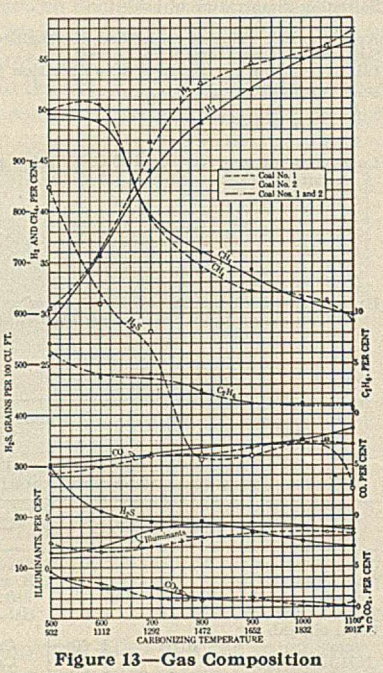

Figure 13—Gas Composition

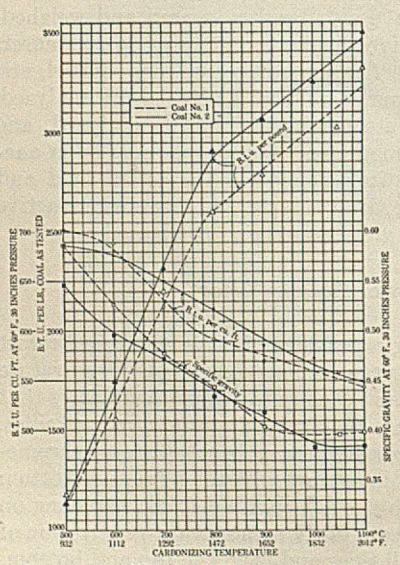

Figure 14—Physical Constants of Gas

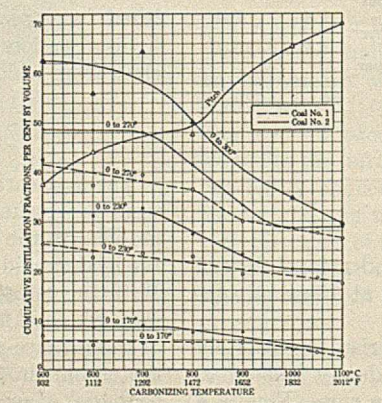

Figure 15—Tar Distillation

as shown by the isothermal zones plotted in Figure 4 which is taken from a test at 1050° C. furnace temperature—i. e., in the space between retort and jacket. Figure 6 shows the extent of carbonization at 1000° C. furnace temperature after 2 hours' heating. The coal was coked uniformly for a distance of 3 inches from the wall of the retort, the center of the charge being loose coal. The plastic layer between coke and loose coal seemed only $^1/_4$-inch thick. Figure 7 shows the appearance of the charge at the end of the coking time in a test of Pittsburgh coal carbonized at 900° C.

Description and Properties of Coals Tested

Pittsburgh bed coal from Ocean No. 2 mine, near Sutersville, Allegheny County, Pa., was selected for the first

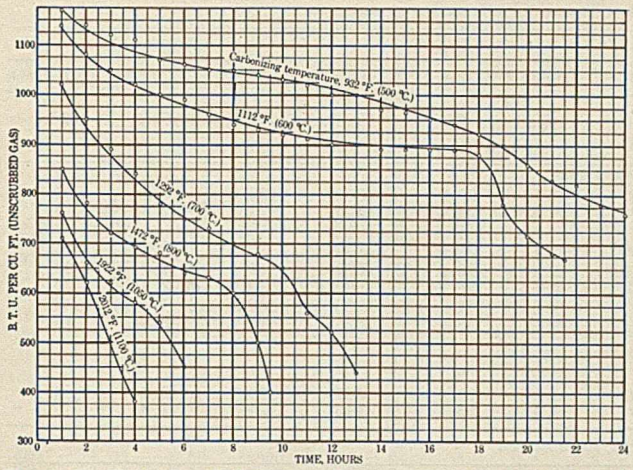

Figure 16—Recording Calorimeter Curves. Coal No. 1, Pittsburgh Bed, Ocean No. 2 Mine

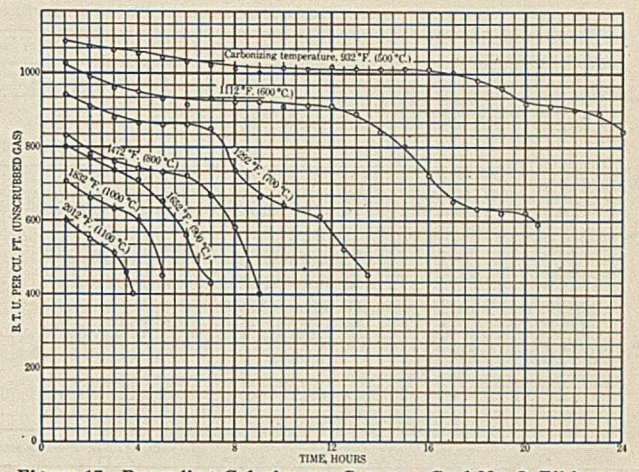

Figure 17—Recording Calorimeter Curves. Coal No. 2, Elkhorn Bed, Mine No. 204

coal to be tested, because this coal was used in large-scale tests of six different types of gas or coke plants by the Carbonization Committee of the American Gas Association in 1925 and 1926 (*1*). Direct comparison could therefore be made of results from the experimental apparatus with those from commercial plants. This coal is designated as Coal No. 1. Coal No. 2, which is also covered in this report, is a well-known gas coal designated in the trade as Elkhorn coal. It comes from the Elkhorn bed, No. 204 mine, near Jenkins, Letcher County, Ky. Approximately 1-ton samples of each coal were shipped from the mines to the Pittsburgh Experiment Station, where the coals were prepared for test as previously described under test procedure.

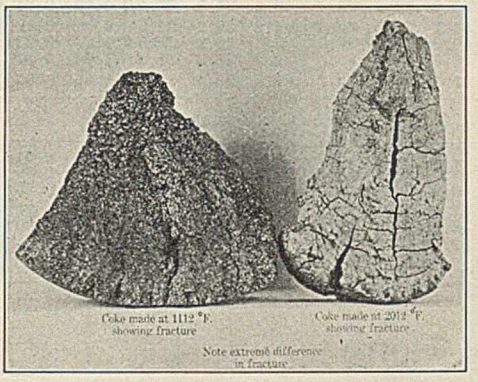

Figure 18—Coke from Coal No. 1, Pittsburgh Bed, Ocean No. 2 Mine, Bureau of Mines Retort

Left, 600° C. Right, 1100° C.

The original lot of coal No. 1, Ocean No. 2, which was unwashed, forked lump all over 4-inch screen, was exhausted before the carbonziation tests at 600° and 500° C. were made. A second lot was therefore obtained, which was from the same mine but was a washed coal all passing through a $^3/_8$-inch screen. The description and properties of the two coals are given in Table I.

Results of Carbonization Tests

The yields and quality of products at various carbonization temperatures measured in the space between the retort and the jacket are given in Tables III to VII and Figures 8 to 17, inclusive. These results are the average of two tests in most instances and refer to the coal as tested. Short tons (2000 pounds) and U. S. gallons are used throughout this paper. The coke is on the as-received basis; the tar is the crude dry product; and the light oil from coal No. 1 is calculated from determinations made by passing an aliquot portion of the gas, after it has passed through the condensing train, through activated charcoal and recovering the light oil from the charcoal by the usual steam-distillation method. For coal No. 2 a light-oil scrubber using wash oil was installed, and all the gas made was passed through this scrubber. None of the light-oil figures include the light oil condensed with the tar. The gas yields are scrubbed gas calculated to 15.6° C. and 760 mm. (60° F. and 30 inches Hg) pressure.

Agreement of Duplicate Tests—In general, the yields obtained in duplicate tests at low temperatures agreed more closely than at high temperatures, especially the tar and gas. The sudden rush of gas when the retort is lowered into the furnace at 1100° C. renders it difficult to collect all the tar and liquor in their proper places in the condensing and scrubbing system. Since running these two coals the condensing equipment has been enlarged to take care of larger gas flows. The

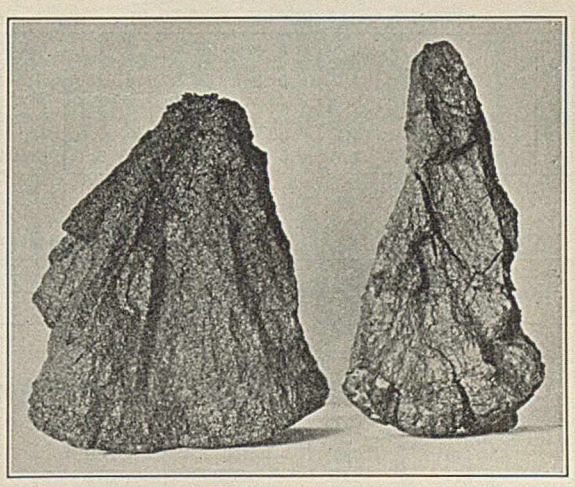

Figure 19—Coke from Coal No. 1, Pittsburgh Bed, Ocean No. 2 Mine, Carbonized in Bureau of Mines Retort

Left, 600° C. Right, 1000° C.

average and maximum differences in results from two or more tests at each carbonization temperature are shown in Table II. The method and apparatus are being improved and future results are expected to show better agreement.

Agreement of Bureau of Mines Results with Those of Commercial Plants

A comparison of the American Gas Association plant results on Ocean No. 2 mine, Pittsburgh coal, with the results of

Table III—Average Yields of Carbonization Tests at Various Temperatures

Carbonization Temperature	Yields, Per Cent of Coal							Yields, per Ton of Coal			
	Coke	Gas	Tar	Light oil	NH_3	Liquor	Total	Gas	Tar	Light oil	$(NH_4)_2SO_4$
° C.	%	%	%	%	%	%	%	Cu. ft.	Gal.	Gal.	Lbs.
COAL NO. 1—PITTSBURGH BED, OCEAN NO. 2 MINE											
Washed coal:											
500	77.6	7.1	8.5	0.00	0.02	6.3	99.5	3543	20.0	0.0	6.3
600	73.9	8.2	9.4	0.42	0.05	6.4	98.4	4539	21.2	1.3	9.5
Unwashed coal:											
700	71.5	11.7	8.1	0.29	0.16	6.2	98.0	7050	18.1	0.9	24.0
800	71.1	13.7	7.5	0.60	0.16	6.9	99.9	8799	17.0	1.9	23.7
900	69.4	14.1	7.4	0.80	0.13	6.6	98.4	10001	15.6	2.4	20.0
1050	69.3	15.0	6.4	0.70	0.16	6.1	97.7	10822	13.2	2.2	19.2
1100	69.4	16.8	4.1	0.90	0.15	4.4	95.9	12237	10.1	2.8	16.9
Tests of washed (5.9% ash) calcd. to unwashed coal (7.6% ash):											
500	78.0	7.0	8.3	0.00	0.02	6.2	99.5	3479	19.7	0.0	6.2
600	74.5	8.1	9.2	0.42	0.05	6.3	98.6	4457	20.9	1.3	9.3
COAL NO. 2—ELKHORN BED, MINE NO. 204											
500	76.4	6.4	9.2	0.06	0.10	7.2	99.4	3271	21.8	0.17	4.8
600	71.1	9.3	9.5	0.15	0.08	6.0	96.1	5149	21.6	0.45	11.8
700	68.6	12.5	8.4	0.40	0.16	6.5	96.6	7258	19.0	1.16	20.3
800	67.7	14.7	8.3	0.37	0.12	6.8	98.0	9323	17.8	1.10	18.4
900	67.3	15.6	7.4	0.38	0.16	6.4	97.2	10461	15.3	1.18	19.7
1000	67.6	15.4	6.9	0.78	0.13	6.1	96.9	11372	14.0	2.26	17.1
1100	66.6	18.3	5.3	1.00	0.14	4.9	96.2	12736	10.6	3.00	14.3

Table IV—Analyses of Coke, As-Received Basis

Carbonization Temp.	Proximate				Ultimate					B. t. u.
	Moisture	Volatile matter	Fixed carbon	Ash	S	H	C	N	O	
° C.	%	%	%	%	%	%	%	%	%	
COAL NO. 1—PITTSBURGH BED, OCEAN NO. 2 MINE										
500	1.2	8.9	82.1	7.8	0.8	3.4	81.7	1.7	4.6	13,565
600	1.7	6.3	84.2	7.8	0.8	2.8	82.6	1.8	4.2	13,440
700	0.9	2.2	86.3	10.6	0.8	1.7	82.9	1.6	2.4	12,895
800	1.3	2.0	86.7	10.0	0.8	1.7	84.1	1.4	2.0	12,925
900	0.1	0.8	88.0	11.1	0.7	0.9	86.3	0.9	0.1	12,650
1050	0.3	0.8	88.0	10.9	0.8	0.9	86.0	1.0	0.4	12,630
1100	0.1	0.6	88.9	10.4	0.7	0.5	86.2	1.0	1.2	12,705
COAL NO. 2—ELKHORN BED, MINE NO. 204										
500	0.5	9.4	87.3	2.8	0.5	3.5	87.4	1.7	4.1	14,525
600	0.5	4.7	91.6	3.2	0.4	2.4	89.4	1.7	2.9	14,465
700	0.7	2.9	93.1	3.3	0.5	2.0	90.5	1.6	2.1	14,145
800	0.5	1.5	94.7	3.3	0.4	1.5	92.4	1.5	0.9	14,035
900	0.2	0.8	95.4	3.6	0.5	1.0	93.4	1.4	0.1	14,005
1000	0.1	1.2	95.0	3.7	0.5	0.9	92.8	1.3	0.8	13,910
1100	0.0	2.1	94.2	3.7	0.5	0.9	93.7	1.1	0.1	13,910

Table V—Physical Properties of Coke, As-Received Basis

Carbonization Temp.	Shatter, Cumulative			Tumbler, Cumulative			Specific Gravity		Cells
	On 2 in.	On 1½ in.	On 1 in.	On 1½ in.	On 1 in.	Through ¼ in.	True	Apparent	
° C.	%	%	%	%	%	%			%
COAL NO. 1—PITTSBURGH BED, OCEAN NO. 2 MINE									
500	75.9	86.0	92.1	29.9	52.6	39.2	1.50	0.71	52.8
600	72.4	85.0	92.9	25.4	43.6	40.5	1.55	0.72	53.6
700	58.0	70.9	83.4	10.6	31.3	37.4	1.79	0.81	54.8
800	61.1	75.2	86.3	15.2	38.2	34.5	1.84	0.82	55.4
900	40.2	67.5	87.0	5.6	36.2	38.5	1.86	0.83	55.4
1050	30.6	62.5	85.5	6.2	37.3	31.4	1.90	0.87	54.1
1100	21.4	46.1	79.7	2.4	28.5	28.4	1.95	0.85	56.3
COAL NO. 2—ELKHORN BED, MINE NO. 204									
500	73.3	86.9	93.1	25.6	39.1	43.5	1.46	0.61	58.2
600	62.6	75.8	88.6	13.1	35.0	36.4	1.57	0.69	56.0
700	60.7	74.3	84.8	15.0	31.7	33.5	1.71	0.73	57.6
800	61.8	80.6	90.4	20.2	45.1	30.1	1.82	0.79	56.8
900	48.2	78.4	91.6	24.1	58.2	23.3	1.83	0.80	56.4
1000	22.5	56.4	87.8	7.2	41.1	23.8	1.81	0.81	55.2
1100	2.7	22.8	71.7	0.9	16.0	21.1	1.83	0.82	55.3

Table VI—Physical and Chemical Properties of Gas

Carbonization Temp.	Sp. Gr.[a]	Heating Value		H_2S	Analysis by Volume						
					CO_2	Ill.	H_2	CO	CH_4	C_2H_6	N_2
° C.		B. t. u./[b] cu. ft.	B. t. u./ lb. coal	Grains/ 100 cu. ft.	%	%	%	%	%	%	%
COAL NO. 1—PITTSBURGH BED, OCEAN NO. 2 MINE											
500[c]	0.532	781	1383	848	4.0	2.4	30.4	4.2	50.0	7.1	1.9
600[c]	0.481	734	1666	618	3.7	1.5	35.7	4.8	50.6	3.7	0.1
700	0.440	666	2346	562	2.0	2.0	46.8	5.8	39.2	4.0	0.2
800	0.414	622	2736	311	1.7	3.0	52.6	6.1	34.5	2.1	...
900	0.375	596	2980	319	2.0	3.3	54.6	6.7	32.4	1.0	...
1050	0.367	584	3160	348	1.1	3.4	56.2	7.3	31.2	0.8	...
1100	0.365	571	3490	252	1.5	3.2	57.7	7.0	29.4	0.7	0.5
COAL NO. 2—ELKHORN BED, MINE NO. 204											
500[d]	0.518	733	1199	288	4.7	1.5	29.0	5.2	49.6	5.9	4.1
600	0.480	715	1837	210	2.9	2.1	35.6	5.6	48.9	4.0	0.9
700	0.460	673	2442	191	3.1	3.7	44.0	6.2	39.3	3.5	0.3
800	0.419	641	2987	189	1.9	4.4	48.5	7.0	35.9	2.3	...
900	0.397	612	3176	168	1.7	4.3	51.9	6.9	34.2	1.0	...
1000	0.360	596	3389	147	1.5	4.0	54.9	7.3	31.2	1.1	...
1100	0.381	561	3572	141	1.0	3.7	56.7	8.5	29.7	0.4	...

[a] Calculated (15.5° C. and 760 mm.; air = 1).
[b] 15.56° C. and 760 mm. pressure; scrubbed for light oil and H_2S.
[c] Washed coal.
[d] Single test.

Unscrubbed for light oil:
Coal No. 1, 1050° C. = 611; 1100° C. = 601
Coal No. 2, 1000° C. = 624; 1100° C. = 593
Coal No. 1, 1050° C. = 3306; 1100° C. = 3677
Coal No. 2, 1000° C. = 3548; 1100° C. = 3776

Table VII—Analyses of Dry Tar

Carbonization Temp.	Sp. Gr. 15.6°/15.6° C.	Free Carbon[a]	Heating Value	Ultimate Analyses					Analytical Distillation, by Volume				Analysis of Fraction			Anthracenes	Naphthalenes
				H	C	N	S	O	0–175° C.	175–225° C.	225–275° C.	Residue	Acids	Bases	Neutral oils		
° C.		%	B. t. u.	%	%	%	%	%	%	%	%	%	%	%	%	%	%
COAL NO. 1—PITTSBURGH BED, OCEAN NO. 2 MINE																	
500	1.02	0.88	16785	8.5	84.3	0.7	0.6	5.9	6.9	18.8	16.6	57.7	15.4	1.4	24.8	..	..
600	1.06	0.94	16540	8.2	84.2	0.8	0.5	6.3	4.8	17.9	14.5	62.8	17.9	2.0	18.4	..	..
700	1.08	2.38	16430	7.7	85.8	1.0	0.6	4.9	5.4	18.2	15.8	60.6	14.6	2.1	22.8	..	..
800	1.10	3.55	16350	7.2	86.2	1.0	0.6	5.0	5.4	17.5	13.3	63.8	13.2	2.1	20.9	0.04	0.00
900	1.13	5.79	...	6.4	87.9	1.3	0.7	3.7	5.6	13.7	10.8	69.9	6.8	1.9	21.3	2.42	1.53
1050	1.16	6.77	16219	6.3	88.4	1.2	0.6	3.5	3.2	15.4	9.2	72.2	5.6	2.3	19.9	1.48	1.93
1100	1.20	9.43	16180	6.0	88.5	1.2	0.7	3.6	2.5	14.8	8.8	73.9	4.3	3.9	17.9	2.15	2.77
COAL NO. 2—ELKHORN BED, MINE NO. 204									0–170° C.	170–230° C.	230–270° C.	270–300° C.					
500	0.99	0.09	17082	9.6	85.0	0.6	0.4	4.4	8.8	23.2	16.7	13.7	37.6	23.0	1.4	37.6	0.0	0.0
600	1.03	0.69	16800	8.8	84.7	0.6	0.4	5.5	8.7	22.5	17.0	7.8	44.0	19.0	1.6	35.4	0.0	0.0
700	1.06	2.76	16530	8.0	85.5	0.9	0.4	5.2	9.0	23.8	15.2	16.3	35.7	20.2	1.9	39.0	0.24	0.0
800[b]	1.11	5.80	16360	7.1	87.0	1.0	0.5	4.4	8.5	20.0	13.6	9.0	46.2	11.5	2.0	29.3	0.47	0.0
900[b]	1.16	10.11	16305	6.5	87.9	1.1	0.5	4.0	7.7	15.8	10.1	..	..	6.5	2.0	24.8	..	2.90
1000	1.18	9.7	16230	6.1	89.7	1.2	0.5	2.5	4.0	16.2	8.1	6.3	65.4	5.0	0.9	22.5	1.25	2.64
1100	1.20	13.6	16220	5.8	88.5	1.1	0.4	4.2	3.9	16.1	8.4	1.3	70.3	3.9	1.1	19.4	0.86	4.72

[a] Residue on extraction with benzene.
[b] One of duplicate tars from 800° C. test and both of 900° C. tests were fractionated with same cuts as tars from coal No. 1.

Table VIII—Agreement of Bureau of Mines Test Results and Plant Yields, Coal No. 1

Type of Plant	Carbonization		Coal Analysis			Yields				Gas[a]	Gas[a]	Sp. Gr. Tar
	Temp.	Time	Moisture	Ash	Volatile matter	Coke	Gas	Tar	$(NH_4)_2SO_4$			
	° C.	Hours	%	%	%	%	Cu. ft./ton	Gal./ton	Lbs./ton	B. t. u./cu. ft.	B. t. u./lb. coal	
Horizontal retorts, Lowell, Mass.	1043	10	1.7	6.5	35.1	68.6	12110	11.6	19.1	542	3282	1.21
Intermittent vertical retorts, Rochester, N. Y.		12	2.5	6.6	35.8	70.7	11347	11.4	23.0	540	3064	1.16
By-product ovens, Utica, N. Y.	1090	12	2.1	7.1	35.2	70.0	11315	12.3	24.7	584	3302	1.16
Test retort, Bureau of Mines	1050	6	1.6	7.5	34.2	69.3	10822	13.2	19.2	611	3306	1.16
Test retort, Bureau of Mines	1100	4	1.6	7.5	34.2	69.4	12237	10.1	16.9	601	3677	1.20
Av. plant tests	1070	12	2.1	6.7	35.3	69.8	11591	11.8	22.3	555	3217	1.18
Av. 1050° and 1100° C., Bureau of Mines tests	1070	5	1.6	7.5	34.2	69.4	11530	11.7	18.0	606	3491	1.18

[a] Unscrubbed for light oil.

Table IX—Comparison of Coke Properties, Bureau of Mines and Plant Tests, Coal No. 1

Type of Plant	Shatter Test, Cumulative			Tumbler Test, Cumulative			Specific Gravity		Cells	Volatile Matter, Moisture- and Ash-Free
	On 2 in.	On 1½ in.	On 1 in.	On 1½ in.	On 1 in.	Through ⅛ in.	Apparent	Real		
	%	%	%	%	%	%			%	%
Horizontal retorts, Lowell, Mass.	58.5	79.6	91.3	15.9	38.8	36.9	0.81	1.89	57.1	1.1
Intermittent vertical retorts, Rochester, N. Y.	53.9	75.0	87.6	13.3	42.7	28.9	0.91	1.87	51.3	1.4
By-product ovens, Utica, N. Y.	57.0	76.3	89.2	12.4	42.0	27.8	0.96	1.88	48.9	1.9
Test retort 1050° C., Bureau of Mines	30.6	62.5	85.5	6.2	37.3	31.4[a]	0.87	1.90	54.1	1.0
Test retort 1100° C., Bureau of Mines	21.4	46.1	79.7	2.4	28.5	28.4[a]	0.85	1.95	56.7	0.7
Av. plant tests	56.5	77.0	89.4	13.9	41.2	31.2	0.89	1.88	52.4	1.5
Av. 1050° and 1100° C., Bureau of Mines tests	26.0	54.3	82.6	4.3	32.9	29.9	0.86	1.93	55.4	0.9

[a] Through ¼-inch screen.

Table X—Agreement of Bureau of Mines Test Results and Plant Yields, Coal No. 2

	Carbonization		Coal Analysis			Coke	Gas	Tar	$(NH_4)_2SO_4$	Gas	Gas	Sp. Gr. Tar	Shatter Test, Cumulative		Volatile Matter in Coke As-Received
	Temp.	Time	Moisture	Ash	Volatile matter								On 2 in.	On 1½ in.	
	° C.	Hours	%	%	%	%	Cu. ft./ton	Gal./ton	Lbs./ton	B. t. u./cu. ft.	B. t. u./lb. coal		%	%	%
Vertical chamber ovens	1055	12	2.0	3.1	37.7	68	11800	12	23.3	573	3377	..	57.2	71.2	1.9
By-product ovens[a]	1066	24½	...	...	..	..	13260	..	..	505	3354	..	68.0	..	1.0
Inclined retorts[b]	1093	6	...	...	..	..	11260	13	..	570	3210	..	..	..	...
Inclined retorts[c]	1010	8	...	...	..	..	10640	13.3	..	605	3219	..	..	..	...
Horizontal retorts	..	..	1.3	3.5	36.3	64.7	10860	13.3	18.9	645	3490	1.26	..	..	1.1
Horizontal retorts[d]	1288[e]	8	...	...	..	65.0	11500	10.8	22.5	610	3507	..	..	..	...
Horizontal retorts[f]	1200[e]	8	4.2	3.4	34.7	67.7	12640	..	..	530	3342	..	..	..	1.3
B. of M. test	1000	3¾	2.2	2.2	36.6	67.6	11372	14.0	17.1	624	3548	1.18	22.5	56.4	1.2
B. of M. test	1100	5	2.2	2.2	36.6	66.6	12736	10.6	14.3	593	3776	1.20	2.7	22.8	2.1
Av. of plant tests	1056	..	...	...	..	66.4	11709	12.5	21.6	577	3357	..	62.6	71.2	1.3
Av. of 1000° and 1100° C. B. of M. tests	1050	..	...	...	..	67.1	12054	12.3	15.7	608	3662	1.19	12.6	39.6	1.6

[a] 18 7/8 to 21 inches wide, 9 feet, 10 inches deep; 37 feet, 6 inches long.
[b] 16 inches × 27 inches × 15 feet.
[c] 15 inches × 25 inches × 18 feet.
[d] D retorts; 16 inches × 26 inches × 16 feet.
[e] Temperature of combustion chamber in setting.
[f] 16½ inches × 26½ inches × 20 feet.

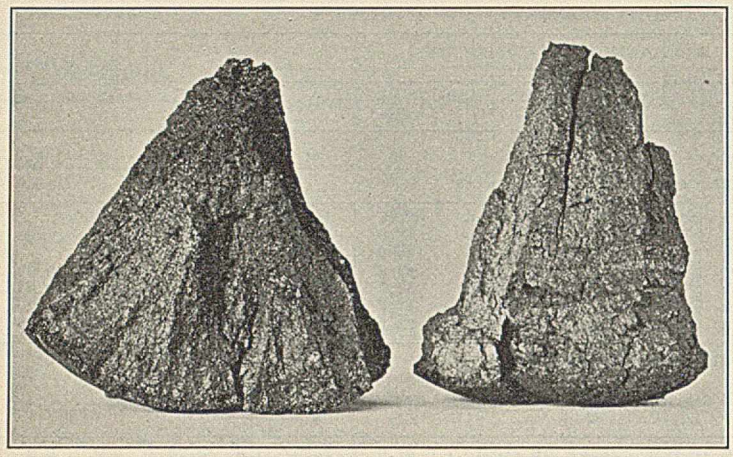

Figure 20—Coke from Coal No. 1, Pittsburgh Bed, Ocean No. 2 Mine, Carbonized in Bureau of Mines Retort

Left, 700° C. Right, 900° C.

the test retort on coal from the same mine at 1050° and 1100° C., is given in Table VIII.

The agreement of gas, coke, and tar yields is surprisingly close. The difference in the averages of the three plants and the average of the Bureau of Mines 1050° and 1100° C. tests is less than 1 per cent. Likewise, the calorific value and B. t. u. of gas per pound of coal agree equally well with the Utica test, but are somewhat higher than Rochester and Lowell results. The experimental retort gives low ammonium sulfate yields owing to the catalytic effect of the iron retort in decomposing ammonia. The experimental retort ammonia yield at 1050° C. was about the same as was obtained in the horizontal retorts at Lowell, but was 30 per cent less than was obtained in the by-product ovens at Utica.

A comparison of the properties of the cokes from plants and test retort is given in Table IX. It will be noted that the test-retort coke made at 1050° C. has nearly the same volatile matter, cell space, and apparent specific gravity as the average of the three plant cokes; also the resistance to abrasion or hardness, as shown by the per cent dust in the tumbler test, is about the same.

Comparison of shatter and tumbler tests shows much less material over the 2- and $1^1/_2$-inch screens on the test retort coke than in the plant cokes. This difference does not mean that the latter were intrinsically weaker cokes. There are two reasons for the difference: First, the test-retort cokes were carefully removed from the retort by hand and placed in the shatter and tumbler machines without any rough handling, whereas the plant cokes were pushed from the ovens while hot, dropped on a wharf, and moved on conveyors before being sampled for testing; second, the rate of heating the charge in a circular retort is different from that of a rectangular retort heated from two sides only. The circular retort produces wedge-shaped pieces of coke, whereas a coke oven produces prismatic pieces. Hence shatter and tumbler figures do not have the same absolute values as are obtained in plants for the same coal. It is believed, however, that they have relative value for comparing different coals and blends of coal in the test retort. Also it is to be expected that the test-retort cokes would have somewhat lower specific gravity and higher porosity than oven cokes owing to less weight on the charge.

Table X shows similar comparisons between yields obtained in several types of carbonization plants and test-retort results obtained at 1000° and 1100° C. for Elkhorn-bed coal. In this case only approximate agreement can be expected, because the coals used in the plant tests were from several different mines in the Elkhorn bed. None was from the same mine as the coal used in the test retort. This difference is shown in the coal analyses. The test-retort coal was of selected high quality having only 2.2 per cent ash, whereas the plant coals represented the usual grade of coal shipped, being 3 to 4 per cent ash. However, even with these differences in coal and in the mode of heat treatment in different types of gas plants, the plant yields of gas, coke, and tar and B. t. u. in gas per pound of coal are, in most cases, between the limits obtained with the test retort at the 1000° and 1100° C. carbonization temperatures. It must be kept in mind that the plant results assembled in Tables X are from miscellaneous sources and were not conducted under the same systematic supervision as were the American Gas Association tests reported in Tables VIII and IX on the Pittsburgh coal. The data are necessarily incomplete, yet they are of value in showing that the test-retort yield figures for gas, coke, and tar may be accepted as representative of large-scale plant yields without the application of any factor.

Discussion of Results

The dominant influence of temperature and rate of heating on yields and properties of the products of carbonization is shown graphically in Figures 5 to 17. In general both coals give similar results, although the higher percentage (2.4) of volatile matter in the Elkhorn coal is evident in its higher yield of gas and tar and lower yield of coke. Also, the higher

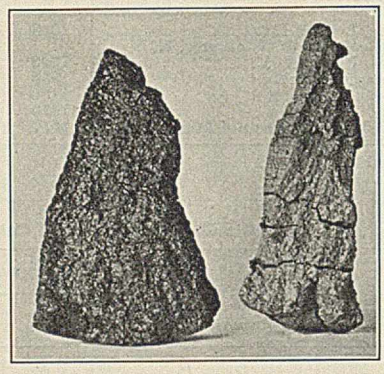

Figure 21—Coke from Coal No. 2, Elkhorn Bed, Mine No. 204, Carbonized in Bureau of Mines Retort

Left, 500° C. Right, 1100° C.

percentage of nitrogen (0.1) in the Pittsburgh coal is reflected in a greater yield of ammonia. From the lower oxygen content of the Pittsburgh coal in comparison with Elkhorn one would expect a lesser proportion of low-boiling fractions and of acids in the tar, a larger proportion of neutral oils, and a stronger coke. Figures 15, 12, and 10 bear out this expectation with one important exception.

The midtemperature coke of Elkhorn coal made at 700–900° C. is more resistant to breakage on both shatter and tumbler tests than the Pittsburgh coke. Figure 10, on physical tests, shows the unique practical value of making these carbonization tests at 100-degree temperature intervals throughout the entire practical range from low-temperature to high-temperature coking practice. In the case of coking 100 per cent Elkhorn coal. Figure 10 shows that the strongest coke is obtained in the range from 800° to 900° C. Above 900° C. the strength falls off sharply owing to the development of shrinkage cracks or cross fractures. Possibly a decrease of coking time would reduce this effect.

On the other hand, Pittsburgh coal produces the strongest

coke, as measured by shatter and tumbler tests at 600° C. The strength is progressively lower as the carbonizing temperature is increased. On the basis of these tests a low-temperature process is most suitable for Pittsburgh coal and a midtemperature process for Elkhorn coal.

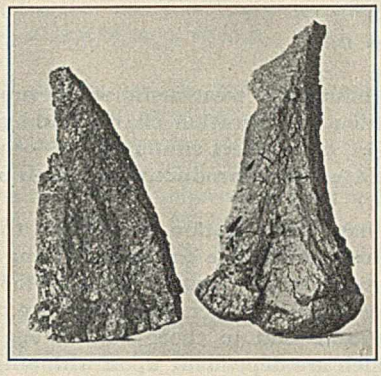

Figure 22—Coke from Coal No. 2, Elkhorn Bed, Mine No. 204, Carbonized in Bureau of Mines Retort

Left, 600° C. Right, 1000° C.

Although the low-temperature cokes from both Pittsburgh and Elkhorn coal are more resistant to breakage than the high-temperature cokes, the low-temperature product is less resistant to abrasion as shown by the larger percentage that passes through a $^1/_4$-inch screen after a tumbler test. Also, as shown in Figure 11, it has a much lower density. The percentage of cells does not vary greatly throughout the entire temperature range, but the cells are much larger at low temperatures. Figures 18 to 23, inclusive, show typical pieces of coke from coals 1 and 2 at various carbonization temperatures.

In order to bring out the contrast of structure, 500° C. coke is compared with 1100° C. coke; 600° C. with 1050° or 1000° C.; and 700° with 900° C. It will be observed that the 1100° C. coke is fine-grained, fingery, and cross-fractured, and has a bright, metallic luster. The 1000° C. cokes are also fingery but less cross-fractured. At 900° C the coke is more blocky and comparatively free from cross checks. It will be noted that in Figure 10 the resistance to breakage on the shatter and tumbler test shows a sharp drop above 900° C. The 500° to 800° C. cokes are coarse-grained, blocky, and free from checks. The 500° C. coke has a dull, black appearance, which gradually changes to the bright, metallic luster as the carbonization temperature reaches 800° C.

Since shrinkage fractures develop above 900° C. and density falls off sharply below 700° C., it appears that the best coke for domestic fuel purposes from 100 per cent Pittsburgh or Elkhorn coal will be produced at carbonization temperatures between 700° and 900° C. The greater reactivity of coke made in this temperature range would also be a desirable characteristic in domestic fuel.

The ultimate analyses of the various cokes plotted in Figure 9 show that with these two coals practically all the volatile matter is distilled off at 900° C. There is comparatively little change in composition of the coke above this temperature.

This observation checks the results of Fieldner and Hall (*4*), who ran volatile-matter determinations on 1-gram samples of Pittsburgh coal at various temperatures up to 1100° C. They found that at temperatures above 900° C. very little additional volatile matter was given off. It was on the basis of their investigation that volatile-matter determinations were standardized at 950° C. The marked increase in gas yield above 900° C., as shown in Figure 8, is from cracking of tar rather than additional gas removed from the coke.

Composition and physical properties of the gas are shown in Figures 13 and 14. It is interesting to note that 1.1 per cent sulfur in the Pittsburgh coal gave 320 grains of hydrogen sulfide in 100 cubic feet of the gas obtained at 900° C., and 0.6 per cent sulfur in the Elkhorn coal gave 165 grains of hydrogen sulfide in the gas, the ratios being 11/6 = 1.83 for the sulfur in the coal, and 320/165 = 1.94 for the hydrogen sulfide in the gas.

Figures 16 and 17 show the calorific values of the gas as recorded by the Thomas calorimeter, and also give the time of carbonization for each test. The tremendous increase of coking time with decrease of temperature and the cracking of hydrocarbons at the higher temperatures are shown in a striking manner by these curves. The downward turn of the curves near the end of the tests indicates the arrival of the zone of coke formation at the center of the retort.

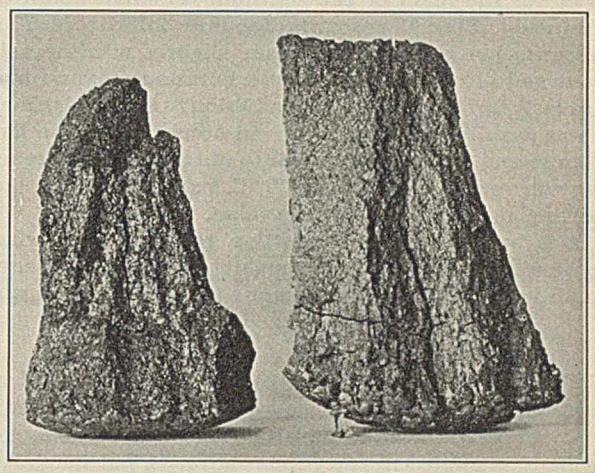

Figure 23—Coke from Coal No. 2, Elkhorn Bed, Mine No. 204, Bureau of Mines Retort

Left, 700° C. Right, 900° C.

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Molasses Used for Alcohol Production in Argentina

More than four-fifths of the total alcohol production in Argentina is reported to be obtained from molasses, the remainder being manufactured from potatoes and corn, according to Assistant Trade Commissioner Charles H. Ducote, Buenos Aires.

There are forty-one sugar mills and refineries in the Republic, twenty-six of which operate alcohol-distilling units. The total production of these plants reached 20,783,910 liters in 1928 and 21,044,437 liters in 1929. The Province of Tucuman is the most important producing area, there being twenty-one distilling plants in operation, whose total output in 1929 amounted to 15,427,379 liters. Approximately 3,500,000 tons of cane are ground annually in the province, which yields 30 to 40 kg. of molasses per ton, making about 120,000 tons of molasses a year. Approximately 230 liters of alcohol are produced from each ton of molasses treated. Alcohol is not imported into Argentina. Exports of alcohol totaled 425,402 and 451,245 liters for the years 1927 and 1928. About 90 per cent of the exports go to Uruguay, with the remainder to Bolivia, Brazil, and Paraguay.

Normal and Modified Foaming Properties of Whey-Protein and Egg-Albumin Solutions[1]

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Measurements of the normal and modified foaming properties of solutions of whey proteins and of egg albumin have been made and comparisons drawn. It has been found that the stability of the foams made from whey liquor or the powdered product may be greatly increased by the addition of (1) small quantities of calcium hydroxide and subsequent neutralization of the alkali, (2) successive small quantities of acid and alkali to the foam while whipping, (3) small amounts of tannic acid to either the foam or the solution, (4) small quantities of saponin, (5) small amounts of sodium sulfite or bisulfite. Precipitation with alcohol from slightly alkaline solutions and filtration from the precipitation medium has a similarly favorable effect. In addition to these treatments it was usually found necessary, in order to obtain a large volume and a maximum stability of the foam, to preheat the whey-protein solutions to 50° C. before whipping; such heating alone was of but little value.

It is believed that, in addition to necessary surface-tension and viscosity relationships, the most essential condition for the stabilization of a foam made from whey proteins is induced by treatments which produce in the interface either denaturation changes and precipitation of the protein, or an effect similar to gel formation, both types of changes being productive of tough or semi-solid films.

A preliminary investigation has shown that solutions of whey proteins also have good emulsifying properties.

Whey-protein powder has an excellent food value and can be made much cheaper than dried-egg products. It appears probable that in those uses of egg albumin or egg yolk which are dependent upon whipping or emulsifying properties, such as in salad dressings, sponge candies, cake icing, ice cream, etc., this whey product may serve as a satisfactory substitute for the egg white or yolk; very favorable results have already been obtained when whey-protein powder was used in salad dressings and in ice cream. In those uses of egg white which are also dependent upon its heat-coagulative properties, such as in baked or cooked products, whey-protein powder, owing to its possession of such properties to an insufficient degree, cannot serve as an egg substitute.

THE foaming and heat-coagulative properties of egg albumin (egg white) add greatly to the commercial importance of this product. By its use not only may air be incorporated in many kinds of foods, but its gelation on heating results in giving a certain rigidity to the cooked or baked product and a consequent retention of the air. Thus a light and desirable texture is obtained. The possession of these characteristics by a much lower-priced product made from whey, either naturally or as a result of permissible physical or chemical treatment, would result, therefore, in its extended use.

The relationship of this property of foaming to emulsification should also be considered (*3, 4*). Both phenomena are dependent upon a concentration of the colloid at the interface and the resulting formation of a gelatinized or semi-solid membrane. For this reason a study of the foaming properties of a solution should indicate, at least to some degree, its value as an emulsifying agent.

Because of its emulsifying properties, egg yolk is used to a considerable extent in such products as mayonnaise dressing. This investigation should consequently be expected to indicate the possibilities of utilizing whey proteins as a substitute for that part of the egg as well as for the white. The results submitted in a later section of this paper substantiate this opinion and offer confirmatory evidence of the relationship between foaming and emulsification with respect to protein solutions.

A discussion of the normal foaming properties of protein solutions, of methods of altering such properties in solutions of egg albumin and whey proteins, their measurement and the results obtained, together with preliminary data upon the emuslifying properties of whey proteins, are presented here. An investigation dealing with the heat-coagulative properties of egg albumin and of whey-protein solutions and their modification has been completed and will be reported in the near future.

[1] Received May 20, 1930.

Foaming or Whipping Properties

The phenomenon of foaming is treated in this paper mainly from the standpoint of stability or permanency, and not as a property of frothing, which may be but temporary in nature.

Freundlich (*6*) considers foams to be disperse structures with a liquid as dispersion medium and a gas as disperse phase. For the development of a fairly permanent foam he believes that the surface tension should be low and the viscosity high. Moreover, it is important that the colloidal solution shall have to a considerable degree "the power of forming tough or amorphous solid surface films, which circumstance is decisive for the formation of a durable foam."

The results of a number of investigations reviewed by Clayton (*3, 4*) agree for the most part with the contention that low surface tension and high viscosity are the principal factors involved in the formation of a stable foam. A soap solution is an example of the effect of these two influences on the foaming ability of a solution.

Ramsden (*15*) has claimed that an adsorption effect, or the concentration of the colloid at the interface and its subsequent precipitation in the foam, is in many instances the most important influence on the permanency of the foam. Here too, however, a change, of which the surface tension is a measurement, is the initiative factor in foam stability.

A review of the literature on foaming shows that the many explanations of this phenomenon can in general be harmonized with the conceptions of Freundlich, Clayton, and Ramsden. The Gibbs adsorption equation (*8*) is a mathematical expression of the relationship of some of these factors involved in foaming phenomena. It defines the relationship of the change of surface tension with concentration of surface depressant to its distribution, or its concentration in the body of the fluid and in the film; this surface concentration in turn, mainly through adsorption changes and subsequent precipitation

(due to denaturation[2] in protein solutions), or the formation of a semi-solid membrane, markedly affects the nature of the film or foam. The "superficial viscosity" (*14*, *20*), the "plasticity of the film" (*21*), and the "structural viscosity" (*13*) can be included under the heading "the nature of the film."

It may thus be seen that the explanations of foaming by previous investigators are principally concerned with the three factors—surface tension, viscosity, and the character of the film.

In an investigation upon the proteins of milk, Seidel and Hesse (*19*) have obtained quantitative proof of the effect of the Ramsden phenomenon of protein adsorption and subsequent precipitation. Holm (*16*) likewise has treated of foaming phenomena with special reference to milk and milk products. Dahlberg and Hening (*5*) have made an extensive investigation of viscosity, surface tension, and the whipping properties of cream.

Experimental

The measurements of the surface tensions of the protein solutions were made with the du Noüy apparatus. Care should be exercised in making such determinations, as du Noüy (*11*) has shown that when surface-tension depressants are added to protein solutions absorption reactions between protein and depressant may, after a short time, neutralize the usually observed lowering of surface tension.

The viscosity measurements were made by determining the time required for a given volume to flow by gravity through a capillary tube with submerged discharge. Viscosities so determined were considered sufficiently accurate for the purpose of this investigation.

The strength and stability tests of the foams or whipped products were performed by measuring the rate of penetration into the whip of a standardized glass tube or penetrometer, the same penetrometer being used in all the tests recorded. This glass tube was of 1.25 cm. inside diameter and sealed at one end; it was 42.25 cm. in length, and at the upper end 12 cm. were drawn out to a diameter of 0.4 cm. The weight was 37.5 grams.

In detail the method of measuring the strength and permanency of the foam was first to whip with an egg beater a 20 per cent solution of the substance to be tested; beating was continued for 5 minutes or until it was thought that more beating would not increase the stability of the whipped product. The foam was then quickly transferred to a 250-ml. cylinder and well shaken down by pounding the bottom of the cylinder upon a rubber stopper. The penetrometer, which passed through a glass guide, thus insuring a perpendicular fall, was so adjusted that it touched the surface of the foam or whip. Upon release of the penetrometer its rate of fall through the whipped product was measured. The initial drop was indicative of the initial strength of the foam, while the fall in centimeters at 10- and 20-minute intervals was a measurement of the foam stability.

A further determination of the permanency of the whip was made by ascertaining the time interval necessary for the appearance of a layer of liquid in the bottom of the container.

The hydrogen-ion measurements were for the most part made by potentiometric methods.

Results and Discussion

The values of the surface tensions and viscosities of certain whey-protein solutions and of egg albumin at a temperature of 24° C. are shown in Table I.

[2] The term "denaturation" is used in this manuscript in the sense of a probable chemical change, hydrolytic in nature, and a definite irreversible physical alteration of a hydrophilic into a hydrophobic colloid, the resulting hydrophobic colloid being insoluble at the isoelectric point, in the presence of electrolytes, and with respect to whey proteins partially so at a pH of 6–7.

Table I—Surface Tensions and Viscosities of Whey-Protein and Egg-Albumin Solutions at 24° C.

Designation	Acidity		Surface Tension	Viscosity
	%	pH	Dynes/cm.	Cp.
Swiss cheese (rennet) whey:				
Neutralized to	0.03	7.25	49.1	0.994
Unneutralized	0.11	6.7	48.5	0.987
Grain-curd casein whey:				
Neutralized to	0.04	7.2	48.3	1.029
Whey liquor	..	6.6	47.6	1.878
Whey liquor, old and slightly jellied	..	..	..	8.100
Egg albumin (12.5% soln.)	..	7.8	49.9	1.646

In this investigation upon the foaming or whipping properties of protein solutions it was particularly desirable to determine whether the proteins of the solution designated in Table I as whey liquor could be used as a substitute for egg products. This liquid product is the mother liquor resulting from the crystallization and removal of most of the milk sugar from neutralized and condensed whey (*2*). It contains approximately 15 per cent protein, 20.0 per cent lactose, and 7.0 per cent milk salts, or a total solids content of approximately 42.0 per cent. About two-thirds of the protein of this liquor is lactalbumin or lactalbumin hydrolytic products (albumoses); the remainder is mostly casein (paracasein).

The solutions of egg albumin were made from dried egg white.

The titratable acidities are expressed as lactic acid, phenolphthalein having been used as an indicator.

It will be seen that there are but slight differences in the surface tensions of the solutions measured, whey liquor in which the albumin is concentrated having the lowest value. Values lower than those measured may be obtained by heating the different types of whey to 50° C. At this temperature, in agreement with other investigations on milk (*17*), it was found that the foaming or whipping properties of the whey products were considerably increased. In experiments on skim milk it has been found that this rise in temperature (25° to 50° C.) corresponded to a surface-tension lowering of approximately 7 dynes per cm. An analogous reduction for whey products would give a value of approximately 40 dynes per cm.

Since the surface tensions of the solutions of whey proteins and of egg albumin are practically the same and since the latter substance possesses excellent foaming and whipping properties, it is believed that, in so far as the surface tension is concerned with foaming properties, whey-protein solutions possess this physical characteristic to an approximately optimal degree. Furthermore, since the addition of surface-tension depressants did not produce an increase in foaming properties equivalent to that produced by heating of the whey-protein solutions, it is likewise believed that the influence of heating on foaming did not primarily involve a surface-tension relationship, but rather produced changes in viscosity, peptization, and in particular an accelerated denaturation of the protein, resulting in a gelatinized or semi-solid film which, as will later be seen, we believe materially influenced the permanency of the foam.

The work of the present writers, as well as that of other investigators, tends to show that a certain degree of surface-tension lowering is necessary to readiness of foaming or to the initiation of a foam. The writers have found that the whey proteins under investigation already possessed to a considerable extent the property of initiating or forming a foam. Since the experiments described in this paper were primarily concerned with methods for improving the stability or permanency of the whipped product, the surface-tension measurements were not extended.

Table I shows that the values for the viscosities of whey liquor and of a 12.5 per cent solution of egg albumin approximate each other. It was found that the slightly jellied product

Table II—Effects of Various Methods of Treatment upon the Strength and Stability of Foams Made from Whey Liquor

Expt.	Treatment[a]	pH	Strength of Foam	Stability of Foam	Character of Foam	Remarks
			Cm.	*Minutes*		
1	Untreated	6.3	Began to break immediately		Poor	
	EFFECT OF HEAT TREATMENT					
2	Heated to 60° C. before beating		Penetrometer sank slowly to bottom in 5 minutes	40	Fair	
3	Forewarmed at 60° C. for 45 minutes		13.5–	50	Fairly good	Moist and frappé-like foam
	EFFECT OF HYDROCHLORIC ACID					
4	+HCl[b]	5.1		45	Fairly good	
5	As in 4 except heated to 55° C.			75	Good	
6	As in 4 except stood for 24 hours		Foam too poor to measure		Poor	High viscosity; product had thickened overnight
	EFFECT OF SODIUM HYDROXIDE					
7	NaOH added	8.3	5–	90	Good	
8	NaOH added and heated to 60° C.	10.2	4–6–9	105	Very good	Foam dried out partially
9	As in 8 except neutralized with HCl	6.9	14–	50	Fairly good	
10	As in 9 except alkali and acid added to foam	7.5	2–		Excellent	Applicable as a general procedure
	EFFECT OF CALCIUM HYDROXIDE AND CALCIUM SALTS					
11	$Ca(OH)_2$ added	11.5	4–7–10		Good	Dried out partially
12	As in 11 except heated to 60° C. and neutralized with HCl	7.2	3–5–7	110	Very good	Dried out partially
13	As in 12 except heating continued for 30 minutes	7.2	No measurement possible		Very poor	Partial coagulation of liquor
14	As in 12 except neutralized before heating	7.2	4–		Good	
15	As in 12 except double quantity of $Ca(OH)_2$ used	7.0	2–4–7	180	Excellent	Dried out
16	$Ca(OH)_2$ and $CaCl_2$ (0.6%) added	9.0	4–8–9	193	Very good	
17	$Ca(OH)_2$ and $CaCl_2$ (1.25%) added	11.0	3–7–10	200	Very good	
18	As in 16 except heated to 45° C. for 10 minutes		1/4–2–4	240	Excellent	
19	$CaCl_2$ (1.25%) added	6.3	12	45	Fair	
	MISCELLANEOUS TREATMENT					
20	Dialysis,[c] alcohol and ether treatment	7.3	2–		Excellent	2.1% ash, a dry foam
21	Dialysis alone[c]	7.0	Very poor foam			2.1% ash, protein swells in water

[a] Except where otherwise noted, all solutions were warmed to 50° C. before whipping.
[b] In the treatment of the protein solutions 10 per cent solutions of acid and alkali were used.
[c] Protein salted out twice with sodium sulfate before dialysis; it was then precipitated by alcohol, from a slightly alkaline solution (pH = 8.5), washed with ether, and dried.

having a viscosity of 8.1 centipoises would not foam or whip. In this case it was evident that the viscosity was so high as practically to preclude the possibility of incorporating air.

It appears that a relatively low viscosity is favorable to foam formation, but it has been found that the films are frequently of insufficient strength to resist rupture. Evidently the ideal condition would be that of a liquid which changed its viscosity from a low to a high value upon passage into the film. The methods to be later discussed which the writers have developed for increasing the stability of a foam probably do effect this change.

In Tables II and III the results of numerous experiments to determine the strength and stability of foams are presented. As has been indicated, both whey liquor and the powdered product made from it have been used in these tests. The various experiments have been grouped, and in a number of cases combined, according to similarity of treatment. Thus the values given often represent the averages of three or four determinations.

The three numerals given under "Strength of Foam" refer to the distance in centimeters to which the penetrometer fell; (1) after 10 seconds, (2) after 10 minutes, and (3) after 20 minutes. In a few experiments only the first determination was made. The values listed under "Stability of Foam" represent the time of watering off or the number of minutes required for the formation by gravity of a layer of liquid from the foam or whipped product. The "Character of the Foam" was judged mainly by holding close to the ear the vessel containing it. Rapid breaking of the films or bubbles could be heard in a poor foam, while in one classed as very good no sound of such collapse could be distinguished.

Good agreement was usually found between the gradings listed under "Character of Foam," "Stability of Foam," and the first figure or initial strength given under "Strength of Foam." The initial strength is therefore considered the characteristic best suited to indicate these properties of a foam.

The results of the foaming experiments are more clearly presented by separately considering the experiments upon whey liquor (Table II) from those conducted upon solutions of the powder (Table III) made from this product.

The first entry in Table II shows that the untreated whey liquor yields poor foams. Heating of the liquor to 60° C. before beating (Expts. 2 and 3) produces some improvement, as does slight acidification (Expts. 4 and 5), whereas the addition of alkali (Expts. 7 to 18) yields considerable improvement, calcium hydroxide having a more pronounced effect than sodium hydroxide. It is likewise true that the effect of added calcium hydroxide solution upon foaming properties (Expt. 12) is not removed when the solution is neutralized, whereas with sodium hydroxide this effect is largely dissipated (Expt. 9). Such a result has also been found in similar experiments with solutions of whey powders. This variation is probably due to the difference in the reversibilities of the two reactions, calcium hydroxide in general possessing to a greater extent the property of producing changes in protein solutions which may be classed as permanent or irreversible.

The addition of calcium salts alone is practically without effect (Expt. 19). However, the presence of a relatively high concentration of Ca^{++} in an alkaline medium, particularly if the solution is warmed (Expt. 18), yields a foam or whip excellent in character and of great strength or stiffness.

It is likewise true that successive additions, during beating, of small quantities of acid and alkali to the foam or whipped product (Expt. 10), and in this way shifting the reaction from acid to alkaline and vice versa, also give a product of very high strength and permanency. These conditions are favorable to changes in the film such as denaturation and precipitation of the protein, which result in a gelatinized or semi-solid film.

Experiment 20 shows that dialysis, followed by precipitation of the protein with alcohol (from a slightly alkaline solution) and washing with ether, gives an excellent whipped product. Dialysis alone (Expt. 21) gives a very poor foam. Here again, as a result of alcohol treatment, the probability of changes such as denaturation, and a resulting gelatinization in the film, is evident.

The number of experiments upon the foaming properties of the powdered liquor was much greater than upon the liquor itself. The results included in Table III will not be discussed in detail, for an inspection shows that in general the two products, when treated in a similar manner, exhibited similar

Table III—Effects of Various Methods of Treatment upon the Strength and Stability of Foams Made from Whey-Protein Powder Solutions

Expt.	Treatment[a]	pH	Strength of Foam	Stability of Foam	Character of Foam	Remarks
			Cm.	*Minutes*		
22	Untreated (25% soln.)	6.6	12–19–	20	Poor	
23	Liquor of pH 6.6 forewarmed to 60° C. for 30 minutes before powdering	6.6	19–21–	22	Poor	
	EFFECT OF HYDROCHLORIC ACID					
24	Liquor + HCl (and powdered)[b]	5.0		15	Poor	
25	As in 24 except liquor forewarmed to 60° C. after acid addition			15	Poor	
	EFFECT OF SODIUM HYDROXIDE					
26	Liquor + NaOH	7.3	8–11–22	40	Fairly good	
27	Liquor + NaOH	7.8	5–12–13	70	Good	
28	Liquor + NaOH	9.3	9–16–17	57	Fairly good	
29	Liquor + NaOH	13.0	14–15–24	55	Fair	Excessive alkali
	EFFECT OF CALCIUM HYDROXIDE AND CALCIUM SALTS					
30	25% powder soln. + $Ca(OH)_2$	8.0	6–11–	45	Good	Dries out partially
31	As in 30 except heated to 65° C. before whipping	8.0	11–12–12			Toughens and becomes gluelike on standing
32	25% powder soln. + $Ca(OH)_2$	9.0	5–9–10	94	Good	
33	25% powder soln. + $Ca(OH)_2$ + $CaCl_2$ (2.5%) and warmed	10.0	1/2–1–2	180+	Excellent	A dry foam
34	25% powder soln. + $Ca(OH)_2$ + $CaCl_2$ (1.25%)	9.5	4–7–14	60	Good	Dries out partially
35	25% powder soln. + $Ca(OH)_2$ (pH 10.0) and neutralized with HCl	7.0	5–8–9	90	Very good	
36	Liquor and $Ca(OH)_2$ (pH 10.5) heated to 45° C. and neutralized with HCl	7.0	3–6–7	90	Excellent	Whips very well, even in cold soln.
37	Liquor + $CaCl_2$ (0.5%)		10–	25	Fair	
	MISCELLANEOUS TREATMENT					
38	Soln. of powder made slightly alkaline, pptd. with alcohol, and washed with ether	7.0	4–		Excellent	Requires a long time to beat up, requires no heating
39	As in 38 but alcohol allowed to remain in contact with albumin overnight	7.0	A poor foam			Denaturation carried too far; protein mostly insoluble
40	25% soln. of whey powder + tannic acid (0.5%)		6–	30	Good	
41	25% soln. + sodium oleate (1.25%)		Poor foam	Foam quickly broke		
42	25% soln. + sodium sulfite (3.0%)		4–	50	Very good	
	EXPERIMENTS WITH POWDERED EGG ALBUMIN					
43	25% soln.		4–15–23	30	Very good	Dries out
44	30% soln.		4–9–20	35	Very good	Dries out
45	15% soln.		6–14–15	30	Good	Dries out

[a] Except where otherwise noted, all solutions were warmed to 50° C. before whipping; all solutions of whey-protein powder were made 25 per cent.
[b] All the experiments in this table were conducted upon solutions of the powdered product. For the sake of brevity the designation "and powdered" is omitted from the treatment of the following experiments.

foaming properties. The essential difference between these products resulted from the heat treatment, the powder being subjected in the process of spray-drying to a temperature of approximately 75° C. A higher temperature would have been obtained in commercial drying on a large scale.

The following comments upon foaming properties relate to those reagents and treatments which were not used in experiments on the whey liquor. Thus it was found that the addition of small quantities of tannic acid (Expt. 40) to solutions of whey-protein powder, either before or during whipping, yields an improved product. Such treatment of a rather concentrated protein solution produces a semi-coagulum of a liquid gel consistency. It is possible that, on beating, these threads of the proteins or the continuous phase give a strength and stability to the foam.

The addition to whey-protein solutions of surface tension depressants such as sodium oleate or sodium ricinoleate (Expt. 41) yields a product with poor foaming properties. It is probable that the hydrolysis of such depressants produces fatty acids sufficient in quantity to diminish these properties to a considerable extent since it is known that the presence of small amounts of fat or of a third liquid phase will cause a rapid collapse in foams and whips which otherwise are excellent with respect to strength and stability. Such is the case even with beaten egg albumin.

Experiments upon solutions of powdered egg albumin (43, 44, and 45) are self-explanatory. These results serve as a very useful guide or measurement of the relative foaming properties of protein solutions. It will be noticed that a number of the treated whey-protein solutions showed a higher stability of foam than did equivalent concentrations of egg-albumin solutions and that some evidenced a greater strength of foam. Experiments which showed the possession by whey proteins of foaming or whipping properties to a high degree were numbers 10, 15, 18, 20, 33, 34, 35, 36, 38, and 42.

Preliminary experiments with saponin showed that the addition of small quantities of this substance to whey-protein solutions produces greatly increased foaming properties. These experiments were not extended, since such a substance could not probably be used in a food product because of the reputedly poisonous nature of some saponin products.

A rather remarkable characteristic is shown in the foams of whey-protein solutions which have been treated with sodium sulfite (Expt. 42). Not only are the foaming properties considerably improved, but the whipped product is able to withstand, even with continued beating, the addition of butter fat or other fats. One of the faults of beaten egg albumin is that in baking it will not permit the thorough admixture of a fat or shortening without at least partial collapse of the whip and consequent loss of air. For this reason beaten whites of eggs must be folded into the cake dough rather carefully in order to obtain proper air incorporation.

The favorable action of sodium sulfite (or bisulfite, made slightly alkaline) probably results from the combined effect of the alkaline reaction, strong reducing properties, and reactive sulfur groupings upon the character of the protein, particularly its degree of hydration, thus increasing the fat-emulsifying power of the solution. The possible relationships of reducing action and of sulfur groupings to the physical properties of protein solutions are discussed by Mathews (*9*). As will be shown in a subsequent paper, the addition of sodium sulfite also increases the heat-coagulative properties of whey protein solutions to a marked degree, and it is one of the few substances which does have such a power.

The results in the foregoing treatment of foaming phenomena indicate that with protein solutions the chief condition—aside from a low surface tension and a high viscosity—which is necessary for foam stability is the capacity to form semi-solid or tough films. Such a condition may be brought about by alterations in the film resembling gel formation and by denatura-

tion and precipitation changes. Suggestions as to the possibility of gel formation in foams are presented by Freundlich (*7*) and Mathews (*10*).

At another type of interface, the fat-protein solution boundary, a membrane or semi-coagulum is likewise formed. In fact such information was presented by Ascherson (*1*) as early as 1838 and the work was verified and extended by Ord (*12*), whose findings were published in 1879.

The results of a preliminary investigation upon mayonnaise dressing show that the whey-protein product is an excellent emulsifying agent. Not only have such emulsions been stable over a period of several months, but it has been found that a greater percentage of oil may be incorporated in the emulsion than is possible with egg yolk. Unpublished results from these laboratories also show that the addition of whey proteins considerably improves the whipping properties of ice-cream mixes, giving both a greater overrun or incorporation of air and a shortening of the freezing time necessary to obtain the proper consistency. As previously stated, the foaming power and emulsifying properties of protein solutions appear to be dependent upon related physical characteristics at the interface.

Since whey-protein products have an excellent food value, it seems probable that in the uses which are dependent upon whipping and emulsification properties these products may, in some cases, serve as a substitute for egg white or egg yolk. Such possible uses may be found in salad dressings similar to mayonnaise, sponge candies, cake icing, ice cream, thickened soups, custards, etc. With respect to those cooked or baked products, in which the heat-coagulative property is the principal consideration and is necessary to the proper texture of the food, however, such substitution will not be possible.

Of the methods developed in this investigation for increasing the whipping properties of whey-protein solutions, it is believed that the addition of small amounts of calcium hydroxide to the concentrated whey liquor, heating of the product to 55° C. for 10 minutes and subsequent neutralization of the alkali, before spray-drying, will be of most practical value for its adaptation to the previously suggested uses as a whipping compound in food products.

Warming of the solution of whey-protein powder to approximately 50° C. before beating, following suitable modifications of the foaming properties of the protein solution insures a large volume of foam and a stable whip. Such heat treatment is recommended as a procedure preliminary to whipping of the solution.

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Composition of European and California Almonds[1]

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NOTE: The investigation reported in this paper was conducted by C. V. Hart and was part of a more extensive study planned by him. Realization of his plans was frustrated by his untimely death. His data have been prepared for publication for the information of those interested in the composition of foods and food products. Doctor Hart received his Ph D. degree with Doctor Franklin, of Stanford University. The work reported in this paper was the first undertaken by him after receiving his degree. Hemicellulose determinations were contemplated but not made before Doctor Hart's death; these are reported by G. A. Pitman elsewhere in this issue.—W. V. CRUESS

ALMONDS used industrially in confectionery, ice cream, and bakery products and those used on the table come principally from the Mediterranean countries, particularly Spain and Italy, and from California. It has been deemed of interest and value to food chemists to ascertain by careful analysis the chemical composition of samples of the more important commercial varieties of imported and domestic almonds.

Through the coöperation of the California Almond Growers Exchange and several importers of almonds, authentic samples of 5 to 25 pounds of each of the leading varieties were obtained. The official methods of the A. O. A. C., in so far as they applied, were followed in conducting the analyses; in other cases standard procedure was followed. Pentosans were determined by the furfural-phloroglucin method. For each variety analysis of ash was made upon a single large sample, ashed in an electric muffle at a moderate temperature in order to reduce loss by volatilization of potassium salts to a minimum.

The results of the analyses are given in the two accompanying tables.

Table I—Composition of Ash of Almonds

Constituent	Foreign			Domestic			
	Jordan	Marcona	Valencia	Nonpareil	Ne Plus	Drake	I. X. L.
	%	%	%	%	%	%	%
SiO_2	0.23	0.12	0.16	0.14	1.15	0.22	0.23
Fe_2O_3	0.30	0.54	0.39	0.32	0.27	0.31	0.37
CaO	6.73	11.01	11.35	14.28	14.61	12.17	11.92
MgO	14.84	13.64	14.91	14.75	13.63	13.61	13.62
P_2O_5	38.99	40.28	38.93	36.76	34.88	39.75	33.21
Na_2O	3.23	2.12	2.36	3.98	2.59	1.45	1.83
K_2O	26.98	24.73	26.59	24.13	23.87	27.71	25.30
SO_3	3.29	2.24	2.36	3.85	3.46	2.62	2.62
CO_2	5.22	4.40	3.01	4.15	3.86	4.11	Not detd.
	99.81	99.08	100.06	102.36	98.32	101.95	

There is apparently very little difference in the composition of imported and California grown almonds. Unfortunately,

[1] Received July 21, 1930.

Table I—Composition of Almonds: Organic Constituents and Total Ash

Sample	Fat	Alcohol Extract	Sucrose in Alcohol Extract	Sucrose in Sample	Unidentified Alcohol Extract	Ash	Pentosans	Nitrogen	Proteins	Pentosans Extracted Basis (Oil-Free Sample)
	%	%	%	%	%	%	%	%	%	%
FOREIGN:										
Valencia	59.65 ± 0.08	7.32 ± 0.2	64.19	4.65	2.67	3.00	3.28	3.32 ± 0.03	20.75	9.92
Jordan	58.45 ± 0.02	6.80 (1)	70.03	4.78	2.02	3.09	3.43	3.83 ± 0.05	23.93	9.88
Marcona	59.30 ± 0.04	5.65 ± 0.15	57.90	3.24	2.41	2.91	3.40	3.91 ± 0.03	24.43	9.70
Aetna	57.00 ± 0.03	8.34 (1)	...	4.48	3.86	3.41	..	3.22 ± 0.01	20.12	...
Alicante	59.05 ± 0.03	7.29 ± 0.08	65.89	4.80	2.49	3.07	3.16	3.87 ± 0.02	24.18	9.40
DOMESTIC:										
Nonpareil	55.32 ± 0.13	7.76 ± 0.23	60.02	4.57	3.19	3.38	3.43	3.70 ± 0.03	23.12	9.50
Drake	55.41 ± 0.10	7.04 (1)	...	4.68	2.36	3.36	3.84	4.07 ± 0.00	25.43	9.91
Ne Plus	57.09 ± 0.16	7.30 (1)	...	4.42	2.88	3.46	...	3.61 ± 0.02	22.56	10.20
Jordan	58.75 ± 0.26	6.67 (1)	70.91	4.73	1.94	3.42	3.56	3.58 ± 0.03	22.37	10.32
I. X. L.	55.93 ± 0.02	8.29 (1)	52.55	4.36	3.93	3.33	..	3.55 ± 0.03	22.18	11.80

most of the European varieties are not grown in California; however, samples of imported (Spanish) and of California Jordan variety almonds were available for comparison; the analyses will be found in Table II. It will be seen that the domestic sample had 58.75 per cent oil, the imported 58.45 per cent oil; alcohol extracts 5.5 and 6.8 per cent; pentosans 3.56 and 3.43 per cent; and protein 22.37 and 23.93 per cent. No difference in behavior on cooking or in quality of the two samples after cooking could be observed. It is believed that such small differences in composition as were observed were due rather to the effect of variety than of locality. The domestic almonds were slightly higher in total protein, an average of 23.13 per cent compared with 22.68 per cent and slightly lower in oil content, an average of 56.5 per cent compared with 58.68 per cent.

The ash of all samples was high in P_2O_5, as would be expected for seeds such as the almond, and high in K_2O and MgO. From the analyses it can be seen that almonds, as food, are a good source of protein, fat, phosphorus, and potassium.

Further Comparison of California and Imported Almonds[1]

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THE work herein reported was undertaken to complete some of the unfinished work of the late C. V. Hart, of this laboratory.[2]

Shearing Stress

The apparatus consisted of two pieces of brass strip, $^3/_{16}$ by 1 inch (5 by 25 mm.), one used as a support, the other as a knife. The knife was inserted vertically through a hole in the support in such manner that a section of a nut could be placed horizontally through a hole in the knife and thus made to support the weight of the knife and any added weight. The edges of the holes were square and sharp to minimize crushing before shearing. The bottom of the knife was provided with a receptacle into which shot was poured until the knife sheared the specimen. The shot was then removed and its weight recorded. The sections of the nuts that were tested were cut by hand and calipered to $^3/_{16}$ by $^3/_{16}$ inch (5 by 5 mm.). They were then placed in the apparatus with the division between the cotyledons in the vertical plane, as varying the position of this plane affected the shearing stress. It was found that an average of twenty-five determinations gave practically the same result as an average of one hundred determinations. The weights given in Table I are for imported Aetna variety almonds and are typical of the shearing stresses as determined in the above manner.

The average shearing stresses found by this method on the uncooked nuts are given in Table II.

Table I—Shearing Stress Data

Kg.	Kg.	Kg.	Kg.	Kg.
3.48	3.19	4.00	3.92	3.47
3.87	3.39	3.60	3.87	3.75
3.92	3.65	4.00	4.05	4.02
4.00	3.95	3.25	4.05	4.02
4.05	3.54	4.55	3.95	3.54

Average, 3.50 kg.

Table II—Shearing Stresses of Uncooked Nuts

Domestic	Kg.	Imported	Kg.
Nonpareil	5.28	Jordan	2.78
I. X. L.	5.50	Alicante	3.82
Drake	3.93	Marcona	3.49
		Valencia	2.95
		Aetna	3.80

The above figures show a somewhat greater shearing stress for the domestic than for the imported varieties and a considerably higher stress for the Nonpareil than for the Drake.

Hemicellulose Content

PROCEDURE—The method used was that proposed by W. H. Dore (unpublished), of the Division of Plant Nutrition, University of California. About 5 grams of the ground and mixed sample were extracted for 16 hours with alcohol in a Soxhlet extraction flask and aliquots equivalent to 1 gram of the original sample were treated as follows: The analysis of the alcohol-insoluble material as proposed by Dore includes a determination of starch which precedes the hemicellulose determination, as starch will respond to the hemicellulose test. By testing with iodine the filtrate of the alcohol-insoluble portion after digestion by boiling the samples was found to be starch-free, so the starch determination was omitted. The aliquot of alcohol-insoluble

[1] Received July 21, 1930.

[2] The work of Doctor Hart is reported on page 1128 of this issue.

material was transferred to a 400-cc. Erlenmeyer flask with a known volume of water and 8 cc. of 12 per cent hydrochloric acid (1:2) and water to make to a volume of 100 cc. The mixture was refluxed for $2^1/_2$ hours and the insoluble residue filtered off and washed and the filtrate transferred to a 250-cc. volumetric flask. After cooling to room temperature the solution was made alkaline to phenolphthalein and then slightly acidified with acetic acid. The solution was made up to volume and reducing sugars were determined in 50-cc. aliquots. The results were calculated to the hexosan formula, $C_6H_{10}C_5$, by multiplying the glucose value by the factor 0.9.

The hemicellulose contents of the almonds examined are given in Table III.

Table III—Hemicellulose Content of Almonds

Domestic	Per cent	Imported	Per cent
Nonpareil	6.60	Valencia	6.76
Drake	6.92	Jordan	5.34
Ne Plus	4.06	Marcona	5.69
Jordan	6.35	Aetna	8.06
I. X. L.	8.68	Alicante	6.16

There are two possible sources of error that should be mentioned. First, during the Soxhlet extraction a small quantity of particles worked through the thimble and was therefore calculated as alcohol-soluble. It is estimated that these particles would not exceed 0.05 gram per sample. Second, the hemicellulose content of the samples was calculated to the hexosan formula. This is not corrected for the pentosans known to be present.

It is evident that the determinations show no consistent differences between the imported and domestic almonds.

Suberin Content

The microchemical tests recommended by S. H. Eckerson for membrane substances were used in this examination. These tests were intended to give qualitative results that could be later verified quantitatively (Table IV).

Table IV—Qualitative Tests for Suberin and Other Membrane Substances

Variety	Cellulose	Galactan	Methyl Pentoses	Pentoses	Cellulose	Pectic Substances	Lignin	Fatty Membrane	Suberin
Nonpareil	+	+	+	+	−	+	+	+	+++++++
Jordan (Imported)	+	−	+	+	−	+	+	+	+
I. X. L.	+	+	+	+	−	+	+	+	+++++
Alicante	+	+	+	+	−	+	+	+	++++++++
Drake	+	−	+	+	−	+	+	+	++
Marcona	+	?	+	+	−	+	+	+	+++
Aetna	+	?	+	+	−	+	+	+	+++

Suberin by the microscopic qualitative tests appeared to vary rather markedly. Accordingly, an attempt was made to determine this constituent quantitatively.

The gaseous chlorine method of delignification was found to be inapplicable to the material at hand, which was so finely ground as to form a vacuum-tight mat when wet. Accordingly, carbon tetrachloride was saturated with chlorine and the material treated with this reagent to effect delignification.

Filtration troubles were very persistent, so centrifuging was tried. During the rather elaborate technic involved in delignification and removal of the cellulose by a method similar to that recommended by Dore (*1*), so much of the solid material was removed in decanting as to render the results valueless.

Analysis of Almonds from Two Principal Districts of California

In two important almond-growing sections of California—namely, the Sacramento Valley and the Paso Robles district—soil and climatic conditions vary considerably, entailing different cultural practices. The Sacramento Valley orchards are irrigated, while those near Paso Robles are not, although the hot, dry summer climate and comparatively low annual rainfall would make irrigation desirable if water were available. It might be expected that these differences in growing conditions would cause differences in the composition of the nuts from these two localities. In order to ascertain whether significant differences in composition exist, samples of four common varieties—the Nonpareil, Ne Plus Ultra, I. X. L., and Drake—were obtained from both of these regions for analysis.

Procedure—The shelled almonds were finely ground and stored at room temperature in sealed glass jars for analysis.

Moisture determinations were made in duplicate by drying 5-gram samples in aluminum moisture dishes in a vacuum oven at 29 inches of vacuum and 72° C. for 16 hours.

Oil was determined by extraction with petroleum ether in an A. S. T. M. rubber-extraction apparatus, duplicate 5-gram samples being extracted in alundum thimbles for 16 hours.

Protein was determined in duplicate 1-gram samples by the Kjeldahl-Gunning method, using the factor $6.25 \times N$ = protein.

Ash was determined by incineration of 5-gram samples in small porcelain crucibles in a muffle until a white ash was obtained.

Invert sugars were determined by the Munson and Walker method, but were so low as to not be appreciable and are not mentioned in the tabulated results.

Total sugars were determined by the Shafer-Hartmann method on 1.25-gram samples using the factor 6.36 for determining the amount of copper reduced.

Data—The results of this set of analyses are presented in tabular form in Table V. The data are also given in several smaller tables to bring out more clearly the differences to be discussed.

Table V—Analysis of Almonds from Sacramento and Paso Robles Districts, California

Variety	H_2O %	Ash %	Oil %	Protein %	Total Sugar %
		1927 TESTS			
PASO ROBLES:					
Nonpareil	3.980	3.80	53.48	22.46	5.98
Ne Plus	4.205	3.20	51.33	24.45	5.55
I. X. L.	4.055	3.31	49.45	22.76	5.30
Drake	4.125	3.30	50.24	21.35	4.81
Average	4.09	3.22	51.12	24.25	5.41
SACRAMENTO:					
Nonpareil	3.230	3.22	52.19	23.84	5.75
Ne Plus	2.130	3.24	53.49	22.48	5.58
I. X L.	4.310	2.97	53.98	21.66	5.52
Drake	4.070	2.95	56.27	21.15	4.75
Average	3.44	3.09	53.90	22.30	5.40
		1928 TESTS			
SACRAMENTO:					
Nonpareil	4.193	3.390	51.47	22.82	5.90
Ne Plus	3.970	3.444	52.81	22.90	5.76
I. X. L.	4.168	3.049	53.44	23.32	5.12
Drake	3.271	3.287	59.73	18.58	4.28
Average	3.90	3.29	54.36	21.90	5.26
PASO ROBLES:					
Nonpareil	5.288	3.209	50.98	24.10	5.51
Ne Plus	4.657	3.392	52.61	25.42	5.03
I. X. L.	5.525	3.534	47.10	26.25	6.76
Drake	4.931	3.400	53.28	26.38	4.57
Average	5.10	3.38	50.99	25.50	5.47
AVERAGE	4.11	3.24	52.6	23.49	5.38

Effect of Locality and Season—The figures in Table VI were obtained by computing the average composition of each group of almonds listed in Table V.

Table VI—Effect of Locality and Season on Composition of California Almonds

Year	Locality	H_2O %	Ash %	Oil %	Protein %	Sugar %
1927	Paso Robles	4.09	3.22	51.12	24.25	5.41
1927	Sacramento	3.44	3.09	53.98	22.30	5.40
1928	Paso Robles	5.10	3.38	50.99	25.50	5.47
1928	Sacramento	3.90	3.29	54.36	21.90	5.26
	Average	4.11	3.24	52.6	23.49	5.38

An examination of this table shows that the differences in ash and sugar are negligible, but the following differences may be noted in water, oil, and protein by averaging the two seasons:

	H_2O	Oil	Protein
	%	%	%
Sacramento	3.67	53.67	22.10
Paso Robles	4.59	51.55	24.87

Thus, while lower in protein and moisture, the Sacramento almonds are high in oil. Though the trees in the Sacramento Valley are irrigated, the Paso Robles almonds had a higher moisture content, owing to storage conditions after harvesting.

Effect of Variety—A comparison of varieties is given in Table VII.

Table VII—Effect of Variety on Composition of California Almonds

Variety	H_2O	Ash	Oil	Protein	Sugar
	%	%	%	%	%
Nonpareil	4.173	3.40	52.1	23.27	5.31
Ne Plus	3.740	3.32	52.6	23.80	5.19
I. X. L.	4.514	3.21	50.9	23.45	5.27
Drake	4.099	3.24	54.8	23.35	4.84
Average	4.11	3.24	52.6	23.49	5.12

There is even less variation according to variety than according to locality. The most noticeable deviation from the average is the value of 54.8 per cent for the oil in Drakes, which is somewhat higher than any of the other varieties. Moisture, ash, protein, and sugar are all very close to the average. Therefore, the season and locality differences are more important than varietal differences.

In Table VIII the analyses averages of two seasons, of the four varieties, are separated into their respective localities.

Table VIII—Effect of Variety and Locality on Composition of California Almonds

Variety	H_2O	Ash	Oil	Protein	Sugar
		Paso Robles			
	%	%	%	%	%
Nonpareil	4.63	3.14	52.23	23.28	5.74
Ne Plus	4.43	3.29	51.92	24.93	5.29
I. X. L.	4.79	3.42	48.27	24.50	6.02
Drake	4.53	3.35	51.71	26.86	4.69
Average	4.59	3.30	51.03	24.89	5.43
		Sacramento			
Nonpareil	3.93	3.25	52.10	24.22	5.58
Ne Plus	3.64	3.26	53.18	24.27	5.14
I. X. L.	4.29	3.07	53.09	24.03	5.10
Drake	4.14	3.10	55.73	22.21	5.07
Average	4.00	3.17	53.52	23.68	5.22

Locality apparently affected composition more than did variety. For example, the Drake from Sacramento was high in oil and low in protein while the opposite is true of the Drake from Paso Robles. The values for the ash and sugar content of the different varieties show no important deviation from the average.

Summary

1—The shearing stresses of almonds were found to substantiate the "tooth-test" in determining texture.

2—Differences in hemicellulose content did not explain differences in texture.

3—The average composition of the nuts from the two leading almond districts was practically identical, with the single exception that the Drakes were slightly higher in oil.

4—The Drake from Sacramento gave the highest average oil content.

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Isolation of the Humic Acids[1]

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In order that the chemical nature of coal may be better understood, there is need for a better understanding of the nature of the humic acids. The present nomenclature and methods of preparing the humic acids leave much to be desired, for we know very little about these very complex colloidal plant decomposition materials. The authors have presented a method of extraction and purification of the humic acids which has yielded good results. The analyses and molecular weights of some of the humic material studied are presented. The absorption spectra of some of the humic acids in the region of visible light have been determined.

In the study of the chemical constitution of coal the study of coal in itself has not proved satisfactory. The coal should be separated into its individual components and these components made the subject of separate investigations. The botanical composition of coal has been very successfully determined by studying peat and then noting the changes the various plant components undergo as the rank of the coal increases. Similarly, the same procedure should prove of value in the determination of the chemical nature of coal, since the constituents of peat are more reactive and easier to handle than those of coal.

Humic acids have probably been the subject of more investigations than any of the other constituents of peat and coal. These are the dark brown, colloidal, alkali-soluble materials which have been formed, according to the most widely accepted theories, by the natural decomposition of lignocellulose. They are very complex substances whose chemistry is intimately bound up with the chemistry of coal, but about which very little is definitely known.

A review of the literature relating to humic acids showed much to be desired in the methods of extracting and purifying these substances. The usual method employed in preparing humic acids for experimental purposes has been to extract them from peat, brown coal, or oxidized bituminous coal.

These sources of humic acids are more or less complex mixtures to start with and vary with the locality from which they are obtained. Furthermore, frequently no account is taken of the fact that alkali solutions, besides extracting the humic acids, also dissolve some resins, lignin, and organic acids.

These impurities may profoundly influence the properties of the humic acids with which they are associated. The attempt was made to devise a satisfactory method for the extraction and purification of humic acids. As a starting material it seemed logical to use a piece of wood which had decayed under the conditions prevailing in a peat bog, instead of the heterogeneous peat. The species of wood should be known and should be a common constituent of peat bogs.

[1] Received May 22, 1930.

[2] Contribution No. 192 from the Department of Chemistry, University of Pittsburgh. Submitted in partial fulfilment of requirements for the Ph.D. degree by G. Thiessen.

Table I—Analyses of Materials at Various Stages of Extraction

Material	Original Analyses						Ash-, N-, and S-Free Basis		
	C	H	O	N	S	Ash	C	H	O
	%	%	%	%	%	%	%	%	%
Decayed wood	56.8	5.4	36.2	0.1	0.2	1.3	57.7	5.5	36.8
Wood after extraction with acetone	57.2	5.7	35.5	0.1	0.2	1.3	58.1	5.8	36.1
Acetone extract	65.7	6.8	26.7	0.3	0.1	0.4	66.2	6.9	26.9
Wood after extraction with acetone, ClO_2, and NaOH	60.0	5.5	33.0	0.0	0.1	1.4	60.9	5.6	33.5
Humic acid	56.4	4.9	34.7	0.2	0.3	2.5	58.8	5.1	36.1
Hymatomelanic acid	57.8	4.9	35.2	0.2	0.3	1.3	59.0	5.0	36.0

Scheme of Extraction

A decayed log of white cedar, *Thuja occidentalis*, from Hawk Island Swamp, Manitowac County, Wis., was chosen as the starting material for this study. Material from this swamp has been the subject of other investigators (*4*) in the laboratories of the United States Bureau of Mines. The log was broken up into small pieces, air-dried, and ground to pass a 12-mesh screen. During the course of the grinding the less decayed material, because of its greater toughness than the friable thoroughly decayed matter, was removed. The

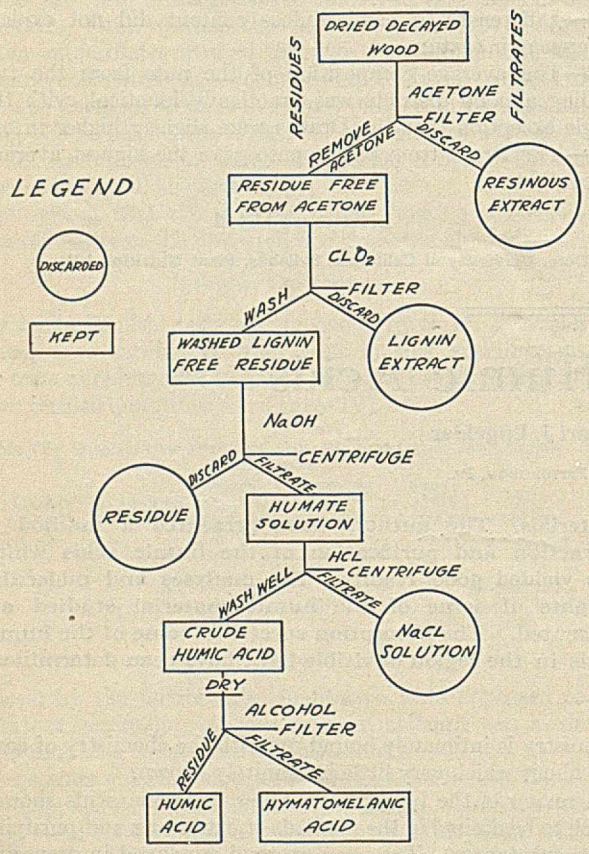
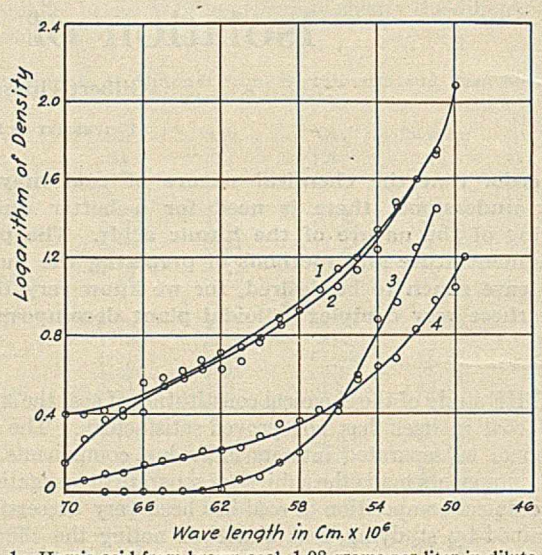


Figure 1—Humic Acid Extraction Flow Diagram

resinous materials were extracted with hot acetone. After extraction was complete, the residual acetone was removed from the extracted mass by evaporation under vacuum over a water bath. The acetone extract was decidedly resinous. The lignin was next removed by extraction with an aqueous chlorine dioxide solution, prepared according to the method of Schmidt (*3*) by saturating cold water with the gaseous products of the reaction of potassium chlorate, oxalic acid, and dilute sulfuric acid. In carrying out the extraction 400 grams of the acetone-treated mass were placed in about 4 liters of the chlorine dioxide solution and allowed to stand about 24 hours. The liquid was decanted off and the extraction repeated twice more in the same manner. After the third extraction the washed residue gave no test for lignin with phloroglucinol and hydrochloric acid. This test is carried out by placing a crystal of phloroglucinol with a small amount of the material to be tested which has been acidified with hydrochloric acid; a reddish coloration of the material is a positive test for the presence of lignin. The residue was well washed with distilled water and was then ready for the extraction of the humic acids with sodium hydroxide.

The use of ammonium hydroxide is apparently not advisable for the extraction in view of the investigations of Fuchs and Leopold (*2*) which show that ammonia is very strongly adsorbed by humic acids and possibly may also introduce amino groups into the humic acid molecule. It is also unpleasant to work with large quantities of strong ammonia solutions.

Sufficient 4 per cent sodium hydroxide solution to form a fairly liquid mass was added to the residue from the previous extraction and allowed to stand, with occasional stirring, for several hours. Upon addition of the caustic soda solution to the previously almost granular decayed wood residue, the mass became very slimy and absorbed most of the solution. It was very difficult to remove the sodium humate solution from this mixture by filtration. Separation was most easily accomplished with a small DeLaval oil-purifying centrifuge. A rough separation was first made



1—Humic acid from brown coal, 1.08 grams per liter in dilute NH_4OH
2—Humic acid from desized wood, 1.08 grams per liter in dilute NH_4OH
3—Brominated humic acid, 1.7 grams per liter in acetone
4—Nitrated humic acid in acetone

Figure 2

by rapidly running the material through the centrifuge. The humate solution was then clarified by running it slowly through the centrifuge several times. The humic acids were precipitated from the clarified solution by the addition of hydrochloric acid and removed from suspension by centrifuging. They were washed by being dispersed in distilled water and reprecipitated by centrifuging. Washing was continued by repeatedly dispersing the humic acids in water and recovering them by centrifuging, until the final wash

water showed only slight amounts of chlorides. As washing proceeded and the electrolytes were removed, the humic acids showed greater and greater tendency to form very fine colloidal dispersions, from which they were removed only with difficulty. The washed humic acids were dried at 30° C. *in vacuo*, first over sulfuric acid and finally over phosphorus pentoxide. A portion of these acids should be soluble in ethyl alcohol. The alcohol-soluble fraction has been given the name "hymatomelanic acid" by Hoppe-Seyler. The alcohol-insoluble fraction has been considered to be the true humic acid. This separation was made using hot absolute ethyl alcohol and evaporating the alcohol from both the extract and the insoluble residue under vacuum. The scheme of separation which was followed is presented diagrammatically in Figure 1.

Analyses

Samples of the materials were taken at various stages and analyzed. These figures were then recalculated to an ash, nitrogen, and sulfur free basis. Both sets of analyses are given in Table I. The two humic acids are very similar in elemental composition. This would lend weight to the theory that they are the same material, differing in their solubilities because of differing colloidal particle size.

The molecular weights of the humic acids themselves are difficult to determine, since they are not soluble in any of the solvents used for molecular weight determinations. A portion of the alcohol-soluble material was soluble in acetone and its apparent molecular weight could therefore be determined. Fuchs (*1*) has prepared the nitro and bromo derivatives of the humic acids. These materials are easy to prepare and are soluble in acetone. It may be that the humic acid complex is broken down during the treatment. The apparent average molecular weights of several of the materials studied are presented in Table II.

Absorption Spectra

All humic acids are colored. This fact has been written into most of the definitions of humic substances which have been put forward. It was thought to be of interest to determine whether the absorption spectra of the various materials studied were the same or similar.

Table II—Approximate Molecular Weights of Humic Acids

Acetone-soluble humic acid	800
Nitro-humic acids	1040
Bromo-humic acids	940

Note—These values were obtained by the method of McCoy, using between 0.4 and 0.9 gram of material in about 20 ml. of acetone. Similar values were also obtained by the microchemical method of Pregl. The individual values from which the average for the nitro humic acids was derived were 988, 990, 1020, 1050, and 1150. These molecular-weight values are of about the same magnitude as those found in the literature.

The absorption measurements were made with a Hilger-Nutting photometer and a Hilger constant-deviation wavelength spectroscope. The curves obtained by plotting the data were all of approximately the same shape. The materials in solution were almost completely transparent to red and yellow light and became less and less transparent to light of decreasing wave length, being practically opaque to blue and violet light. Figure 2 shows some typical curves obtained. An absorption spectrum curve for a humic acid obtained from brown coal is included for comparison. It was found that the brominated and nitrated acids were less highly colored, as were also the more soluble fractions. The authors did not notice the black almost always said to be characteristic of humic acids, when the materials were carefully prepared. Instead, they were all of various shades of brown. The absorption spectra of humic materials in the ultraviolet region of the spectrum would probably be more interesting than those in the visible region. Lignin shows some very interesting properties in this region.

Acknowledgment

The authors wish to express their appreciation to G. St. J. Perrott for permission to use the facilities of the Pittsburgh Experiment Station of the United States Bureau of Mines, and to Reinhardt Thiessen for his help and suggestions during the course of the work.

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Action of Rotenone upon Mammals When Taken by Mouth—Preliminary Report[1]

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ROTENONE is the principal insecticidal constituent of *Derris elliptica*, of the South American plant "cube" (*Lonchocarpus nicou*), and of certain other tropical fish poisoning plants. It is a white crystalline compound having the formula $C_{23}H_{22}O_6$. It is insoluble in water, but soluble in acetone, chloroform, and many other organic solvents. Rotenone is extremely toxic to fish, 1 part in 20,000,000 parts water killing goldfish in 3 hours; and it is also highly toxic to insects. It is effective both as a contact and as a stomach insecticide.

Derris extract has been used as an ingredient of an arrow poison by the Borneo head hunters. According to Newbold (*2*), a tiger died within 3 hours of being wounded with three arrows tipped with this mixture. This toxic action may have been due to constituents in the arrow poison other than those from derris. Campbell (*1*) made tests with derris upon various animals and reported that the sap from only 2 grams of the root when administered by mouth is sufficient to kill a monkey.

The usefulness of rotenone as an insecticide would be seriously curtailed if it were markedly toxic to warm blooded animals, if for instance its action were similar to that of strychnine, curare, or similar drugs. The ideal agricultural insecticide is one that is toxic to insects but harmless to man and domestic animals eating fruits, vegetables, or grass that has been sprayed or dusted. The object of the investigation here reported has been to determine what action rotenone, when taken by mouth, has upon farm animals, such as cows, horses, pigs, sheep, goats, and chickens, as well as upon household pets, such as cats, dogs, and canary birds. In these tests the rotenone was administered mainly by mouth, as only in that way do domestic animals normally come into contact with insecticides that have been applied to vegeta-

[1] Received August 26, 1930.

tion. A few dusting experiments, from which the action on the skin could be judged, and one intravenous injection were also made.

Dogs

Five pound puppies of the hound type, four weeks old, were given 1 grain each of pure rotenone[2] in capsule, with no ill effects. Later the dose was increased to 2 grains. There was no vomiting, which shows that in small amount rotenone is not a stomach poison to dogs; nor was there any purging, which indicates that rotenone does not irritate the intestines nor stimulate glandular activity. The puppies showed no loss of appetite, and there was nothing to indicate that rotenone causes gastric depression.

The same results were obtained when 10 grains of the solid extract of derris was given adult dogs of the terrier type, weighing about 30 pounds.

A terrier bitch weighing 10 pounds was given 10 grains pure rotenone in capsule by mouth without any effect.

A small wire-haired bitch nursing five puppies was thoroughly dusted with a dusting powder of talcum containing 2.5 per cent of derris extract. Both the bitch and her puppies were heavily infested with fleas and were thin and stringy in flesh, owing partly to starvation by their negro owner and partly to feeding so many blood-sucking insects. Within 24 hours of applying this powder not a living flea could be found upon the dogs, which suffered no ill effects from this treatment but on the contrary showed profound comfort. On the following day each puppy was dusted in the mouth with the powder and on succeeding days 10 grains of powder in capsule were given each puppy and 20 grains to the mother without causing any deleterious effect.

A litter of Esquimau Spitz puppies literally skin loaded and covered with dog lice were dusted with the same powder, which relieved them of the pests in about 24 hours.

The effect of this dusting powder upon the flea or lice eggs was not noted, but as long as some of the powder remained on the skins of the dogs they were not reinfested. An injection of 2 grains of rotenone into the peritoneal cavity of a 15-pound dog had no injurious effect.

Normal 35-pound dogs given 4 grains of pure rotenone in capsule showed no reaction whatever.

Cats

Cats showed no reaction when heavily dusted with a talcum dusting powder containing 2.5 per cent of derris extract. This test extended over an entire summer and was made on a large number of pure bred Persian cats and kittens. No irritation either to the skin or when licked off by the cat and swallowed was noticed in any case.

[2] The rotenone used in all the tests reported in this paper was recrystallized from alcohol and melted sharply at 163° C. It was obtained from F. B. LaForge, of the Insecticide Division, Bureau of Chemistry and Soils, Washington, D. C.

Pigs

Ten 60-pound young pigs were used in these tests. Each animal was given 4 grains of pure rotenone in capsule, without producing any visible effects. Assuming that rotenone is used in an insecticidal spray at the same strength as lead arsenate, it would be necessary for an animal to eat 40 pounds of the most heavily sprayed apples in order to consume 4 grains of rotenone. Although a spray schedule for rotenone has not yet been developed, it is reasonable to assume that less rotenone than lead arsenate will be used per 100 gallons of spray, which means that probably 100 or more pounds of sprayed fruits or vegetables would have to be consumed in order to ingest 4 grains of rotenone. There is very little likelihood of spray residue poisoning to man from rotenone in view of the non-toxicity of this compound to pigs.

Sheep and Cows

Five Hampshire lambs, 6 months old, were each given 4 grains of pure rotenone in capsule without producing any effects.

In South America aqueous extracts of derris are used as antifly sprays on dairy cattle and as a mange remedy. No ill effect from this use of rotenone has ever been observed.

Post mortems on animals given 4 grains of pure rotenone showed no sign of gastro-intestinal inflammation. The fate of rotenone in warm-blooded animals is not yet known.

Chickens

In addition to the animals mentioned, the author has tried the effect of pure rotenone upon chickens. No injurious action was observed in any case. The author ate one of the chickens and experienced no ill effects.

Effect on Persons Handling Rotenone

In grinding derris root the mill operator may notice a numbness of the lips, tongue, and throat, which is due to the anesthetic action of some unknown constituent. This effect may persist for 2 hours, but is not serious. The author has produced the same symptoms on himself by chewing a minute portion of the root.

Conclusions

When administered by mouth, pure rotenone produced no visible effects in dogs, cats, pigs, or sheep in doses (for dogs) up to 1 grain per pound of bodyweight. It is believed that even larger doses would be harmless.

Derris extract (the ether extract of derris root evaporated to dryness) when administered by mouth was likewise without effect.

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Friability of Midtemperature Cokes[1]

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THE shatter test has long been used to give comparative information concerning the strength of cokes. It is used in particular to compare cokes used for blast-furnace or metallurgical practice and gives data which are useful in estimating the ability of a coke to withstand breakage due to handling as well as to carry the burden in the blast furnace.

The standard method of the A. S. T. M. and U. S. Bureau of Mines was used in making these tests. In brief, it con-

[1] Received August 1, 1930. Presented before the Division of Gas and Fuel Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

sists of taking 50 pounds (22.6 kg.) of coke above 2 inches (5 cm.) representing by careful sampling the coke as it comes from the coke oven, and placing it in a specially constructed box, raising the box to a height of 6 feet (1.8 meters) and dropping the coke on a steel plate. The box has a specially constructed spring bottom, so that when it is released the coke drops in mass as one piece. This procedure is repeated four times. The coke is then screened by hand, using a square-mesh screen, and the percentage remaining on a 2-inch (5-cm.) screen is taken as the shatter index.

The above procedure was followed closely except that a box 30 by 28 inches (76 by 71 cm.) was used instead of the standard one, 30 by 18 inches (76 by 46 cm.). The larger box permits of placing the coke in a single layer in the box and practically eliminates any tendency for cushioning to take place, which might occur in a smaller box.

The coke samples used were taken from cokes made in an experimental outfit of semi-plant size, at Champaign-Urbana, using a standard 12-inch (30.5-cm.) oven, and operated according to the more or less definite conditions of the Parr process, the special characteristics being quick carbonization and use of the midtemperature range. All coals were preheated in the neighborhood of 300° C. and then charged hot into the coke oven, the coke-oven temperatures ranging from 750° to 900° C., the coal being charged in 1-ton lots. The samples upon which the tests were run were selected as being representative of a great number of coals coked at this plant.

The coals from which these cokes were made were not cleaned in any way; in fact, most of the samples carried considerable free impurities in the form of slate and pyrite. Undoubtedly these same coals cleaned would make a much stronger coke.

Table II—Shatter Tests—50-Pound Samples

(Percentage retained on square mesh screens)

Sample	Origin	2-Inch[a] (5-cm.)	1-Inch (2.5-cm.)	1/2-Inch (1.3-cm.)	Through 1/2-Inch (1.3-cm.)	Remarks
		%	%	%	%	
1146	Illinois	75.2	11.4	7.1	6.3	Made from same coal as No. 883, short preheating time
1127	Iowa	70.8	10.0	10.0	9.2	
1040	Illinois	57.0	20.5	11.5	11.0	
750	West Virginia	78.5	15.6	3.1	2.8	
1141	Illinois	68.3	17.7	7.0	7.0	Made from same coal as 1142; 5-hour coke
775	West Virginia	73.6	17.3	2.8	6.3	
1142	Illinois	64.6	17.4	7.9	10.1	4-hour coke
883	Illinois	72.4	16.9	6.3	4.4	
1156	25% West Virginia, 75% Illinois	62.6	21.7	9.1	6.6	

[a] Shatter index.

Table I gives the proximate analyses of the coals used, together with the ash and B.t.u. of the resultant coke. It is to be noted that most of these samples are high in ash. It is well known that free impurities in coal tend to produce planes of weakness in the cokes made from them.

Table II gives results of the shatter tests on nine different cokes made by the Parr process. The shatter index varies from a low of 57.0 to a high of 78.5. Samples 1146 and 883 were taken from cokes made from the same coal, the only difference being that sample 1146 had a short preheating time. This short preheat seems to have slightly increased the strength of the coke. Samples 1141 and 1142 were also cokes made from the same coal, sample 1141 having had a little longer coking time. This seems to have aided in making a stronger coke; in fact, the carbonization reaction may not have been entirely complete in sample 1142.

Table I—Proximate Analyses of Coal and Coke as Received

Sample	Locality	Coal						Coke (calcd.)	
		Moisture	Volatile matter	Fixed carbon	Ash	Sulfur	Calorific value	Ash	Calorific value
		%	%	%	%	%	B.t.u.	%	B.t.u.
1146	Illinois	10.20	37.00	40.80	12.00	3.06	11270	20.9	11520
1127	Iowa	16.47	33.21	35.73	14.59	4.17	9542	22.20	11330
1040	Illinois	8.43	33.75	48.51	9.31	0.95	11900	14.95	12400
750	West Virginia	1.40	34.23	55.37	8.99	2.29	13680		
1141	Illinois	7.22	34.21	50.21	8.36	0.84	12194	12.45	12700
775	West Virginia	1.61	27.20	62.92	8.26	1.00	14040	10.90	12980
1142	Illinois	7.22	34.21	50.21	8.36	0.84	12194	12.45	12700
883	Illinois	10.20	37.00	40.80	12.00	3.06	11270	20.9	11520

For comparative purposes Table III is given which is the result of some tests made on English cokes by Bramholtz, Nave, and Briscol (*1*) using practically the same sized testing box as used in these tests. It is to be noted in comparing the shatter indices as given in the two tables that the midtemperature cokes have a high average shatter index. This is the more remarkable in that most of the cokes tested were made from Illinois and Iowa coals, which are ordinarily classed as non-coking. This would tend to show that midtemperature cokes were somewhat tougher than cokes made from high-temperature processes. Cokes made at 750–900° C. contain from 4 to 5 per cent volatile matter, and make a very desirable domestic fuel, being smokeless, having a low ignition temperature, and, as seen from the foregoing tests, of high physical strength.

Table III—Shatter Tests of English Cokes

Coke	Origin	Shatter Index	Ash
		%	%
1	Cumberland	50.2	8.91
4	Cumberland	65.5	9.84
5	Cumberland	53.5	10.58
6	Cumberland	57.0	9.43
7	Durham	62.9	9.75
11	Durham	70.8	10.64
12	Durham	55.9	8.76
13	Durham (Beehive)	83.3	7.02
15	South Yorkshire	54.0	8.63
16	South Wales	96.3	6.82
8	Westphalia	88.9	8.85

The values here presented are consistent with the results of investigations carried out by the U. S. Bureau of Mines, which demonstrate the importance of these two factors of speed and temperature in methods for determining the agglutinating value, but also in actual coking experiments, as carried out by the bureau under precisely controlled conditions. Fieldner and Davis, in a report under date of May 21, 1930, state: "Tests now complete for representative gas coals (unmixed with lower volatile coals) clearly show that cokes made at carbonization temperatures 500° to 900° C. are considerably stronger than those made at higher temperatures."

Literature Cited

(1) Bramholtz, Nave, and Briscol, *Fuel*, 7, 100 (1928).

Resistance to Tackiness of Certain Paint, Varnish, and Lacquer Coatings on Interior of Cedar-Lined Receptacles[1]

Frank Rabak

BUREAU OF PLANT INDUSTRY, U. S. DEPARTMENT OF AGRICULTURE, WASHINGTON, D. C.

MANUFACTURERS of metal cedar-lined safes and cedar chests used for the storage of clothing and furs for protection against moth damage are confronted with the serious objection of the trade to the stickiness or tackiness of the painted or varnished metal surfaces inside these receptacles, with possible resultant damage to the material stored in them.

Investigation of the problem disclosed that the inside surfaces of the doors, hinges, locks, and jambs of the safes or chests lined with red cedar are coated at the time of manufacture with oil-base colors or varnishes of standard usage. These coated surfaces soon soften and become sticky, often with considerable resultant damage and expense to the articles stored in the receptacles. The cedar lining, which consists largely of the heartwood of red cedar, *Juniperus virginiana*, was suspected of being the cause of the trouble, which was explained by the fact that the vapors of red cedar, which are concentrated within the interior and which consist of the volatile oil of cedar, act as a solvent for the oils in the coatings used on the inside metal surfaces, thus softening the same to a point of extreme stickiness or tackiness.

It is evident that in order to correct the trouble certain types of protective coatings must be used that will resist softening in a concentrated atmosphere of cedar vapors. A small replica of a cedar-lined safe was constructed for use in testing numerous steel panels to be coated with various types of coatings, such as paints, varnishes, and lacquers, and then placed in the safe for observation. It was hoped that some inexpensive yet effective coating would thus be revealed which could be used instead of the usual paint or varnish to overcome the objectionable tackiness with its resultant damage to materials placed in the safe.

A total of seventeen materials, representing several types of coatings, mostly products purchased in the open market, were chosen for the tests. Small steel panels were coated with the materials and when thoroughly dry were placed in the safe. The tests were conducted over a period of 18 months, examination of the panels being made at three intervals of approximately 2, 6, and 18 months. The accompanying table shows the results of the tests.

Of the four general types of coatings—paints, varnishes, lacquers, and bronzes—those containing untreated drying oils in considerable quantities were found to be least effective, while all coatings free from drying oils as color vehicles or containing only very small quantities of drying oils were most effective. Flat paints, such as undercoat white, interior wall finish, and flat wall paint, all of which contain a minimum quantity of drying oils, were found very effective, being distinctly non-tacky after 18 months. These apparently afford a cheap yet effective coating for the interior metal surfaces of the safes. Enamels and varnishes, as well as asphaltum, it will be observed, were ineffective. The tackiness of these panels was attributed to the linseed oil used in the preparation of the products. Radiator bronze with a non-oil vehicle was found to be very effective in preventing the objectionable stickiness. The lacquers used were uniformly effective, with one exception, a panel coated with black lacquer, the history of which was not known. Brushing or spraying lacquers of any desired color can apparently be used with safety and effectiveness on the interior metal surfaces of the safes, combining ease of application, quick drying, and smooth attractive appearance. Flat paints, like those previously mentioned, are perhaps equally as effective and somewhat less expensive than lacquers, but produce a less attractive appearance and require more time to dry to a hard film.

It is apparent from the above tests that the cedar vapors emanating from the cedar lining in the receptacles act as a slow solvent of the oil vehicle of certain coatings, softening the film to the point of extreme stickiness, much as would red cedar oil itself if it were brushed on the coated surface. This is proved by the fact that flat paints made with turpentine, as the principal vehicle for carrying the pigment, and containing practically no oil, are not softened by the vapors. Likewise, radiator bronze, and lacquers with special vehicles or thinners, are unaffected because of the absence of appreciable quantities of oils in the films of these products with their consequent insolubility in the cedar vapors.

Tests on Steel Panels Coated with Paints, Varnishes, Lacquers, and Bronze Placed in Cedar-Lined Safe

Description of Coating	First Examination (July 29, 1928)	Second Examination (Nov. 29, 1928)	Third Examination (Nov. 29, 1929)
	PLACED IN CHEST MAY 21, 1928		
Gray lacquer	Non-tacky, no change	Non-tacky, no change	Non-tacky, no change
Black lacquer	Tacky	Very tacky	Tacky
Silver gray lacquer	Non-tacky, no change	Non-tacky, no change	Non-tacky, no change
Brown enamel	Tacky	Very tacky	Very tacky
Auto color varnish	Slightly tacky	Very tacky	Very tacky
Gold radiator bronze	Non-tacky, no change	Non-tacky, no change	Non-tacky, no change
Clear lacquer	Non-tacky, no change	Non tacky, no change	Non-tacky, no change
Coach varnish	Very slightly tacky	Slightly tacky	Tacky
Asphaltum	Non-tacky, no change	Tacky	Very tacky
	PLACED IN CHEST JUNE 25, 1928		
Interior wall finish (flat)	Non-tacky, no change	Non tacky, no change	Non-tacky, no change
Spar varnish	Non-tacky, no change	Non-tacky, no change	Non-tacky, no change
China wood oil paint (white lead)	Slightly tacky	Very tacky	Very tacky
Flat wall paint	Non-tacky, no change	Non-tacky, no change	Non-tacky, no change
Undercoat white paint (flat)	Non-tacky, no change	Non-tacky, no change	Non-tacky, no change
Hempseed oil paint (lead carbonate)	Slightly tacky	Very tacky	Very tacky
Safflower seed oil paint (lead carbonate)	Tacky	Very tacky	Very tacky
Linseed oil paint (white lead)	Non-tacky, no change	Slightly tacky	Tacky

It is unlikely that the stickiness or tackiness is due to an exudation from the paint films or that condensation of cedar vapors, followed by resinification, takes place on the metal surfaces, which has been claimed by some, since neither the flat painted surfaces nor the lacquered or bronzed surfaces exhibit the slightest sign of tackiness due to the condensation and resinification of cedar-oil vapors on these surfaces.

[1] Received July 9, 1930.

The Investigation of Atmospheric Pollution. Report on Observations in the Year Ended 31st March, 1928. Fourteenth Report. Department of Scientific and Industrial Research. 67 pp. H. M. Stationery Office, London. Price, 3 s. 6 d.

AMERICAN CONTEMPORARIES

Arthur Michael

FEW chemists, except those who browse through the publications in which organic chemistry research is recorded or those who read books which review critically the progress in this branch of chemistry, know Arthur Michael, or his place among great American chemists. He has never written a book, rarely attends meetings, serves on no committees, makes no popular addresses, nor speaks to the radio public. On the other hand, those who have read the literature of organic chemistry know the productivity and versatility of Professor Michael. The wide scope and great variety of subjects in which this investigator has done authoritative work can only be realized by going over the author index of *Centralblatt* and *Chemical Abstracts* beginning in the late seventies and continuing down to about ten years ago. It is doubtful whether any one has successfully accomplished the appalling task of reading, digesting, and becoming familiar with all of the published work of Professor Michael and his students.

This sketch, therefore, does not have as its object a critical review of the work of Arthur Michael. Few men in the chemical world of today are capable of undertaking such a review, and one that was properly done would require a volume of considerable size. Since those who have not read chemical literature hardly know him, and to those who have read extensively Arthur Michael is almost a legendary figure, one of those giants of the days of the dawn of organic chemistry, this brief sketch has as its purpose the introduction of the man to chemists of today as one of the most interesting figures that has ever appeared in the scientific world.

Professor Michael's early association and recollections are characteristically American. As a small boy in Buffalo, he remembers Abraham Lincoln's visit there, and particularly playing with Lincoln's son, Tad. He also knew Grover Cleveland as an easy-going young lawyer. Young Michael attended the Buffalo Latin School, but in his teens his father's business called him abroad, and the family made its temporary home in England. When a lad of eleven Michael had a laboratory of his own, playing at chemistry much as boys of a later generation played with wireless and radio. His choice of a university was Heidelberg. There the brilliant American boy attracted the attention of the great Bunsen, and he soon brought him into his own laboratory as an assistant. Gabriel was then a student at Heidelberg, and he and Michael became fast friends, being generally known to their associates as "two-thirds of the archangel trio." Together they left Heidelberg and went to Berlin to work with A. W. Hoffmann. These two clever youngsters had hardly started on their work together when they prepared in a single evening a new and important organic compound, which Gabriel analyzed early the next morning and the two presented to the astonished Hoffmann. Michael then took his own field and published several papers, being associated with several young Americans, among whom was Thomas F. Norton.

Being blessed with abundant means, Michael went wherever a great figure in chemistry attracted him. He worked with Wurz at Paris, and recalls LeBel perched on an enormous stepladder watching the thermometer at the top of a fractionating column of his own devising. He made a pilgrimage to Russia to be with Mendelejeff. Michael's students of later years will recall that his reminiscences made to live again many of the great men who did so much to make chemical history.

In spite of the charm of the Continent, Professor Michael was devoted to his own country, and when he felt that his period of training was over he began to look about for a permanent location in the United States. He chose Tufts College, then a small institution under the shadow of Harvard and M. I. T., and with very little money for chemistry. For more than a quarter of a century of nearly continuous service, Michael not only taught at Tufts under surroundings that would have been the despair of a modern research worker, but turned out the larger part of that great mass of notable investigation on which his fame rests. His own money provided apparatus, chemicals, books, journals, and the salaries of his corps of assistants.

An American student, Miss Helen Abbott of Philadelphia, already quite well trained in biochemistry, sought admission to a German university. Women were not received in those days, but the question was asked: "Why do you seek to work in Germany when you have in your own country such a great man as Michael?" Miss Abbott was admitted to the Tufts laboratory, and the next year as Mrs. Arthur Michael accompanied her husband on a world tour.

In 1909 Professor Michael was called to the new Clark University as director of the Chemical Laboratory. He soon found that the task of slowly building a university was not to his liking after the long years of freedom at old Tufts, and his stay at Worcester was very brief. The idea of a laboratory at his home had always appealed to him. At one time he had lived on the Isle of Wight, and mystified the rural population by carrying on his research at his home. Harvard University was quick to recognize the prestige which Michael would bring to the chemistry faculty, and elected him professor of chemistry with the privilege of doing his work when and where he pleased. Probably not once a year did he visit Cambridge, but the young research workers who filled his laboratory close by his beautiful home in Newton Center had the privilege of receiving the doctor of philosophy degree from Harvard.

In the latter years of the past century a very considerable number of American chemists went to Germany for graduate work. It is very striking to note that a large proportion of Professor Michael's assistants came to him from Germany. While always a loyal American, and ardently devoted to the cause of the Allies, Michael often spoke very regretfully of his "boys" who had returned and who were fighting in the German army.

The name of Michael recalls to readers of chemical journals some very lively and interesting controversies with some of the best known men in Germany, and it was very rarely that the American did not win in the eyes of the chemical world. Professor Michael used to quote with great glee two phrases, one from a lecture at Berlin and the other from a standard work on organic chemistry: "There is a young American named Michael who holds another view," and "The masterly researches of Michael have rendered the older theory untenable."

No student of Professor Michael found him an easy taskmaster. Men who had been led by earlier successes to think of themselves as "pretty good" were brought to the verge of despair by his exacting standards both of technic and thinking. He himself was a master of manipulation and resented vigorously sloppy work and, even more so, sloppy thinking. "If you do not know why, your work is not worth a rotten apple." "Perhaps you had better stop so much advanced reading and study an elementary text again." Professor Michael was fond of quoting

the phrase in Goethe's "Faust" in which "a little word" is said to take the place of missing ideas.

One is particularly struck in the work of Michael with the constant emphasis on principles. He was never content to make compounds, however interesting and valuable. Unless a problem had in it the possibility of establishing a principle, it was soon abandoned for one more promising. As he went on Michael grew as a chemical philosopher—in fact, a number of his papers published in recent years had to do very largely with fundamental physical chemistry. Many of his students have spoken of his marvelous memory, and his ability to cite articles by journal, year, and even page. They were still more impressed by what one man has called his "almost uncanny ability to predict the course of an organic chemical reaction," and refer to it as a "chemical instinct" and a "sixth sense" with which few men, even great research workers, have ever been blessed.

Professor Michael has done little active laboratory work in the last ten or twelve years. For many years before that time he had begun to transfer some of his interest to several most delightful hobbies. There are few more beautiful grounds in all the suburbs of Boston than those of Professor Michael in the Newtons. To the west of his lovely house there is a great grove of magnificent trees, and nearby a little summer house. His tulips rival those of the Public Gardens. During the outdoor season his flower beds are gorgeous, and even in the dead of winter his greenhouse yields its treasures for his desk and table.

Being a most enthusiastic golfer, Professor Michael would occasionally desert his laboratory in the late winter for a few weeks at Pinehurst. He once rigged up a complicated canvass screen and a small putting green in his laboratory attic in order not to get "off his game" in the winter. He is a member of the "hole-in-one" fraternity.

The Michael home in Newton is a perfect treasure house of the most discriminatingly chosen and varied museum pieces. There are a few paintings, chief among them a Blakelock; there are jade carvings and lacquered chests; there is a great cabinet full of silverware, masterpieces of early American skill; but the most valuable of all are innumerable Chinese and Japanese paintings on scrolls and screens. Professor Michael is no amateur as a collector. Much of this material was gotten from out-of-the-way places of the earth, where the dealer in antiques never penetrates.

Professor Michael will be remembered by his students as a perfect host, and dinner at his home was an event to be treasured as a memory. No matter how heavily he had "landed" on a student for some mistake or lack of thought, in his home he was always charming and delightful. Hardly a part of the world where he had not been; few great works of art he had not seen; most operas were familiar to him; a keen student of world affairs, his conversation was an education in itself to younger men.

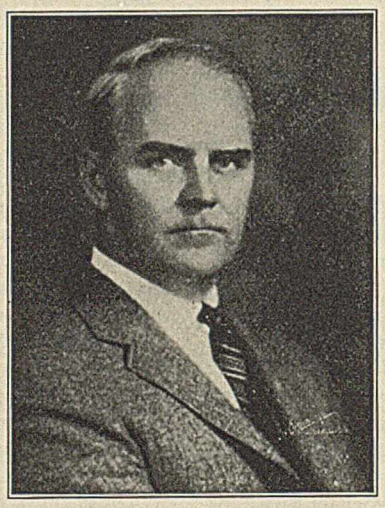
The progress of chemistry for four decades owes much to Arthur Michael. Scores of men were trained in his laboratory. He will always be a memorable figure in the scientific world. With all of this, the few who have been privileged to know him will remember him as a broad and well-rounded citizen of the world.

W. T. Read

AMERICAN CHEMICAL INDUSTRIES

The Champion Fibre Company

IT IS a little more than twenty-two years since operations began at The Champion Fibre Company's plant at Canton, N. C. The location of a pulp plant in the mountains of western North Carolina was something of an adventure and a departure from the path which up to that time led the pulp industry westward from New England. Although the potential lumber resources of the South were, and still are, enormous, most of the standing timber in the southern Appalachians is chestnut wood, which is rich in tannin and not suitable for pulp unless the tannin is first extracted.



Reuben B. Robertson, President, The Champion Fibre Company

The Champion Fibre Company's objective was primarily the production of soda and sulfite wood pulp, but to employ chestnut wood as the raw material for soda pulp involved the construction of a plant to extract the tannin and prepare the wood for the soda-pulp mill. Side by side with the pulp mill the largest single unit for the manufacture of tannin extract was built, having a capacity of 500 barrels of liquid tannin extract per day. This combination of plants, one to serve the paper industry and the other to serve the tanning industry, was unique in the history of industrial development. The coördination of the requirements of these two separate and distinct industries presented many difficulties at the outset, but as experience was gradually gained the products of the respective plants achieved a high distinction for quality.

A sulfite-pulp mill was erected to accompany the soda mill and the extract plant in order to make use of the supply of hemlock and spruce wood from the higher altitudes of the surrounding mountain region, and thus enable the plant as a whole to furnish all the essential wood pulp for the production of higher grade paper at the plant of the parent organization, The Champion Coated Paper Company, at Hamilton, Ohio. In 1917 a sulfate-pulp mill was erected alongside the other two pulp mills, to produce kraft pulp from short-leaf pine, which is available in large quantities from the lower altitudes within easy reach of Canton.

Because of an interruption in the supply of chlorine in the early days of the Great War, it became imperative to build an electrolytic plant for the production of this very necessary material for the bleaching of pulp. So for several years The Champion Fibre Company has produced its own chlorine from a plant having a capacity of 70 tons daily and it has available a supply of caustic soda which is produced in liquid, solid, and fused forms and furnished to the southern textile mills. The other by-product of the electrolytic plant, hydrogen gas, is now being recovered and will be used for hydrogenated products.

The next development was the erection of a mill for the production of book, bond, tablet, and envelope papers. After

a short period of operation, this unit was doubled to permit a daily production of 100 tons of high-grade paper.

In the variety of its wood-pulp products and their derivatives the Canton plant is unique. This variation gives the plant a certain flexibility and adaptability which permits many advantages in a changing market.

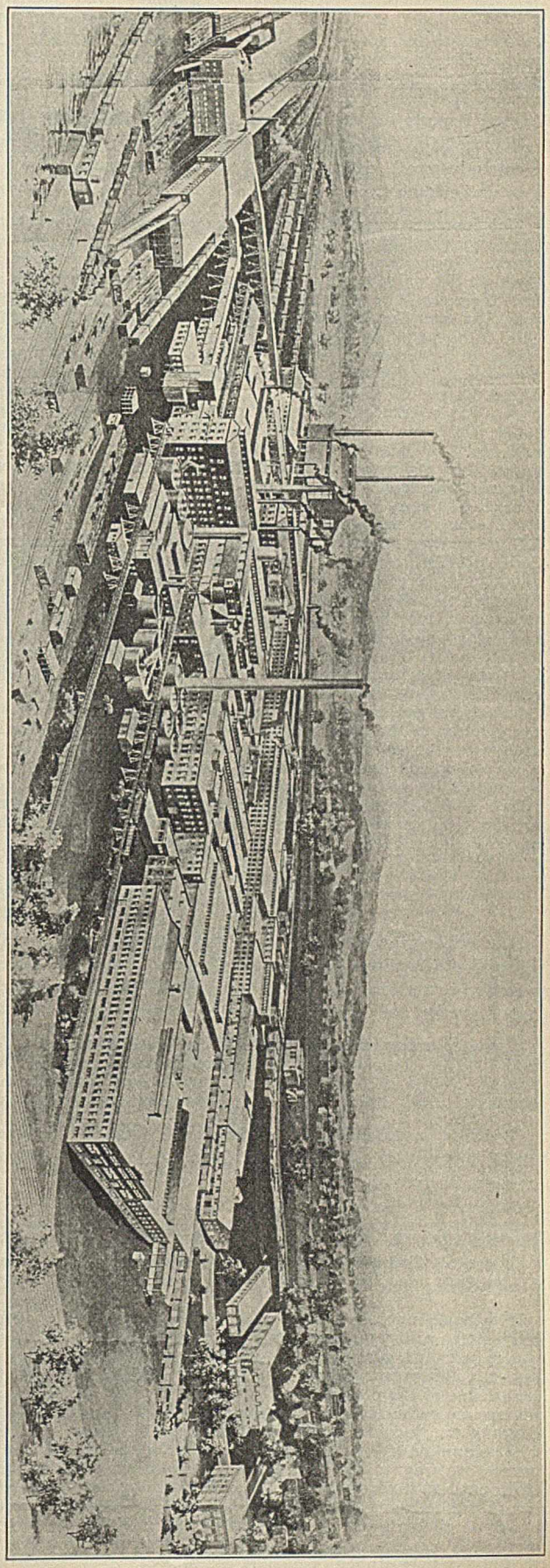
On the matter of the supply of raw material The Champion Fibre Company has for many years inaugurated a forest policy on its timber land-holdings, which consist of over 150,000 acres, which assures indefinitely a continuity of the supply of much of its wood.

The operations of the company are essentially those of a chemical industry and the laboratory controls every step in each department. Efficiency demands a close attention to details and every effort is made to recover all materials having any market value. The production of tannin extract from chestnut wood is a primary process, so that it does not partake of the nature of by-product recovery. In the cooking of pine wood for sulfate pulp, three separate by-products are obtained. Besides the highly volatile methyl compounds, the cooking liquors yield turpentine and sodium resinate. In refining the crude turpentine, dimethyl sulfide is obtained, and this is finding a use as a warning agent in natural gas. The removal of the dimethyl sulfide leaves the turpentine entirely free from objectionable odor. The recovered sodium resinate is used as a size and also in the making of soap. The recovery of the cooking liquor from the sulfite process still presents a problem which has only been partially solved, by concentrating the liquor into heavy extract and dry powder, in which form it finds use as a cheap adhesive under the name of "Bindex."

The cooking of all woods by the soda process involves the recovery of the materials employed, and these are returned to the process and constitute a continuous cycle of operations which call for close chemical supervision to insure economy.

Most of the executives of The Champion Fibre Company's organization have been with the company since it was founded, and under the leadership of Reuben B. Robertson, who took charge as general manager in 1910 and became president in 1926, the history of the company has been one of progress and steady growth. In spite of a record of achievement which would justify a pause for its contemplation, the management of The Champion Fibre Company have plans for development which promise still greater economies and which will enable the company to continue that service to the public which is now recognized as the real basis of progress.

R. W. Griffith



The Champion Fibre Company, Canton, N. C.

Half-Million-Volt X-Ray Tube

X-rays at 500,000 volts, more than twice as high a voltage as is being used in today's most powerful therapy tubes, have been attained by W. D. Coolidge, associate director of the General Electric research laboratory at Schenectady. Such a decided increase in voltage, and hence increase in penetrating power of the rays, was made possible by a system of "cascading" the tube.

Earlier attempts to build experimental x-ray and cathode-ray tubes for voltages appreciably in excess of 250,000 ran into difficulties due to a "cold cathode" effect, whereby current flowed through the tube even when the cathode filament was not heated. Continued investigations showed that this limitation could be removed by dividing the voltage applied to the tube between different pairs of tubular electrodes. Such a cascade or multisectional system, Doctor Coolidge found, promises to permit the building of vacuum discharge tubes for as high voltage as can be generated. The use of the cascade tube applies equally well to x-ray and cathode-ray tubes, since the latter may be converted into the former by the addition of a suitable target.

The highest-voltage Coolidge x-ray tubes used commercially at the present time are of 200,000 volts peak capacity, and are of two types—water-cooled and air-cooled. Both are adaptable for x-ray therapy. The air-cooled type has been used to considerable advantage in industrial applications of x-rays, since the high voltage gives the necessary penetration required for examining the heavier metal objects.

BOOK REVIEWS

Annual Reports on the Progress of Applied Chemistry, 1929. Volume XIV. 775 pages. Published by the Society of Chemical Industry, London. Price, 7 s. 6 d. to members; 12 s. 6 d. to non-members.

This fourteenth annual report on the progress of applied chemistry is arranged in conformity with the plan followed in previous issues. Under the chapter on General, Plant, and Machinery there are 25 pages covering 120 references; under the chapter on Fuel there are 31 pages covering 178 references; Gas, Carbonisation, Tar, and Tar Products, 34 pages, 124 references; Mineral Oils, 14 pages, 42 references; Colouring Matters and Dyes, 36 pages, 310 references; Fibres, Textiles, Cellulose, and Paper, 25 pages, 135 references; Bleaching, Dyeing, Printing, and Finishing, 22 pages, 125 references; Acids, Alkalis, and Salts, 43 pages, 238 references; Glass, 10 pages, 57 references; Refractories, Ceramics, and Cements, 18 pages, 85 references; Iron and Steel, 30 pages, 142 references; Non-Ferrous Metals, 23 pages, 146 references; Electro-Chemical and Electro-Metallurgical Industries, 40 pages, 257 references; Oils, Fats, and Waxes, 44 pages, 317 references; Paints, Pigments, Varnishes, and Resins, 45 pages, 152 references; India-Rubber, 42 pages, 187 references; Leather and Glue, 64 pages, 108 references; Soils and Fertilisers, 49 pages, 185 references; Sugars, Starches, and Gums, 22 pages, 131 references; Fermentation Industries, 37 pages, 94 references; Foods, 16 pages, 143 references; Sanitation and Water Purification, 16 pages, 59 references; Fine Chemicals, Medicinal Substances, and Essential Oils, 31 pages, 99 references; Photographic Materials and Processes, 26 pages, 213 references; and there is a good author and subject index covering 44 pages.

In general, so far as the reviewer can determine from a hasty examination of the book and bearing in mind his lack of familiarity with many of the subject matters treated, this appears to be a very thorough résumé of the work which has been published in applied chemistry during 1929 and the latter part of 1928. It is noted, however, that a number of more or less important articles dealing with the terpenes, especially with turpentine and rosin, have been omitted.—F. P. VEITCH

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Correction

The heading over the review of the Annual Reports on the Progress of Chemistry issued by the Chemical Society of London, which appeared on page 685 of the June issue of INDUSTRIAL AND ENGINEERING CHEMISTRY, should read as follows:

Annual Reports on the Progress of Chemistry for 1929. Volume XXVI. Issued by the Chemical Society, London. 336 pages. 13.5 + 20.5 cm. Richard Clay & Sons, Ltd., Suffolk, England, 1930. Price, 10 s. 6 d. net; postage 6 d. extra.

The data on this book were confused with those on the Annual Reports issued by the Society of Chemical Industry, a review of which is given on this page.

Bacteriology. A Text Book of Fundamentals. BY STANLEY THOMAS. 2nd edition, 301 pages. McGraw-Hill Book Company, Inc., New York, 1930. Price, $3.00.

This book is designed for a very special purpose. The author has written a text for students of engineering, in particular, and others who are almost entirely unfamiliar with the biological sciences, but who need as part of their working equipment a knowledge of the elements of bacteriology. The subject is presented in a rather popular fashion, emphasizing the general principles of the science and its broad relations to human activities. The volume should serve very well to introduce bacteriology in an interesting way to students whose previous training has been along entirely different lines. The text does not include the laboratory methods and notes on technic found in the more advanced books on the subject. It is intended that it should be supplemented by a course of lectures and the laboratory work necessary to round out the student's grasp of the subject.

The book devotes eight chapters to general phases of the life of microörganisms and follows these with six chapters on bacteria characteristic of certain habitats, such as soil, water, sewage, etc. There is a chapter on immunity, one on pathogenic organisms, one on hygiene and sanitation, and one on bacteria in industry. In the chapter on immunity the author has the difficult task of covering a complex subject in a few pages. It is felt that this portion of the text could be improved considerably from the standpoint of clarity. Also, there are several unfortunate errors in the chapter on bacteria in industry.

In general, the material of the book is well arranged and presented, and it should serve quite well as an introductory text to the science of bacteriology.—F. M. HILDEBRANDT

Handbook of Chemistry and Physics. A Ready-Reference Pocket Book of Chemical and Physical Data. 14th edition. Compiled by CHARLES D. HODGMAN AND NORBERT A. LANGE. 1386 pages. Chemical Rubber Publishing Company, Cleveland, Ohio. Price, $5.00.

Continuing their policy of annual revision in order to furnish up-to-date information and to incorporate suggestions of users for increasing its value, the compilers of this handbook have enlarged the fourteenth edition by more than 170 pages.

The principal addition is a table of the wave lengths and other characteristics of the principal lines in the emission spectra of the elements produced by the arc, spark, or Geissler tube. This table alone occupies 72 pages and is followed by a 2-page table of the spark spectrum of air.

The section on ceramics has been increased from 12 to 43 pages by the addition of shrinkage conversion tables and various tables giving the properties of dry and saturated air.

The mathematical section includes anti-logarithm and simple and compound interest tables.

New tables are given on the heat of combustion of organic compounds and the combustion constants for gases and the heat of combination and combustion of representative coals. Tables on the physical and chemical constants of resins, thermal expansion of glasses, new density tables; an enlarged table on physical constants of common minerals; tables on composition of antifreeze solutions, constant humidity, temperature conversion; and an enlarged table of indicators are other new features of the fourteenth edition. Several pages of equations of representative qualitative volumetric reactions with gravimetric equivalents have also been added.

The new volume contains such a variety of new data that this material alone should be well worth the cost of the handbook, and its increased value to ceramic chemists and to those concerned with emission spectra should be especially noted.

Elektrothermie. Die elektrische Erzeugung und technische Verwendung höher Temperaturen. Compiled by M. PIRANI. 293 pages. 268 illustrations. Julius Springer, Berlin, 1930. Price, 36 marks.

"Elektrothermie" is a volume of lectures by several authors, which are intended to furnish a survey of the more important applications of electrothermy, or electrically produced heat.

Electrothermy of iron (74 pages), by R. Gross, contains an intimate discussion of transformers, regulators of the height of electrodes above the furnace charge, and details of clamping devices. A tall oven for pig iron, which might be called a blastless blast furnace, since we do not use the exact equivalent of "Hochofen," is shown completely in three drawings, and is followed by a "low" furnace for pig iron. In the tall oven graphite electrodes bring alternating current of 70 to 120 volts to a point just above the hearth; for each ton of pig iron 2500 kilowatt-hours are required. For a furnace of 40-ton capacity 5000 to 6000 kilovolt-ampere transformers are necessary. This first chapter alone has 81 illustrations.

Electrical fusion ovens for non-ferrous metals (20 pages), by M. Tama, describes ovens for the production of copper, brass, nickel, nickel alloys, and aluminum. The next division (14 pages), by R. Schneidler, discusses the preparation of silicocarbide, electrocorundum, and electrofused cement, the latter a truly fused and not merely sintered material, high in alumina.

The electrocorundum furnaces are particularly well shown in the pictures.

Electrographite (7 pages), by M. Pirani, is followed by calcium carbide (4 pages), by R. Gross. Fused quartz, by Felix Singer, has 31 pages; its production is well detailed and illustrated. Quartz installation of condensers, cooling pipes, and towers for sulfuric acid concentration, for nitric acid, and for hydrochloric acid are shown.

Electrothermy of the gases (28 pages), by Harry Pauling, in reality confines itself to nitrogen oxide. The Pauling, Birkeland, Moscicki, and Schönherr systems, with certain recent improvements, are well presented. To American readers this chapter would have been more exciting twenty years ago.

The next division is perhaps the most stimulating one. It deals with research or development work in electrothermy (34 pages), by M. Pirani. It contains, among other items, specifications and information on ten types of laboratory ovens, in tabular form.

The last chapter, methods of measurement (64 pages), by Georg Keinath, is an intimate discussion of instruments of measurements, their construction, capacity, adaptability, and degree of accuracy. There is no index.

This attractively printed and neatly bound book will be welcome to engineers and chemists busy with electrothermal processes, and to students of the transformation of electrical energy into useful heat.—E. Raymond Riegel

Einführung in die technische Behandlung gasförmiger Stoffe. By W. Bertelsmann and F. Schuster. 411 pages. 288 illustrations. 16.5 × 24.5 cm. Julius Springer, Berlin. Price, paper, 38 marks; bound, 40 marks.

As stated in the title, this book is a brief introduction to the technology of gases and vapors. The subject is treated from the standpoint of methods rather than materials. The authors attempt to show the practical technologist what ways and means have been developed and used in various industries for the production, handling, and treatment of gases.

Following an introduction on physico-chemical fundamentals, the text is arranged in the following nine chapters: heating, cooling, compression, and liquefaction; the winning of gases from the air and from the earth, including separation of constituent gases by liquefaction and fractionation, solution in liquids and adsorption in solids; the generation or formation of gases from other gases, liquids, and solids; the purification of gases from dust, mist, and other gases; gas measurements; storage; transportation; sampling, testing, and analysis; and tables of physical and chemical constants. Obviously a book could be written on each chapter. Therefore one cannot expect more than a bare introduction to the subject, and possibly a bird's-eye view of gas technology as a whole. Within these limitations the authors have succeeded in their objective.

The various chapters consist of brief but to-the-point descriptions and discussions of processes and methods with special reference to the physico-chemical principles involved. The text is illustrated with numerous diagrammatic sketches of various types of apparatus.

Each chapter subdivision is followed by a list of references to the literature, so that the reader may follow up the subject in detail. Naturally most of the references are to German technical literature, although many important French, English, and American references are included.

Most of the subject matter is well selected. However, the authors have made the usual error of compilers with reference to the composition of natural gas in quoting certain incorrect analyses of North American natural gas. They give from 0 to 3 per cent unsaturated hydrocarbons, 0 to 3 per cent carbon monoxide, and 0 to 12 per cent hydrogen. None of these constituents have been found in American natural gas by correct methods of analysis. A chapter on gas hazards covering toxicity and explosibility should have been included in the book. The chapter on examination of gases contains an excellent review of methods for determining dust, mist, and vapor in gases, but it omits the modern forms of Orsat apparatus for complete analysis.

The book is probably of most value to the German-reading chemical engineer who desires in one book brief reference to the technology of industrial gases and an introduction to the literature in this field.—A. C. Fieldner

Les Applications des Rayons X. By J. J. Trillat. 294 pages. Les Presses Universitaires de France, 49, Boulevard Saint-Michel, 49, Paris, 1930.

The book is divided into two main parts. The first, composed of three chapters, gives a general discussion in simple language of the nature of x-rays and of various types of x-ray equipment, and a brief statement of the various methods of crystal analysis. The second part, composed of seven chapters, deals with the application of crystal structure technic under the following topics:

I—Application of X-Rays to the Study of Metals and Alloys.
II—Studies on Long-Chain Organic Compounds.
III—General Studies of Colloidal Substances.
IV—Studies of Cellulose and Its Derivatives.
V—Studies of Rubber, Gelatin, Resins, Proteins, etc.
VI—The Liquid State and Oriented Films.
VII—Qualitative and Quantitative Analysis by Means of X-Rays; Radiography.

The book is clearly written, and is especially valuable to any one working with colloids or with organic compounds such as cellulose. The author has drawn quite widely on the published work of specialists in the various branches of x-ray work. This, together with the author's own well-recognized contributions to crystal structure studies, makes the book worth owning by anyone interested even indirectly in the field. The only drawback to the book is its wretched binding, which scarcely survives a single reading.—Wheeler P. Davey

GOVERNMENT PUBLICATIONS

Notice—*Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate.*

Bureau of Foreign and Domestic Commerce

The Chemical Industry in Czechoslovakia. *Trade Information Bulletin* 708. 33 pp. Paper, 10 cents.

Bureau of Mines

Acrolein as a Warning Agent for Detecting Leakage of Methyl Chloride from Refrigerators. W. P. Yant, H. H. Schrenk, F. A. Patty, and R. R. Sayers. *Reports of Investigations* 3027. 11 pp.

A New Flame Safety Lamp Testing and Demonstration Apparatus. W. P. Yant, L. B. Berger, and G. S. McCaa. *Reports of Investigations* 3017. 10 pp.

Asphalt and Related Bitumens in 1928. A. H. Redfield. *Mineral Resources of the United States, 1928.* Part II, pp. 391–422. Paper, 10 cents.

A Study of the Lubricant Fractions of Cabin Creek (W. Va.) Petroleum. H. M. Smith. *Technical Paper* 477. 48 pp. Paper, 15 cents.

A Study of the Marshall-Bird Test for Determining the Agglutinating Value of Coal. K. A. Johnson and H. F. Yancey. *Reports of Investigations* 3011. 7 pp.

A Study of the Properties of Texas Polyhalite Pertaining to the Extraction of Potash. H. H. Storch and Loyal Clarke. *Reports of Investigations* 3002. 19 pp.

Bauxite and Aluminum in 1928. *Mineral Resources of the United States, 1928.* Part I, pp. 423–27. Paper, 5 cents.

Check Determinations of Fusibility of Coal Ash with the De Graaf Electric Coal-Ash Fusion Furnace. W. A. Selvig. *Reports of Investigations* 3003. 17 pp.

Cobalt. P. M. Tyler. *Information Circular* 6331. 33 pp.

Coke and By-Products in 1928. F. G. Tryon and H. L. Bennit. *Mineral Resources of the United States, 1928.* Part II, pp. 705–801. Paper, 15 cents.

Coöperative Research between the United States Bureau of Mines and the Safety in Mines Research Board. R. V. Wheeler and G. S. Rice. *Reports of Investigations* 3010. 4 pp.

Dissolution of Various Manganese Minerals. C. W. Davis. *Reports of Investigations* 3024. 11 pp.

Fluorspar and Cryolite in 1929. H. W. Davis. *Mineral Resources of the United States, 1929.* Part II, pp. 1–21. Paper, 5 cents.

Fuel Briquets in 1929. O. E. Kiessling and J. M. Corse. *Mineral Resources of the United States, 1929.* Part II, pp. 23–33. Paper, 5 cents.

Gold, Silver, Copper, and Lead in South Dakota and Wyoming in 1928. C. W. Henderson. *Mineral Resources of the United States, 1928.* Part I, pp. 429–39. Paper, 5 cents.

Gold, Silver, Copper, Lead, and Zinc in Montana in 1928. C. N. Gerry. *Mineral Resources of the United States, 1928.* Part I, pp. 563–606. Paper, 10 cents.

Gold, Silver, Copper, Lead, and Zinc in Nevada in 1928. V. C. Heikes. *Mineral Resources of the United States, 1928.* Part I, pp. 441–78. Paper, 10 cents.

Gold, Silver, Copper, Lead, and Zinc in New Mexico and Texas in 1928. C. W. Henderson. *Mineral Resources of the United States, 1928.* Part I, pp. 529–61. Paper, 10 cents.

Increased Recoveries of Phosphate in the Land-Pebble District of Florida. H. M. Lawrence. *Reports of Investigations* 3023. 9 pp.

Laboratory and Field Tests of a Permissible Indicating Methane Detector. A. B. Hooker, W. J. Fene, and R. D. Currie. *Reports of Investigations* 3008. 14 pp.

Lead in 1928. E. W. Pehrson. *Mineral Resources of the United States, 1928.* Part I, pp. 607–43. Paper, 10 cents.

Mineral Resources of the United States, 1927. F. J. Katz. Part I—Metals. 782 pages. Cloth, $1.25.

Same. Part II—Non-Metals. 687 pages. Cloth, $1.00.

Monazite, Thorium, and Cerium. R. M. Santmyers. *Information Circular* 6321. 43 pp.

Natural-Gasoline Plants in the United States, January 1, 1930. G. R. Hopkins and E. M. Seeley. *Information Circular* 6279. 28 pp.

Petroleum in 1928. G. R. Hopkins and A. B. Coons. *Mineral Resources of the United States, 1928.* Part II, pp. 615–703. Paper, 15 cents.

Radium. P. M. Tyler. *Information Circular* 6312. 55 pp.

Results of Air Repressuring and Engineering Study of Williams Pool, Putnam-Moran District, Callahan County, Tex. H. B. Hill. *Technical Paper* 470. Paper, 15 cents.

Roasting of Chromite Ores to Produce Chromates. H. A. Doerner. *Reports of Investigations* 2999. 30 pp.

Selenium and Tellurium. R. M. Santmyers. *Information Circular* 6317. 23 pp.

Stock Distribution and Gas-Solid Contact in the Blast Furnace. C. C. Furnas and T. L. Joseph. *Technical Paper* 476. 73 pp. Paper, 30 cents.

Sulfur Dioxide in the Air at the Pittsburgh Experiment Station of the U. S. Bureau of Mines. E. G. Meiter and C. E. Trauvert. *Reports of Investigations* 3005. 5 pp.

Summarized Data of Silver Production. C. W. Merrill. *Economic Paper* 8. 58 pp. Paper, 20 cents.

Survey of Cracking Plants January 1, 1930. G. R. Hopkins. *Information Circular* 6305. 16 pp.

The Lower Limits of Inflammability of Natural Gas–Air Mixtures in a Large Gallery. J. E. Crawshaw. *Reports of Investigations* 3016. 13 pp.

The Use of Boiler Feed-Water Heater with Steam-Powered Rotary Drilling Equipment. C. E. Reistle, Jr. *Reports of Investigations* 3022. 14 pp.

Use of Ethyl Mercaptan to Detect Leaks in Natural-Gas Distribution Systems. R. R. Sayers, A. C. Fieldner, W. P. Yant, R. D. Leitch, and S. J. Pearce. *Reports of Investigations* 3007. 13 pp.

Bureau of Standards

A Comparison of Resolving Power and Sensitivity of Photographic Plates with Varying Development. B. H. Carroll and Donald Hubbard. *Bureau of Standards Journal of Research*, 5 (July, 1930), 1–11.

A New Consistometer and Its Application to Greases and to Oils at Low Temperatures. Ronald Bulkley and F. G. Bitner. *Research Paper* 188. 14 pp. Paper, 5 cents.

Flow Characteristics of Special Fe-Ni-Cr Alloys and Some Steels at Elevated Temperatures. H. J. French, William Kahlbaum, and A. A. Peterson. *Research Paper* 192. 59 pp. Paper, 25 cents.

Method of Measuring Strains between Glazes and Ceramic Bodies. H. G. Schurecht and G. R. Pole. *Bureau of Standards Journal of Research*, 5 (July, 1930), 97–104.

Photo-Ionization of Caesium by Line Absorption. F. L. Mohler and C. Boeckner. *Bureau of Standards Journal of Research*, 5 (July, 1930), 51–71.

Relationships between Rockwell and Brinell Numbers. S. N. Petrenko. *Research Paper* 185. 30 pp. Paper, 10 cents.

The Preparation of Fiber Test Sheets. M. B. Shaw, G. W. Bicking, and L. W. Snyder. *Bureau of Standards Journal of Research*, 5 (July, 1930), 105–14.

Department of Agriculture

Potassium Iodide as a Mineral Supplement in Paired Feeding Experiments with Growing Swine. W. E. Carroll, H. H. Mitchell, and G. E. Hunt. *Journal of Agricultural Research*, 41 (July 1, 1930), 65–77.

Review of United States Patents Relating to Pest Control. R. C. Roark. Vol. 3, No. 5 (May, 1930). 13 pp. Paper, 10 cents.

Same. Vol. 3, No. 6 (June, 1930). 20 pp. Paper, 10 cents.

The Limits of Error of the Babcock Test for Cream. W. H. Martin, A. C. Fay, and K. M. Renner. *Journal of Agricultural Research*, 41 (July 15, 1930), 147–59.

The Vitamin-C Content of Commercially Canned Sauerkraut, Together with Some Observations on Its Vitamin-A Content. Bertha Clow, Helen T. Parsons, and Ina Stevenson. *Journal of Agricultural Research*, 41 (July 1, 1930), 51–64.

Variations in Content of Sugars and Related Substances in Olives. P. F. Nichols. *Journal of Agricultural Research*, 41 (July 1, 1930), 89–96.

Geological Survey

Contributions to Economic Geology, 1929. H. D. Miser. Part II—Mineral Fuels. *Bulletin* 812. 338 pp. Paper, $1.25.

Geology and Ore Deposits of the Wood River Region, Idaho. J. B. Umpleby, L. G. Westgate, and C. P. Ross. *Bulletin* 814. 250 pp. Paper, 90 cents.

Mineral Resources of Alaska, 1927. P. S. Smith and Others. *Bulletin* 810. 172 pp. Paper, 50 cents.

Surface Water Supply of the United States, 1926. Part XII—North Pacific Slope Basins. C—Pacific Slope Basins in Oregon and Lower Columbia River Basin. *Water-Supply Paper* 634. 236 pp. Paper, 25 cents.

Same. Part XI—Pacific Slope Basins in California. N. C. Groner. *Water-Supply Paper* 631. 419 pp. Paper, 65 cents.

Public Health Service

Acute Response of Guinea Pigs to Vapors of Some New Commercial Organic Compounds. IV—Ethylene Oxide. C. P. Waite, F. A. Patty, and W. P. Yant. *Public Health Reports*, 45 (August 8, 1930), 1832–43.

Experimental Studies of Water Purification. H. W. Streeter. IV—Observations on the Effects of Certain Modifications in Coagulation-Sedimentation on the Bacterial Efficiency of Preliminary Water Treatment in Connection with Rapid Sand Filtration. A—Observed Effect of Variations in the Period of Sedimentation. *Public Health Reports*, 45 (July 4, 1930), 1521–36.

Same. B—Observed Effect of Certain Modifications in the Conditions of Coagulation. *Public Health Reports*, 45 (July 11, 1930), 1597–1623.

Pharmacological and Chemical Studies of the Cause of So-Called Ginger Paralysis. A Preliminary Report. M. I. Smith, E. Elvove, P. J. Valaer, Jr., W. H. Frazier, and G. E. Mallory. *Public Health Reports*, 45 (July 25, 1930), 1703–16.

Perfumes, Cosmetics, and Soaps. With Especial Reference to Synthetics. Volume I. By William A. Poucher. 3rd edition. 394 pages. D. Van Nostrand Co., Inc., New York, 1930. Price, $6.50.

The third edition of this dictionary, when compared with the last edition, is found to contain 30 additional natural products and nearly 250 more synthetics, making a total of more than 1000 perfumery raw materials. The dictionary testifies to the continued search in the domain of aromatic chemicals for a still wider assortment of perfumery raw materials from which to choose. The present volume especially emphasizes synthetics and in Appendix I devotes nearly 20 pages to nomenclature and structural formulas of synthetics. The dictionary proper gives, where possible, chemical formulas and physical constants, and the author points out that, while such data may be regarded as desirable standards, the necessity for odor evaluation as the final choice cannot be emphasized too strongly. The volume contains a vast amount of information gathered throughout the world and the constants given have been determined on samples supplied by manufacturers everywhere.

A second appendix is devoted to simple methods for the determination of physical constants and is intended to be of greatest use to perfumers who may have had no chemical training. A third appendix comprises a series of conversion tables.

The volume appears to be unusually complete, is illustrated with a number of plates, and is unquestionably a valuable addition to the literature in this field.

MARKET REPORT—SEPTEMBER, 1930

THESE PRICES, UNLESS OTHERWISE SPECIFIED, ARE THOSE PREVAILING IN THE NEW YORK MARKET, SEPTEMBER 15, FOR COMMERCIAL GRADES IN CARLOAD QUANTITIES

Newer Chemicals

Acetaldehyde, drums, lc-l., wks.	lb.	.18½
Acetaldol, 50-gal. drums	lb.	.27
Acetylene tetrachloride, *see* Tetrachloroethane		
Amyl furoate, 1-lb. tins	lb.	5.00
Aroclors	lb.	.20
Butyl carbitol, *see* Diethylene glycol monobutyl ether		
Cellosolve, *see* Ethylene glycol monobutyl ether		
Furoate, tech., 50-gal. drums	lb.	.50
Carbitol, *see* Diethylene glycol monoethyl ether		
Cellosolve, *see* Ethylene glycol monoethyl ether		
Acetate, *see* Ethylene glycol monoethyl ether acetate		
Cellulose acetate, 50-lb. kegs	lb.	1.20
Crotonaldehyde, 50-gal. drums	lb.	.32
Dichloroethyl ether, 50-gal. drums	lb.	.06
Diethylene glycol, drums	lb.	.11
Monobutyl ether, drums	lb.	.28
Monoethyl ether, drums	lb.	.16
Diethylene oxide, 50-gal. drums	lb.	.50
Dioxan, *see* Diethylene oxide		
Diphenyl	lb.	.30
Ethyl acetoacetate, 50-gal. drums	lb.	.65
Carbonate, 90%, 50-gal. drums	gal.	1.85
Chlorocarbonate, carboys	lb.	.30
Ether, absolute, 50-gal. drums	lb.	.50
Furoate, 1-lb. tins	lb.	5.00
Ethylene chlorhydrin, 40%, 10-gal. cbys	lb.	.75
Dichloride, 50-gal. drums	lb.	.05
Glycol, 50-gal. drums	lb.	.25
Monobutyl ether, drums, wks.	lb.	.25
Monoethyl ether, drums, wks.	lb.	.17
Monoethyl ether acetate, drums, wks.	lb.	.19½
Monomethyl ether, drums	lb.	.21
Oxide, cyl.	lb.	2.00
Furfuramide (tech.), 100-lb. drums	lb.	.30
Furfuryl acetate, 1-lb. tins	lb.	5.00
Alcohol, tech., 100-lb. drums	lb.	.50
Furoic acid (tech.), 100-lb. drums	lb.	.50
Isopropyl ether, drums	lb.	.10
Lead dithiofuroate, 100-lb. drums	lb.	1.00
Magnesium peroxide, 100-lb. cs.	lb.	1.00
Methyl acetate, drums	gal.	.95
Cellosolve, *see* Ethylene glycol monomethyl ether		
Furoate, tech., 50-gal. drums	lb.	.50
Paraldehyde, 110–55 gal. drums	lb.	.20½
Phosphorus oxychloride, 175 cyl.	lb.	.20
Propyl furoate, 1-lb. tins	lb.	5.00
Strontium peroxide, 100-lb. drums	lb.	1.25
Sulfuryl chloride, 600-lb. drums, crude	lb.	.10
Distilled	lb.	.35
Tetrachloroethane, 50-gal. drums	lb.	.09
Trichloroethylene, 50-gal. drums	lb.	.10
Triethanolamine, 50-gal. drums	lb.	.40
Vinyl chloride, 16-lb. cyl.	lb.	1.00
Zinc dithiofuroate, 100-lb. drums	lb.	1.00
Perborate, 100-lb. drums	lb.	1.25
Peroxide, 100-lb. drums	lb.	1.25

Chemicals Previously Quoted

Acetanilide, tech., bbls.	lb.	.28
Acetic anhydride, 92–95%, cbys.	lb.	.25
Acetone, C. P., drums, wks.	lb.	.11
Acetphenetidin, bbls.	lb.	1.25
Acid, acetic, 28%, c/l., bbls.	100 lbs.	3.11
56%, c/l., bbls.	100 lbs.	5.85
Glacial, c/l., bbls.	100 lbs.	11.01
Glacial, technical, c/l., carboys	100 lbs.	11.51
Acetylsalicylic, bbls.	lb.	.85
Anthranilic, 99–100%, drums	lb.	.98
Benzoic, tech., bbls.	lb.	.43
Boric, bbls.	lb.	.06¾
Butyric, 100% basis, cbys.	lb.	.85
Chloroacetic, mono-, bbls., wks.	lb.	.18
Di-, cbys.	lb.	1.00
Tri-, bbls.	lb.	2.50
Chlorosulfonic, drums, wks.	lb.	.04½
Chromic, 99%, drums	lb.	.16½
Cinnamic, bottles	lb.	3.25
Citric, U. S. P., kegs, bbls.	lb.	.46
Cresylic, pale, drums	gal.	.55
Formic, 90%, cbys., N. Y.	lb.	.10½
Gallic, U. S. P., bbls.	lb.	.60
Glycerophosphoric, 25%, 1-lb. bot.	lb.	1.40
H, bbls., wks.	lb.	.65
Hydriodic, 10%, U. S. P., 5-lb. bot.	lb.	.67
Hydrobromic, 48%, cbys., wks.	lb.	.45
Hydrochloric, 20°, tanks, wks.	100 lbs.	1.35
Hydrofluoric, 30%, bbls., wks.	lb.	.06
60%, bbls., wks.	lb.	.13
Hydrofluosilicic, 35%, bbls., wks.	lb.	.11
Hypophosphorus, 30%, U. S. P., 5-gal. demis.	lb.	.85
Lactic, 22%, dark, bbls.	lb.	.04
48%, light, bbls., wks.	lb.	.11
Mixed, tanks, wks.	N unit	.07
	S unit	.008
Molybdic, 85%, kegs	lb.	1.25
Naphthionic, tech., bbls.	lb.	nom.
Nitric, C. P., cbys.	lb.	.11
Nitric, 36°, c/l., cbys., wks.	100 lbs.	5.00
Oxalic, bbls., wks.	lb.	.11¼
Phosphoric, 50%, U. S. P.	lb.	.14
Picramic, bbls.	lb.	.65
Picric, bbls., c/l.	lb.	.30
Pyrogallic	lb.	1.50
Salicylic, tech., bbls.	lb.	.33
Stearic, d. p., bbls., c/l.	lb.	.13½
Sulfanilic, 250-lb. bbls.	lb.	.15
Sulfuric, 66°, c/l., cbys., wks.	100 lbs.	1.60
66°, tanks, wks.	ton	15.50
60°, tanks, wks.	ton	11.00
Oleum, 20%, tanks, wks.	ton	18.50
40%, tanks, wks.	ton	42.00
Sulfurous, U. S. P., 6%, cbys.	lb.	.05
Tannic, tech., bbls.	lb.	.30
Tartaric, U. S. P., cryst., bbls.	lb.	.34½
Tungstic, kegs	lb.	1.40
Valeric, C. P., 10-lb. bot.	lb.	2.50
Alcohol, U. S. P., 190 proof, bbls.	gal.	2.55
Amyl, Imp. drums	gal.	1.75
Butyl, drums, c/l., wks.	lb.	.17¼
Cologne spirit, bbls.	gal.	2.69
Denatured, No. 5, comp. denat., c/l., drums,	gal.	.41
No. 1, comp. denat., drums	gal.	.43
Isoamyl, drums	gal.	4.00
Isobutyl, ref., drums	lb.	1.00
Isopropyl, ref., drums	gal.	.60
Propyl, ref., drums	lb.	1.00
Wood, *see* Methanol		
Alpha-naphthol, bbls.	lb.	.65
Alpha-naphthylamine, bbls.	lb.	.32
Alum, ammonia, lump, bbls., wks.	100 lbs.	3.30
Chrome, casks, wks.	100 lbs.	5.00
Potash, lump, bbls., wks.	100 lbs.	3.30
Soda, bbls., wks.	100 lbs.	3.50
Aluminum, metal, N. Y.	lb.	.24
Aluminum chloride, anhyd., commercial, wks., drums extra, c/l.	lb.	.05
Aluminum stearate, 100-lb. bbl.	lb.	.25
Aluminum sulfate, comm'l, bags, wks.	100 lbs.	1.40
Iron-free, bags, wks.	100 lbs.	1.95
Aminoazobenzene, 100-lb. kegs	lb.	1.15
Ammonia, anhydrous, cyl., wks.	lb.	.15½
Ammonia water, 26°, drums, wks.	lb.	.03¼
Ammonium acetate, kegs	lb.	.33
Bifluoride, bbls.	lb.	.21
Bromide, 50-lb. boxes	lb.	.48
Carbonate, tech., casks	lb.	.09
Chloride, gray, bbls.	100 lbs.	5.25
Lump, casks	lb.	.11
Iodide, 25-lb. jars	lb.	5.20
Nitrate, tech., cryst., bbls.	lb.	.08½
Oxalate, kegs	lb.	.28
Persulfate, cases	lb.	.26
Phosphate, dibasic, tech., bbls.	lb.	.11½
Sulfate, bulk, wks.	100 lbs.	1.82½
Thiocyanate, tech., kegs	lb.	.36
Amyl acetate, tech., drums	lb.	.22
Aniline oil, drums	lb.	.15
Anthracene, 80–85%, casks, wks.	lb.	.60
Anthraquinone, subl., bbls.	lb.	.50
Antimony, metal	lb.	.07¾
Antimony chloride, drums	lb.	.13
Oxide, bbls.	lb.	.08
Salt, dom., bbls.	lb.	.24
Sulfide, crimson, bbls.	lb.	.25
Golden, bbls.	lb.	.16
Vermilion, bbls.	lb.	.38
Tartrolactate, bbls.	lb.	.45
Argols, red powder, bbls.	lb.	.07½
Arsenic, metal, kegs	lb.	.30
Red, kegs, cases	lb.	.09
White, c/l., kegs	lb.	.04
Asbestine, bulk, c/l.	ton	15.00
Barium carbonate, bbls., bags, wks.	ton	58.00
Chloride, bbls., wks.	ton	63.00
Dioxide, drs., wks.	lb.	.12
Hydroxide, bbls.	lb.	.04¾
Nitrate, casks	lb.	.07½
Barium thiocyanate, 400-lb. bbls.	lb.	.27
Barytes, floated, 350-lb. bbls., wks.	ton	23.00
Benzaldehyde, tech., drums	lb.	.60
F. F. C., cbys.	lb.	1.40
U. S. P., cbys.	lb.	1.15
Benzene, pure, tanks, mills	gal.	.21
Benzidine base, bbls.	lb.	.65
Benzoyl chloride, cbys.	lb.	1.00
Benzyl acetate, F. F. C., bottles	lb.	.75
Alcohol, 5-liter bot.	lb.	.95
Chloride, tech., drums	lb.	.30
Beta-naphthol, bbls.	lb.	.22
Beta-naphthylamine, bbls.	lb.	.53
Bismuth, metal, cases	lb.	1.00
Bismuth, nitrate, 25-lb. jars	lb.	1.85
Oxychloride, boxes	lb.	2.95
Subnitrate, U. S. P., 25-lb. jars	lb.	1.35
Blanc fixe, dry, bbls.	ton	70.00
Bleaching powder, drums, wks.	100 lbs.	2.00
Bone ash, kegs	lb.	.06
Bone black, bbls.	lb.	.08¼
Borax, bags	lb.	.02½
Bordeaux mixture, bbls.	lb.	.12
British gum, com., c/l.	100 lbs.	4.37
Bromine, bot.	lb.	.45
Bromobenzene, drums	lb.	.50
Bromoform, jars	lb.	1.80
Butylacetate, drums, c/l.	lb.	.181
Cadmium bromide, 50-lb. jars	lb.	1.40
Cadmium, metal, cases	lb.	.70
Cadmium sulfide, boxes	lb.	.95
Caffeine, U. S. P., 5-lb. cans	lb.	2.75
Calcium acetate, bags	100 lbs.	3.00
Arsenate, bbls.	lb.	.07
Carbide, drums	lb.	.05
Chloride, drums, wks.	ton	20.00
Cyanide, 100-lb. drums	lb.	.30
Lactate, tech., bbls.	lb.	.42

Nitrate, bbls.	ton	42.00
Phosphate, monobas., bbls.	lb.	.08
Tribas., bbls.	lb.	.11
Calcium carbonate, tech., bgs.	100 lbs.	1.00
U. S. P., precip., 175-lb. bbl.	lb.	.06½
Camphor, Jap., cases	lb.	.56½
Camphor, monobrom., cs.	lb.	1.85
Caramel, bbls.	gal.	.63
Carbazole, bbls.	lb.	.75
Carbon, activated, drums	lb.	.08
Carbon bisulfide, drums	lb.	.05½
Carbon black, cases	lb.	.12
Carbon dioxide, liq. cyl.	lb.	.06
Carbon tetrachloride, drums	lb.	.06¼
Casein, stand. gr., bbls.	lb.	.13½
Cellulose acetate, kegs	lb.	1.20
Cerium oxalate, kegs	lb.	.32
Charcoal, willow, powd., bbls.	lb.	.06
China clay, bulk	ton	8.00
Chloral hydrate, drums	lb.	.60
Chloramine, U. S. P., 5-lb. bot.	lb.	1.50
Chlorine, liq., c/l., cyl.	lb.	.04
Chlorobenzene, mono-, drums	lb.	.10
Chloroform, tech., drums	lb.	.15
Chromium acetate, 20° soln., bbls.	lb.	.05
Coal tar, tanks, bbls., wks.	gal.	.07
Cobalt, metal, kegs	lb.	2.50
Cobalt oxide, bbls.	lb.	2.10
Cod-liver oil, bbls.	bbl.	30.00
Collodion, drums	lb.	.22
Copperas, c/l., bulk	ton	13.00
Copper, metal, elec.	100 lbs.	10.50
Copper carbonate, bbls.	lb.	.10
Chloride, bbls.	lb.	.22
Cyanide, drums	lb.	.41
Oxide, red, bbls.	lb.	.15½
Sulfate, c/l., bbls.	100 lbs.	4.75
Cotton, soluble, bbls.	lb.	.40
Cream tartar, bbls.	lb.	.26¼
Cyanamide, bulk, N. Y.	Nitrogen unit	1.45
Diaminophenol, kegs	lb.	3.80
Dianisidine, bbls.	lb.	2.35
Dibutylphthalate, drums, wks.	lb.	.24½
Diethylaniline, drums	lb.	.55
Diethylene glycol, drums	lb.	.11
Diethyl phthalate, drums	lb.	.24
Diethyl sulfate, tech., drums	lb.	.30
Dimethylaniline, drums	lb.	.26
Dimethylsulfate, drums	lb.	.45
Dinitrobenzene, drums	lb.	.15½
Dinitrochlorobenzene, bbls.	lb.	.13
Dinitronaphthalene, bbls.	lb.	.34
Dinitrophenol, bbls.	lb.	.29
Diphenylamine, bbls.	lb.	.40
Diphenylguanidine, bbls.	lb.	.30
Epsom salt, tech., bbls., c/l., N. Y.	100 lbs.	1.43
Ether, nitrous, bot.	lb.	.80
Ether, U. S. P., drums	lb.	.14
Ethyl acetate, drums, c/l.	lb.	.096
Bromide, drums	lb.	.50
Chloride, drums	lb.	.22
Methyl ketone, drums	lb.	.30
Ethylbenzylaniline, 300-lb. drums	lb.	.88
Ethylene dichloride	lb.	.05
Chlorohydrin, anhyd., drums	lb.	.75
Glycol, c/l., wks.	lb.	.25
Feldspar, bulk	ton	20.00
Ferric chloride, tech., bbls.	lb.	.05
Ferrous chloride, cryst., bbls.	lb.	.06
Ferrous sulfide, bbls.	100 lbs.	2.50
Fluorspar, 98%, bags	ton	41.00
Formaldehyde, bbls.	lb.	.07¼
Formaniline, drums	lb.	.37½
Fuller's earth, bags, c/l., mines	ton	15.00
Furfural, drums, tech., contract, works	lb.	.10
Glauber's salt, bbls.	100 lbs.	1.00
Glucose, 70°, bags, dry	100 lbs.	3.14
Glycerol, C. P., drums	lb.	.14
G salt, bbls.	lb.	.42
Hexamethylenetetramine, tech., drums	lb.	.46
Hydrogen peroxide, 25 vol., bbls.	lb.	.06½
Hydroquinone, kegs	lb.	1.20
Indigo, 20%, paste, bbls.	lb.	.12
Iodine, crude, 200-lb. kgs.	lb.	4.20
Iodine, resubl., jars	lb.	4.65
Iodoform, bot.	lb.	6.00
Iridium, metal	oz.	280.00
Kieselguhr, bags	ton	60.00
Lead, metal	100 lbs.	7.75
Lead acetate, bbls., white	lb.	.12
Arsenate, bbls.	lb.	.13
Oxide, litharge, bbls.	lb.	.08¾
Peroxide, drums	lb.	.25
Red, bbls.	lb.	.11
Sulfate, bbls.	lb.	.07¼
White, basic carb., bbls.	lb.	.09¼
Lime, hydrated, bbls.	100 lbs.	.85
Lime, live, chemical, bbls., wks.	100 lbs.	1.05
Limestone, ground, bags, wks.	ton	4.50
Lithium carbonate, 100-lb. kgs.	lb.	1.35
Lithopone, bbls.	lb.	.05¼
Magnesite, crude	ton	36.00
Calcined, 500-lb. bbls., wks.	ton	50.00
Magnesium, metal sticks, wks.	lb.	.85
Magnesium carbonate, bags	lb.	.06
Chloride, drums	ton	36.00
Fluosilicate, cryst., bbls.	lb.	.10
Oxide, U. S. P., light, bbls.	lb.	.42
Manganese chloride, casks	lb.	.08
Dioxide, 80%, bbls.	ton	80.00
Sulfate, casks	lb.	.07
Mercury bichloride, cryst., 25 lbs.	lb.	1.66
Mercury, flasks, 75 lbs.	flask	120.00
Meta-nitroaniline, bbls.	lb.	.67
Meta-phenylenediamine, bbls.	lb.	.80
Meta-toluylenediamine, bbls.	lb.	.67
Methanol, pure	gal.	.48
Denaturing grade, tanks	gal.	.43
Methyl acetone, drums	gal.	.57
Salicylate, cases	lb.	.42
Methyl chloride, cylinders	lb.	.45
Michler's ketone, bbls.	lb.	3.00
Naphtha, solvent, tanks	gal.	.35
Naphthalene, flake, bbls.	lb.	.05½
Nickel, metal	lb.	.35
Nickel salt, single, bbls.	lb.	.13
Double, bbls.	lb.	.13
Niter cake, bulk	ton	15.00
Nitrobenzene, drums	lb.	.09
Oil, castor, No. 1	lb.	.09
China wood, bbls.	lb.	.12½
Coconut, Ceylon, tanks	lb.	.07
Cod, N. F., tanks	gal.	.54
Corn, crude, tanks, mills	lb.	.07¾
Cottonseed, crude, tanks	lb.	.07⅛
Lard, edible, bbls.	lb.	.13
Linseed, bbls.	lb.	.14
Menhaden, crude, tanks	gal.	.30
Neat's-foot, pure, bbls.	lb.	.12¾
Oleo, No. 1, bbls.	lb.	.10½
Olive oil, denat., bbls.	gal.	.70
Foots, bbls.	lb.	.06
Palm, Lagos, casks	lb.	.05¾
Peanut, crude, bbls.	lb.	nom.
Perilla, bbls.	lb.	.12⅛
Rapeseed, bbls., English	gal.	.76
Red, bbls.	lb.	.09¾
Soy bean, crude, bbls.	lb.	.10¾
Sperm, 38°, bbls.	gal.	.84
Whale, bbls., natural, winter	gal.	.74
Ortho-aminophenol, kegs	lb.	2.15
Ortho-anisidine, drums	lb.	2.50
Ortho-dichlorobenzene, drums	lb.	.08
Ortho-nitrochlorobenzene, drums	lb.	.28
Ortho-nitrophenol, bbls.	lb.	.85
Ortho-nitrotoluene, drums	lb.	.16
Ortho-toluidine, bbls.	lb.	.27
Palladium, metal	oz.	46.80
Para-aminophenol, kegs	lb.	.92
Para-dichlorobenzene	lb.	.17
Para-formaldehyde, cases	lb.	.40
Paraldehyde, tech., drums	lb.	.23
Para-nitroaniline, drums	lb.	.48
Para-nitrochlorobenzene, drums	lb.	.25
Para-nitrophenol, bbls.	lb.	.45
Para-nitrosodimethylaniline, bbls.	lb.	.92
Para-nitrotoluene, bbls.	lb.	.29
Para-phenylenediamine, bbls.	lb.	1.15
Para-toluidine, bbls.	lb.	.40
Paris Green, 250-lb. kegs	lb.	.25
Phenol, drums	lb.	.14¾
Phenolphthalein, drums	lb.	1.10
Phenylethyl alcohol, 1-lb. bot.	lb.	7.00
Phosphorus, red, cases	lb.	.60
Phosphorus trichloride, cyl.	lb.	.35
Phthalic anhydride, bbls.	lb.	.15
Platinum, metal	oz.	57.00
Potash, caustic, drums	lb.	.06⅛
Potassium acetate, kegs	lb.	.27
Bicarbonate, casks	lb.	.09½
Bichromate, casks	lb.	.09
Binoxalate, bbls.	lb.	.14
Bromate, cs.	lb.	.35
Carbonate, 80–85%, calc., casks	lb.	.05¼
Chlorate, kegs	lb.	.08½
Chloride	ton	34.55
Cyanide, cases	lb.	.55
Meta-bisulfite, bbls.	lb.	.12
Permanganate, drums	lb.	.16
Prussiate, red, casks	lb.	.38
Yellow, casks	lb.	.18½
Titanium oxalate, bbls.	lb.	.21
Pyridine, drums	gal.	1.50
Quinine bisulfate, 100 oz.	oz.	.40
Sulfate, 100-oz. cans	oz.	.40
Resorcinol, tech., kegs	lb.	1.00
Rochelle salt, bbls., U. S. P.	lb.	.20
R salt, bbls.	lb.	.42
Saccharin, cans	lb.	1.75
Salt cake, bulk	ton	25.00
Saltpeter, gran., bbls.	lb.	06⅛
Silica, ref., bags	ton	22.00
Silver nitrate, 16-oz. bot.	oz.	.46¼
Soda ash, 58%, light, bags, contract, wks.	100 lbs.	1.34½
Soda, caustic, 76%, solid, drums, contract, wks.	100 lbs.	2.90
Sodium acetate, bbls.	lb.	.05
Benzoate, bbls.	lb.	.45
Bicarbonate, bbls.	100 lbs.	2.25
Bichromate, casks	lb.	.07
Bisulfite, bbls.	lb.	.04
Bromide, bbls.	lb.	.42
Chlorate, kegs	lb.	.06¼
Chloride, bags	ton	12.00
Cyanide, cases	lb.	.16
Fluoride, bbls.	lb.	.08¼
Metallic, drums, 12¼-lb. bricks	lb.	.27
Naphthionate, bbls.	lb.	.54
Nitrate, crude, bags, N. Y.	100 lbs.	2.07
Nitrite, bbls.	lb.	.07½
Perborate, bbls.	lb.	.18
Peroxide, cases	lb.	.27
Phosphate, trisodium	lb.	.03½
Picramate, kegs	lb.	.69
Prussiate, bbls.	lb.	.11½
Silicate, drums, tanks, 40°	100 lbs.	.75
Silicofluoride, bbls.	lb.	.04
Stannate, drums	lb.	.34
Sulfate, anhyd., bbls.	lb.	.02
Sulfide, cryst., bbls.	lb.	.02½
Solid, 60 %	lb.	.03½
Sulfocyanide, bbls.	lb.	.28
Thiosulfate, reg., cryst., bbls.	lb.	.02½
Tungstate, kegs	lb.	.81
Strontium carbonate, bbls.	lb.	.07¼
Nitrate, bbls.	lb.	.09
Strychnine alkaloid, 100 oz., powder	oz.	.56
Sulfate, powder	oz.	.52
Sulfur, bulk, mines, wks.	ton	18.00
Sulfur chloride, red, drums	lb.	.05
Yellow, drums	lb.	.03½
Sulfur dioxide, commercial, cyl.	lb.	.07
Sulfuryl chloride, drums	lb.	.10
Thiocarbanilid, bbls.	lb.	.22
Tin, Amer., stand.	lb.	.30
Tin bichloride, 50% sol., bbls.	lb.	.14½
Oxide, bbls.	lb.	.35
Titanium oxide, bbls., wks.	lb.	.22
Toluene, tanks	gal.	.35
Tribromophenol, cases	lb.	1.10
Triphenylguanidine, drums	lb.	.58
Triphenyl phosphate, bbls.	lb.	.60
Tungsten	Wo₃ unit	15.50
Urea, pure, cases	lb.	.15
Whiting, bags	100 lbs.	1.00
Xylene, 10°, tanks, wks.	gal.	.28
Xylidine, drums	lb.	.37
Zinc, metal, N. Y.	100 lbs.	5.55
Zinc ammonium chloride, bbls.	lb.	.05½
Chloride, granulated, drums	lb.	.05¾
Oxide, Amer., bbls.	lb.	.06½
Stearate, bbls.	lb.	.25
Zinc dust, bbls., kegs, c/l.	lb.	.06¾

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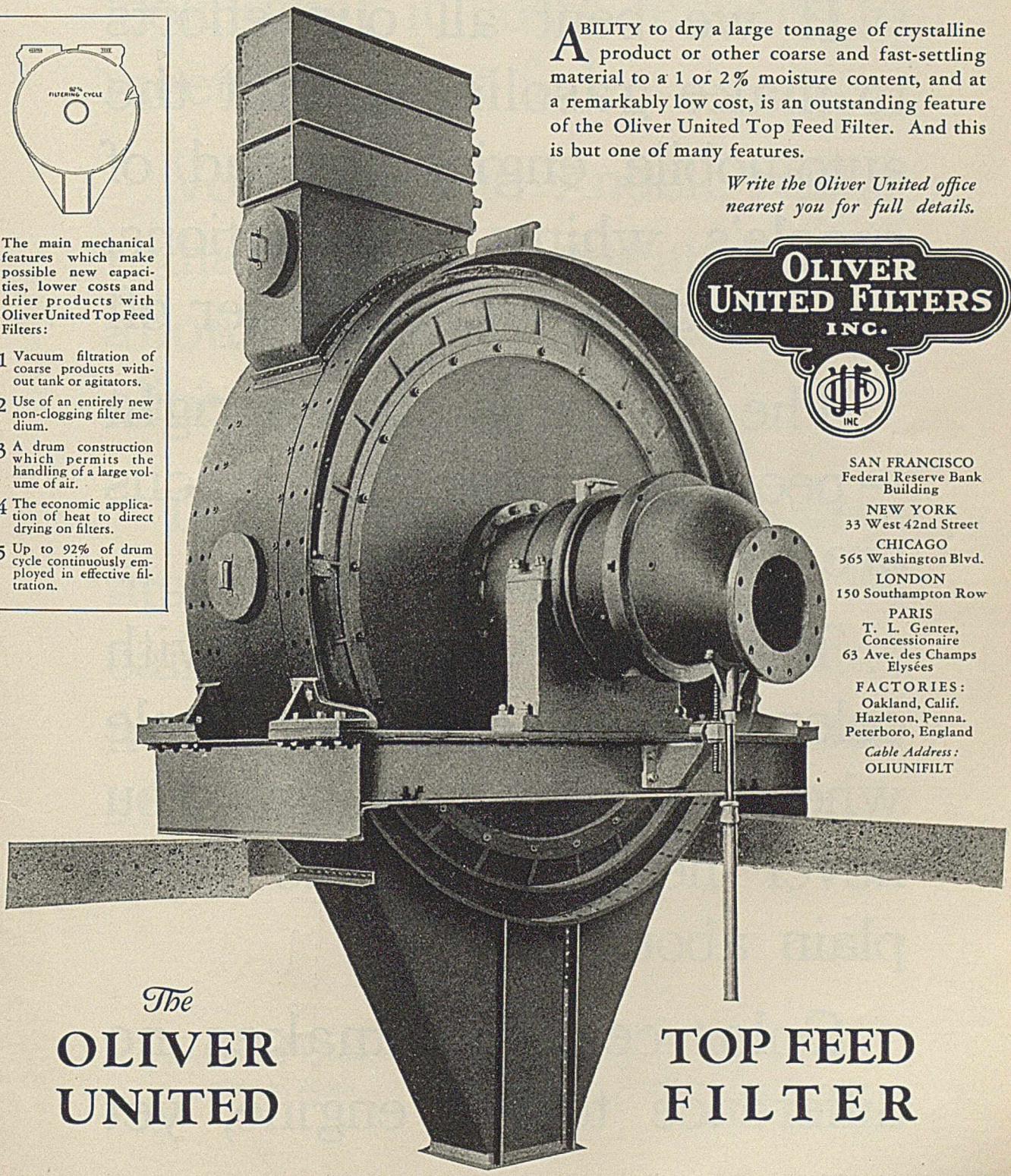

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