Industrial and Engineering Chemistry

Vol. 20, No. 3 MARCH 1, 1928

Foreign Cartels and American Industries

THE above was the title of an address delivered by William J. Donovan, Assistant Attorney General, before the conference of the executives of the chemical industry, which met in Washington February 16, in response to an invitation from the Secretary of Commerce extended at the request of the Chemical Advisory Committee to the Department of Commerce. The various features of the cartel movement abroad have been presented to the chemical industry on a number of occasions, and Colonel Donovan simply undertook to indicate the view of the Department of Justice concerning the operation of these combinations, monopolies, and cartels in the field limited by the laws of the United States. We shall quote extensively from his remarks.

In Article I, Section 8, of the Constitution is to be found the power of Congress to regulate commerce from which is derived the right to enact so-called antitrust statutes. The section states that Congress shall have the power "to regulate commerce with foreign nations and among the several states and with the Indian tribes." It was under this authority that the Sherman Act was passed. This is the primary statute regulating the foreign and interstate commerce of this country. Since the passage of the act it has been interpreted as to its purpose, and its scope has been defined by various decisions of the Supreme Court, with the result that there has been evolved a philosophy of the relation that should exist between business and government.

The Supreme Court has pointed out that, whether the existence of competition is wholesome or not, it nevertheless is the settled law of this country that such competition shall exist and that the natural lines of competition be left undisturbed, holding that the control of prices through combinations tends to restrain trade and is an evil thing. The law further recognizes that competition may be so conducted as to become destructive and may generate evils. However, those consolidations which seek only to secure advantages that come through economical management and do not aim to dominate the particular industry are recognized as proper and even necessary. The American policy, then, is based upon the principle of competition, which includes ideas of equal opportunity, maintenance of individual initiative, freedom from government regulation, and absence of power to control prices or allocate territory or customers. This is in direct conflict with European theories.

As Colonel Donovan pointed out, amendments to American laws permitting combinations in industry resulting in monopoly would lead to more government in business, for the people of this country would not permit monopolistic power to go unregulated. He argued that there is greater opportunity for more effective and unhampered development of our industry under existing laws.

We can find no fault with a foreign government which chooses to evolve a trade policy quite the opposite of our own, and we cannot deny such a monopoly the right to do business here. When, however, a foreign monopoly comes into the jurisdiction of our courts and attempts to perform those acts which are forbidden under our laws and by collusion with our citizens enters into agreements for the restraint of trade and the enhancement of prices, then such acts and such agreements are just as illegal and just as much subject to our laws as they would be if the corporation and individuals involved were themselves creatures of our own Government. The basis for this point of view is found in the antitrust provisions of the Wilson Tariff Act, enacted in 1894, although its provisions were never invoked until two years ago and were not passed upon and interpreted by the Supreme Court until 1927. The act deals with the importation of goods and provides that every contract between two or more persons or corporations, either of whom is engaged in importing any article from a foreign country, is illegal and void if it is intended to operate in restraint of trade or designed to increase the market prices in the United States of any article imported or intended to be imported. The Wilson Act, therefore, as interpreted by the Supreme Court, constitutes a measure of protection against the illegal activities of foreign trusts in our jurisdiction.

Another piece of constructive legislation is the Webb Export Trade Act, commonly known as the Webb-Pomerene Act. This legalizes combinations of American industries for export business, recognizing that in regions where antitrust laws are not in force, American business should be able to compete on a favorable basis with foreign cartels and monopolies. The act specifies that antitrust laws shall not be construed to prohibit associations formed for the sole purpose of engaging in export trade, provided they do not enter into any agreements which artificially enhance or depress prices or substantially lessen competition within the United States. The report of the Federal Trade Commission shows that fifty-five associations filed reports during the past fiscal year indicating the activity of our export associations in shipping raw materials and manufactured goods, the total exports so handled during 1926 amounting to more than $200,000,000. Through such associations member companies have been able to reduce their selling costs, effect standardization, improve the quality of their products, stabilize prices, eliminate cut-throat competition, and present a solid front to European competition.

Now comes the third piece of constructive legislation. A bill has been introduced in the form of an amendment to the Webb-Pomerene Act, expressly sanctioning the collective purchasing of raw materials in foreign markets. It seems quite clear that Congress contemplates the enactment of constructive legislation as needed, not only to protect American industry from unwarranted attacks from abroad, but to enable American industry to have a fair opportunity of meeting foreign competition in neutral markets. But, as Colonel Donovan pointed out, the statutes and all the aid that governmental departments may give are of no avail unless there is an intelligent conduct of business itself.

Coöperation in industry is not forbidden, and it has been shown by the Supreme Court that the Sherman law did not intend to place a penalty upon intelligence in business.

As we looked about the council chamber of the Chamber of Commerce of the United States, kindly loaned for the occasion, we saw representatives of many chemical groups working in various chemical trade associations, of which the industry supports some forty. Why cannot a greater, all-inclusive organization be formed in which there would be adequate and complete representation of the American chemical industry in its many branches and specialties? On two occasions the executives of the industry have met in large numbers, have found such contacts good, and have considered the time most profitably spent. If these conferences could lead to the creation of such an association, permanent good to the industry would result in a degree to dwarf what has thus far been achieved, and afford easy channels for still further coöperation between the Department of Commerce and industry which, in itself, would be invaluable. Such a representative trade association could foster the coöperation which Colonel Donovan described as essential, and make the most of the assistance which a helpful Government offers a legitimate industry.

A Man Passes

THE wide circle of friends and acquaintances made by Robert W. Neff during a life of intense activity was shocked at the news of his passing. There will be some chemists who did not know Neff, for he was not a contributor to the technical press. But men of his type are necessary leaders in the success of any organization, and particularly of the AMERICAN CHEMICAL SOCIETY. Neff wrote no learned scientific articles and he seldom took part in scientific discussions, though he was always an attendant upon sectional, regional, and national meetings. He was not given to much speaking, but to much doing. He was never too busy to find the time necessary for some service to the SOCIETY and to the public. He was a member of the "Old Guard." He could be counted upon as a "wheel horse," and perhaps some people would say he belonged to the "clique"—a term often applied by those unwilling to work to those who carry the burdens incident to any successful enterprise. Neff gave generously not only of his time but of his means and of his seasoned advice, made valuable by extensive experience in the business world.

Neff had been below par physically for a long time, but only his close friends knew it, and how he really felt was well masked beneath his cheery greeting and pleasant smile. He was not the complaining sort. He was a true Rotarian—was "Bobbie" Neff—always practicing the teaching of "Service above Self," and turned his hand to many a kind deed of philanthropy, of which others knew little.

There are always too few men of Neff's stamp, and while he was successful in his chosen specialty of finishes for cotton goods and in many instances had found and eliminated difficulties which had eluded men of broader technical training, he was not the extreme specialist which, to some, represents the standard by which members of a scientific organization should be judged. Not only will the Northeastern Section miss Neff sadly in the conduct of its work, but the whole SOCIETY will be the loser. He pioneered in constructive publicity for chemistry and was invaluable in securing for the A. C. S. News Service the coöperation of important New England papers. He actively furthered the Prize Essay Contest, and often came to the assistance of the committee in difficult situations and when monumental tasks faced it.

The work which men like Neff can do is so important that we take this opportunity to present his example, particularly to our younger members. While we all recognize the inestimable value of those engaged in more fundamental work, we also know that our science and the projects of the SOCIETY would be furthered if we could but enjoy the services of more men of the type of Robert W. Neff.

Institute Conferences

IF a vote were to be taken on the most profitable single feature of the Institute of Chemistry of the SOCIETY as conducted in 1927, it would undoubtedly show the daily general conferences to be an overwhelming favorite. Guided by this experience, the committee has given particular attention to conferences in planning the work for 1928. While the entire program of the Institute is to be kept as flexible as possible, that it may be easily adjusted to meet needs that may arise, certain topics have been selected as of greatest interest for general conference discussion.

Since some fields are too broad to permit a really detailed discussion, the time will be devoted to establishing broad principles. In the general conference on alloys the aim will be to discuss facts quite generally applicable to that type of metals. Seven conferences will be devoted to a discussion of agricultural products as raw materials in the chemical industry or, stated differently, uses other than for food of agricultural products. Beginning with a survey of the problem from the point of view of agriculture, chemistry, and engineering, these conferences will proceed to a discussion of fermentation processes applied to corn, corn products of other types, possible use of corn stover, and thence to the industrial uses of small grains. Special emphasis will be placed upon sources of cellulose, from which one should obtain a clear picture of the future place of wood, cotton, and annual stalks with reference to cellulose supplies. The new competition in agriculture will bring out pertinent facts as to the extent to which tropical oils in their various forms are competing with animal fats—to mention a single example. Finally, a conference will be devoted to research as applied to these industrial products, extended uses of which in many cases await a greater and more fundamental knowledge.

Antioxidants, thermionic emission, and irradiation as applied to catalysis, vitreous enamels, modern thermodynamics, and the use of energy at high potential, the latest word on the new fertilizers, two selected topics on health and chemistry, the sciences in national defense, hydrogenation, hazards attributable to new materials, leather, chemistry and physics as related to life processes, carbohydrates, a topic in petroleum, the packing industry, paint and protective coatings, resins, chemistry of sanitation, and a conference on literature and library work in chemistry are the other topics.

When it is remembered that the subject matter is to be handled by specialists, that groups identified with such work will be present to lead the discussion, and that all in attendance will be given an opportunity both to ask and to answer inquiries, it is evident that there is justification for the popularity of these general conferences.

It is the concentration upon a single topic with assurance of ample time for thorough discussion that makes these daily sessions, for which two hours and forty minutes are available, of such great value. They have demonstrated their utility in the Institute of Chemistry and their form can be recommended for more general application in arranging scientific meetings. In due course through the News Edition we shall announce those who are to conduct the conferences

and lead the discussion. It is one of the high points in the chemistry of the year. You will want to note future announcements.

Industries, Attention

THE annual report for 1927 of E. I. du Pont de Nemours & Company, carries much that is of interest, but what arrests our attention are the paragraphs relative to fundamental chemical research. No one can question the success of the du Pont Company. Its affairs have been so conducted throughout the years since its establishment in 1802, that it has properly escaped much of the criticism levied by a poorly led and at times unthinking public against business organizations. Of course there are other factors which contribute to the advance of such an organization, but surely its attitude toward fundamental chemical research is one of the outstanding reasons for its success. We call the attention of industry generally to the following paragraphs quoted from page 15 of the report cited:

> The diversified chemical industries which constitute your company's business are basically closely related. This relationship consists of similarity or identity of raw materials and processes of manufacture.
>
> The more far-reaching changes and improvements in chemical processes and products go back to the fundamental facts in chemical science and have usually come about through the application of fundamental research to the problems of chemical industry.
>
> In addition to a vast amount of applied research, your company has always carried on a certain amount of fundamental chemical investigation. Since it is so essential to the development of the art, it has recently been decided to place increased emphasis on fundamental research. Accordingly, additional equipment essential to this type of investigation is being provided from time to time as the need arises, and a personnel especially adapted to carrying on investigations of this nature, and selected with particular reference thereto, has under investigation definite problems in the category of fundamental research.
>
> The proper conduct of fundamental research of this nature furnishes added assurance of consistent progress, making available to our applied research information of prime importance not otherwise obtainable.

We recommend the repetition of these paragraphs by the directors of industry to their stockholders and the widespread adoption of the principles enunciated.

An Attainable Objective

THE Petroleum Division of the SOCIETY, now numbering three hundred and thirty-two, has decided that its membership should include at least two members for each of the three hundred and twenty-eight petroleum refineries now in operation. It has undertaken to spread the gospel that to keep abreast of the developments in petroleum industry the technical men must participate in the activities of the Division, use its facilities for furthering acquaintanceship, and benefit directly by participation in programs and by following the discussions presented at the meetings of the Division.

In a recent letter to Division members was included a membership and refinery survey, showing the number of plants in the various states, the daily crude capacity of these refineries where plants are operating, the number of members that should be obtained, and the number of members now in these refineries. Five states and the District of Columbia are without refineries yet have members in the Division, while four foreign countries are represented in Division membership. There are but twelve states where no members of the Petroleum Division are to be found.

We congratulate the Petroleum Division upon its efforts and the vision of its officials which, with the backing of the membership, will enable them to achieve even greater things for American chemistry as applied to our great petroleum industry.

St. Louis Expects You

OF COURSE for months you have carried in your engagement book the item of the seventy-fifth meeting of the SOCIETY, St. Louis, April 16 to 19. You have now noted the preliminary program which appeared in the February 10 News Edition, and if you are at all forehanded have long since made your hotel reservation. You have noted particulars with respect to reduced railroad rates, and if you intend to present a paper, you have by now notified the secretary of your division. See to it that without delay you forward to him at least an abstract and, better yet, the complete paper itself, to aid in the advance publicity for the meeting and to facilitate the publication work of the SOCIETY.

The increase in the number of members attending the semiannual meetings indicates the growing conviction that one cannot afford to be absent. A nucleus of a few hundred may always be counted upon, and it is gratifying to find how eager those in the vicinity of a meeting place are to take advantage of the opportunity offered. The older members need no special urging to be present at these meetings, and even the younger have rapidly come to evaluate properly the advantages afforded. Fortunately, the number of those who feel that they can work on successfully without intimate contact with their profession is decreasing to the vanishing point. One might almost say that increase in attendance, publication, and chemical activity are proportional.

St. Louis expects you. Of course you will not disappoint our hosts.

Failure Despite Research

THAT a little knowledge is a dangerous thing is another way of saying that failures in business begun upon what seemed to be an adequate research foundation occasionally occur.

We have in mind a firm which began production just as soon as enough research had been completed to indicate one method of manufacturing its commodity. This concern had a full six years' start in its field, but when it came into production attention was centered upon problems incident thereto and upon sales, advertising, business policy, and the like. Research work was not continued on an adequate basis. Other methods of making its sole item of commerce were not perfected or even seriously investigated. Its business grew, but more slowly than would have been anticipated.

Six years later another group began to put into commercial production material developed over the entire period of time. It had found other ways of making the product. It had concentrated upon the various scientific phases of a complex problem. It had been undiverted from its principal ambition to know as much as possible about the subject before the plant was erected. Today this group is the leader and the first concern, unable to compete with its younger rival, has gone into a different type of business.

The moral is plain. Resist the temptation to go into commercial production before you are really ready. Under no circumstances undertake a new project until you are prepared to continue active research which will make it impossible, or at least extremely difficult, for another group to be enough better trained to displace you in your chosen business.

Heat Transfer for Oils and Water in Pipes[1]

F. H. Morris and Walter G. Whitman

STANDARD OIL COMPANY (INDIANA), WHITING, IND.

Film coefficients of heat transfer have been determined for three petroleum oils and for water flowing through the tube of a horizontal double-pipe heat exchanger. The experiments cover both heating with steam and cooling with water under similar conditions.

The flow was in the turbulent or semiturbulent regimes. Linear velocity varied from 1 to 20 feet per second, viscosity ran from 0.5 to 55 centipoises, and the heat-transfer coefficients on oil covered a range from 10 to 700 B. t. u. per hour per square foot per degree Fahrenheit.

The data for oils and water can be correlated on the basis of Nusselt's theoretical equation, which states that the heat-transfer coefficient is a function of the velocity, viscosity, density, thermal conductivity, specific heat, and pipe diameter, arranged in dimensionless groups. The quantitative conclusions are expressed graphically, since no simple equation has been found which will apply over the whole experimental range.

Physical properties of the liquid are taken at the temperature of the main body of the liquid rather than at the customary film temperature. On this basis the cooling coefficients fall about 25 per cent lower than those for heating.

The results from heating water with steam agree reasonably with those published by other investigators. Data on coefficients for heating and cooling oil are not available for comparison.

ALTHOUGH the heating and cooling of liquids in pipes are fundamental to many industrial operations, scarcely any investigations of the heat-transfer rates have been published which consider liquids other than water. Most of the data on the heating of water have been correlated by McAdams and Frost[2] in the form of an equation which adequately handles this important case. The chemical engineer, however, deals with many other liquids and is interested in cooling as well as heating them. In the petroleum industry, especially, the rational design of equipment such as pipe stills, heat exchangers, and coolers demands a reliable method for predicting heat-transfer coefficients for oil flowing in pipes.

The work described in this paper was undertaken to supply a basis for a general determination of such coefficients. In order to make sure that the experimental method and apparatus gave results in accord with those of others, a few runs were made heating water, but the greater part of the work was with petroleum products having a wide range of viscosities and in half of the experiments the oils were cooled.

Theoretical Considerations

The modern treatment of heat flow through a series of resistances by evaluating each resistance independently of the others is now so generally accepted that its discussion here appears unnecessary. Following this principle, the problem of heat transfer with liquids in pipes devolves into a study of the coefficient between the liquid and the pipe itself, disregarding the particular heating or cooling phenomena which occur on the other side of the pipe. Coefficients of this sort are often designated as "film coefficients," a term derived from the convenient concept of fluid films at the boundaries of a fluid.

The variables which might be expected to govern the film coefficient for liquids flowing in turbulent motion in pipes are the diameter of the pipe, the density, specific heat, viscosity, and thermal conductivity of the liquid, and the velocity of flow. In a given piece of experimental apparatus the first is fixed. Furthermore, the four physical properties of the fluid are not mutually independent but are determined by the nature of the particular liquid and by its temperature.

The problem of so generalizing data taken on one heat exchanger and with a limited number of liquids that they can be used to predict coefficients for wholly different conditions is best handled with the aid of dimensional analysis. By this principle, which has been applied to the closely related problem of fluid friction with notable success, the independent and dependent variables assumed to be important to the problem are gathered into dimensionless groups. The analysis shows that a particular variable affects the others only as it affects the group or groups in which it occurs.

Dimensional analysis has two limitations. It throws no light on the validity of the assumptions as to which variables are important to the problem. Furthermore, it gives no hint of the functional relationship between the various dimensionless groups. Its great power lies in the inferences it allows regarding the effect of variables which are constant in a given set of experiments. In this particular case the diameter of the pipe, for instance, is the same throughout and the density of the liquids is so nearly constant that no independent determination of its effect is possible, yet if the analysis is properly made the effect of both can be predicted from an experimental determination of the group functions. Another advantage of the analysis is that the problem is simplified to a determination of a functional relationship between three variables instead of seven.

The application of the analysis, first made by Nusselt,[3] yields the equation

$$\frac{hD}{k} = \phi\left(\frac{Du\rho}{z}\right) \cdot \psi\left(\frac{cz}{k}\right)^{*}$$

* For the nomenclature used throughout article see end of paper.

It should again be emphasized that the functions ϕ and ψ can be determined only by experiment, since the analysis places no limit whatever on their form.

Another dimensionless group sometimes introduced into the equation is the ratio of the clear length of the pipe to its diameter. There is no question that excessive turbulence near a sudden contraction in cross section or an elbow, for instance, causes a local increase in coefficient. Hence, a higher value of the average coefficient would be obtained in a short pipe than in a long one. In the experiments here reported only one pipe was used. Since, therefore, no inde-

[1] Presented before the Division of Petroleum Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

[2] *Refrigerating Eng.*, **10**, 323 (1924).

[3] Mitt. über Forschungsarbeiten, Heft 80–96 (1910); *Z. Ver. deut. Ing.*, **53**, 1750, 1808 (1909).

pendent evaluation of end effects could be made, end effects were avoided as far as possible by extending the pipe twenty diameters on either side of the heating surface with unchanged cross section—i. e., by introducing two so-called "calming" sections. For this reason uniform velocity conditions may be expected throughout the portion of the tube where heat is being transferred and the calculated coefficients may be considered as applying to pipes of infinite length.

McAdams and Frost have shown that for water being heated the function $\psi(cz/k)$ can be dropped without great error and $\phi(Du\rho/z)$ can be expressed as constant $\times$ $(Du\rho/z)^{0.80}$. However, where oils of widely varying viscosity are considered, and particularly when a correlation is attempted between the data on oil and on water, it is quite conceivable that neither of these simplifications may be permissible.

An immediate question that arises in the application of the theoretical equation to experimental data concerns the selection of the values of the physical properties to be used in the correlation. Previous experimenters have in general taken the properties at the mean film temperature—that is, at the arithmetic mean between the average temperature of the liquid and that of the inner pipe surface. This selection is admittedly arbitrary, however, and the published data are inadequate to support it against numerous other assumptions which might be advanced. The theoretical considerations involved appear to be too complicated to permit a rigorous solution of the problem which is also simple enough for engineering use. Hence, a practical approximation based on experimental data is probably the best compromise. Evidence will be given later to show that the use of the properties of the main body of the liquid affords a better correlation of data for heating and cooling and gives a method of calculation more easily applied to design problems. Another advantage accrues from this procedure in that the type of flow, laminar or turbulent, probably depends on the properties of the body of the liquid and there is therefore less uncertainty in the applicability of the data in and near the critical range.

Apparatus and Method

The heat exchanger used for the determination of coefficients is shown diagrammatically in Figure 1. The tube through which the liquid under investigation flowed was a standard $^1/_2$-inch steel pipe with internal and external diameters of 0.62 and 0.84 inch. The jacket was of $1^1/_2$-inch standard pipe, having an actual inside diameter of 1.61 inches. The tube extended a foot on either side of the heating surface with unchanged cross section. Turbulence chambers, *A*, were inserted in order to obtain a thorough mixing of the stream leaving the exchanger, so that the temperature read would be a true average for the stream. It was thought that the changes in direction and velocity of the heating or cooling medium leaving the jacket would insure sufficient mixing to accomplish the same purpose for the outside fluid. The exchanger was thoroughly lagged with asbestos pipe-covering extending past all thermocouples.

All temperatures were measured with No. 24 gage iron-constantan thermocouples calibrated in place. A Leeds and Northrup Type K potentiometer was used, giving a least reading of one microvolt which corresponds to about 0.03° F. Seven temperatures were read. In addition to the couples in both streams entering and leaving, three couples were peened into slots in the tube wall with lead scraped flush with the outer surface of the tube. Since they were short-circuited by the lead, they were assumed to give the temperature of the outer surface of the tube. To carry the wires through the wall of the outer jacket three $1^1/_2$-inch by $^3/_4$-inch crosses were inserted in the $1^1/_2$-inch pipe opposite the couples. Each wire passed through an insulated stuffing box screwed into one of the $^3/_4$-inch branches which lay horizontally. This construction permitted the use of fairly high pressures in the annular space when desired. The actual box construction is not shown in Figure 1, but the location of the thermocouples is given.

The exchanger was connected up for continuous recycling of the liquid under investigation. For the heating runs it was pumped from a small tank through a calibrated orifice to the heat exchanger and back to the tank through a water-cooled coil. In cooling runs the liquid was heated to the desired temperature in a gas-fired pipe still before passing to the exchanger. The heating or cooling medium flowed countercurrently through the jacket.

No readings were taken until the system had come to equilibrium as shown by the constancy of the temperature of the liquid entering the exchanger tube. A run consisted of five sets of readings of temperatures and orifice data, occupying about 5 minutes a set. The time necessary to reach equilibrium for a new run was from half an hour to several hours in some cases.

The heat flowing through the wall of the tube was calculated from the change in temperature of the central stream, its quantity, and its specific heat. Errors from radiation and conduction were thereby reduced to the heat passing through the lagged portion of the tube extending beyond the heating surface, and a few sample calculations showed this to be negligible.

The temperature difference through the wall of the tube was calculated from the heat flow and dimensions of the tube, using 35 B. t. u. per hour per square foot per degree Fahrenheit per foot for the thermal conductivity of the (low-carbon) steel. For oil runs this temperature difference

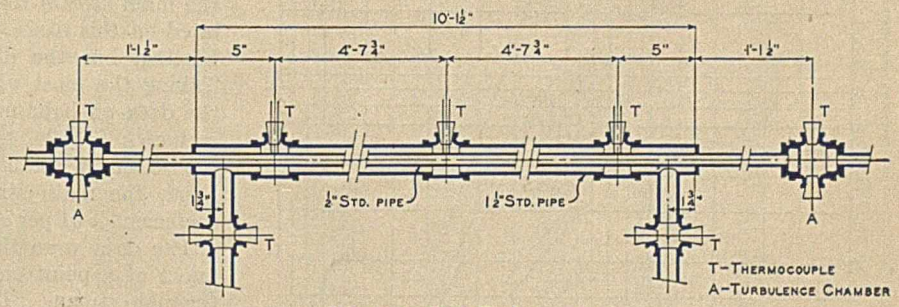


Figure 1—Heat Exchanger

never exceeded 16 per cent of the difference between the temperature of the inner tube surface and that of the body of the liquid.

When, as in most oil runs, the rise or fall in temperature of the central stream was less than 30° F., the average stream temperature was taken as the arithmetic mean of the initial and final readings. When the change was greater the average temperature was obtained by means of a graphical integration assuming the internal film coefficient to vary inversely as the square root of the viscosity. This correction in no case made a change in the calculated coefficient greater than 4 per cent.

In the runs where water was heated by steam the temperature of the inner surface of the pipe was calculated as above. The average temperature of the water was obtained by subtracting from the steam temperature the logarithmic mean

of the temperature differences between water and steam at the entrance and exit of the tube.

Knowing the quantity of heat exchanged, the temperatures of the inner pipe wall and of the body of the stream, the film coefficient could be calculated from the equation

$$Q/\Theta = hA\,\Delta t$$

Data

The range of the data is given in Table I.

Table I—Range of Data

	Heating Runs			Cooling Runs		
	High	Low	Ratio	High	Low	Ratio
Linear velocity, u	19.5	0.9	22	16.9	1.1	15
Viscosity, z	55	0.5	110	15.6	0.5	31
Temperature of liquid, ° F.	169	83		512	115	
DV/z	313	5.0	63	365	7.6	48
cz/k	310	1.2	260	94	4.2	22
hD/k	4890	300	16	5590	110	51
h	1560	40	39	700	14	50
Total number of runs		56			62	

Gravities and designations of the oils used in the experiments are shown in Table II.

Table II—Data on Oils

Runs	Oil	°A. P. I.	Sp. Gr., 60°/60° F.
B1–B13	No. 1 gas oil	36.8	0.841
E1–E15	No. 2 gas oil	35.8	0.846
C1–C22, F1–F4, F10–F26	No. 1 straw oil	29.4	0.879
F5–F9	No. 2 straw oil	29.5	0.879
D1–D9, G1–G21	Light motor oil	22.9	0.917

The viscosities of these oils are plotted on Figure 2.

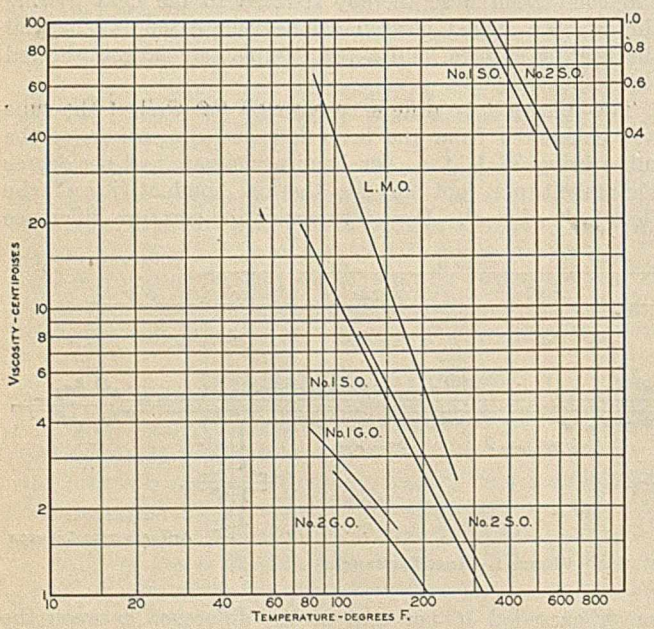


Figure 2

Specific heats were taken from the equation of Fortsch and Whitman.[4]

$$c = \frac{(t + 670)\,(2.10 - \text{sp. gr.})}{2030}$$

where

c = specific heat
t = temperature in ° F.
sp. gr. = specific gravity of the oil at 60° F.

k for oils was taken as 0.078 independent of the temperature. As the data in the literature are meager and contradictory, it was thought best to use a constant value for all cases. That this procedure does not lead to great error is indicated by the agreement, within the experimental error, of data on the three oils with film temperatures from 80° to 370° F.

The values of k for water given by Jakob[5] were used in computing the water runs. His equation, converted to English units, is as follows:

$$k = 0.304\,(1 + 0.00175\,t)$$

where t is the temperature in ° F.

The data from the runs are shown in Table III with important calculated results. These calculations were simplified by the use of plots and, taking into account the accuracy of the data, a precision greater than 3 per cent was not attempted in the calculations.

In this table $V = u\rho$ = average mass velocity of the liquid in the tube. t_1 and t_2 are the temperatures of the liquid entering and leaving. t_p is the external temperature of the tube wall at the center of the heating section. T_1 and T_2 are the temperatures of the heating or cooling medium entering and leaving the exchanger. Q/Θ is the quantity of heat flowing through the tube wall in B. t. u. per hour. Δt is the temperature difference between the *internal* surface of the tube and the average liquid temperature. All temperatures are expressed in degrees Fahrenheit. The meaning of the other symbols is given in the table of nomenclature at the end of the paper.

Correlation of Data

The Nusselt theoretical formulation for analyzing the results having been tentatively accepted, it was first necessary to select the temperature at which the physical properties of the liquid are to be taken. It has been generally assumed in the past that the heat-transfer coefficient is governed by the properties of the liquid at the mean film temperature. If this were true an oil flowing through a given pipe at a given velocity would have the same coefficient whether it were being heated or cooled provided the film temperatures were the same.

When the data were calculated using the film properties, it was found that for given values of DV/z and cz/k, the value of hD/k for cooling runs was more than double that for heating. It was seen that the two sets of data would be brought toward each other if the properties were taken at the main stream temperature; hence all runs were recalculated on this basis. This threw the cooling data below the heating, but the divergence was not so great as before. Taking the most viscous oil, for example, interpolation of the data on light motor oil shows that, when $DV/z = 25$ and $cz/k = 100$, the cooling coefficient is 270 per cent of the heating if the film properties are used. If, on the other hand, the main stream properties are taken, the cooling coefficient is 61 per cent of the heating.

The data were then recalculated, the temperature being taken at a point one-fourth the thickness of the film from the main stream. This gave the best correlation of the data as a whole, but the heating data, which are the more reliable, were not so consistent as when the main stream temperature was used.

The properties of the main stream were adopted for the correlation here presented for the following reasons:

(1) The heating data are most consistent on that basis.
(2) While the cooling coefficients average about 25 per cent below the heating, the agreement in each set is satisfactory for engineering practice.
(3) The use of main stream properties is much easier for the designer, since either of the other methods necessitates a calculation of the pipe temperature by trial and error.
(4) Since the type of flow probably depends on the main stream properties, there is less uncertainty in the application of the data in the critical range.

Heating Runs—The method of correlating the heating data described below consists essentially of successive

[4] *Ind. Eng. Chem.*, **18**, 795 (1926).

[5] *Ann. Physik*, **63**, 537 (1920).

Table III—Data and Calculations

Run	V	t_1	t_2	t_p	T_1	T_2	Q/Θ	Δt	h	$\frac{hD}{k}$	$\frac{DV}{z}$	$\frac{cz}{k}$
					SERIES A—RUNS HEATING WATER WITH STEAM							
A1	58.6	91.6	181.5	198.4	210.9	210.6	39,800	46.4	534	869	81.5	1.17
A2	60.5	92.7	180.3	198.0	210.7	210.2	40,100	46.6	535	870	83.7	1.18
A3	84.3	102.2	175.3	196.5	210.6	210.3	46,600	44.8	646	1050	116	1.18
A4	115	103.1	171.3	194.5	210.4	209.9	59,200	43.8	841	1370	155	1.22
A5	118	103.4	168.2	194.9	210.9	210.5	58,000	46.3	788	1290	157	1.24
A6	145	105.0	165.9	194.0	210.7	210.2	66,700	45.3	927	1520	195	1.25
A7	168	107.2	163.3	192.4	210.7	210.4	71,200	43.8	1020	1670	220	1.26
A8	171	106.7	164.6	191.1	210.5	210.1	74,600	41.6	1140	1870	224	1.25
A9	200	108.5	160.1	190.0	210.8	210.4	78,200	42.2	1160	1910	258	1.27
A10	214	106.3	158.9	188.3	210.4	210.1	85,200	41.2	1320	2180	272	1.28
A11	216	110.1	160.2	190.2	211.0	210.5	81,600	41.6	1210	2000	276	1.29
A12	247	107.6	158.2	186.3	211.2	210.8	94,400	37.7	1560	2570	313	1.30
					SERIES B—RUNS HEATING GAS OIL WITH STEAM							
B1	95.5	77.1	106.9	210.1	211.0	210.9	10,150	115.7	53.6	426	18.4	19.5
B2	117	77.9	109.3	209.0	211.0	210.8	13,150	112.6	71.4	566	22.8	19.3
B3	139	85.6	117.6	208.9	211.0	211.0	16,100	104.0	94.5	751	29.9	17.9
B4	166	89.8	121.9	208.0	211.0	210.9	19,350	98.5	120	954	37.2	17.1
B5	197	91.6	123.3	207.5	211.1	210.9	22,700	96.0	144	1140	46.6	16.8
B6	237	99.1	129.2	207.2	211.2	210.6	26,200	88.5	181	1440	57.6	15.9
B7	285	102.3	131.7	206.9	211.0	210.9	30,900	84.7	223	1770	71.3	15.6
B8	339	106.5	134.3	206.4	211.0	211.0	35,000	80.3	266	2120	87.5	15.1
B9	430	111.5	137.1	205.0	211.0	210.9	41,100	74.2	338	2680	115	14.6
B10	514	113.9	138.2	203.8	210.9	210.7	46,600	70.6	403	3200	140	14.5
B11	605	116.8	139.7	203.0	211.0	210.8	51,900	66.9	474	3760	169	14.1
B12	705	122.2	142.9	202.9	210.6	210.8	54,900	62.3	538	4270	206	13.6
B13	816	124.8	144.1	202.2	211.2	211.3	59,500	59.1	615	4890	242	13.5
					SERIES C—RUNS HEATING STRAW OIL WITH STEAM							
C1	147	77.4	93.7	210.6	211.0	211.1	8,190	123.9	40.4	321	6.08	87
C2	205	77.3	89.1	210.9	211.7	211.0	8,240	126.6	39.7	316	8.00	92.5
C3	210	78.8	90.8	210.2	211.3	211.1	8,650	124.2	42.5	338	8.50	89
C4	261	77.6	89.0	209.2	211.0	210.7	10,200	124.5	50.4	400	10.4	90.5
C5	262	79.0	87.8	210.8	211.6	211.6	7,880	126.3	38.0	302	10.2	92.5
C6	316	78.1	88.8	208.9	211.1	210.8	11,600	123.8	57.3	455	12.4	92
C7	352	90.2	102.6	207.0	211.1	210.9	15,200	108.5	85.5	680	18.6	69
C8	382	100.0	115.4	206.3	210.2	210.3	20,700	95.8	132	1050	25.90	55
C9	385	86.7	99.3	208.0	211.4	211.8	16,800	112.7	91.1	725	19.0	74
C10	441	101.7	117.6	206.0	210.4	210.3	24,800	92.9	163	1300	30.8	53.5
C11	465	100.5	115.7	205.5	211.2	211.2	25,000	94.0	162	1290	31.3	55
C12	491	163.0	175.1	220.1			22,600	47.9	288	2290	82.4	23.9
C13	501	160.5	173.6	220.5	225.3	225.8	24,900	50.0	304	2420	81.9	24.5
C14	506	109.0	124.4	205.7	210.5	210.3	27,800	85.2	199	1580	40.0	47.5
C15	622	112.0	127.3	205.3	210.8	210.6	34,100	81.0	257	2040	51.8	45.5
C16	690	154.9	167.6	217.7			33,100	51.9	389	3090	106	26.0
C17	694	150.9	164.3	217.0			34,900	54.7	389	3090	101	27.1
C18	696	142.3	156.8	216.7			37,500	62.0	369	2930	90.9	30.0
C19	700	132.3	148.1	215.9			40,600	70.2	353	2810	80.4	33.7
C20	739	118.8	133.1	204.7	211.0	210.8	38,200	73.5	317	2520	67.9	41.5
C21	885	122.2	135.9	204.3	211.2	210.8	43,900	69.2	387	3080	85.7	39.5
C22	1030	124.1	137.0	204.4	211.3	211.0	47,900	67.3	434	3450	102	38.5
					SERIES D—RUNS HEATING LIGHT MOTOR OIL WITH STEAM							
D1	444	86.1	91.9	210.3	211.1	211.0	8,590	120.1	43.6	347	5.00	310
D2	519	85.7	92.0	209.7	210.9	210.9	10,900	119.3	55.7	433	5.85	310
D3	649	85.4	90.8	209.5	211.0	210.8	11,800	119.8	60.1	478	7.05	320
D4	766	139.6	148.0	222.2	225.9	225.6	23,000	75.1	187	1490	34.7	84
D5	768	107.7	113.5	223.7	225.8	225.9	15,300	111.0	84.0	667	16.2	171
D6	790	117.2	124.7	221.9	225.5	225.3	20,600	98.1	128	1020	21.7	134
D7	793	124.2	131.7	221.7	225.2	225.1	20,900	90.9	141	1120	25.9	114
D8	801	99.2	105.1	222.7	225.1	225.0	16,100	118.3	83	660	13.4	218
D9	895	88.7	93.5	209.6	211.6	211.6	14,400	116.5	75.5	600	10.8	290
					SERIES E—RUNS COOLING GAS OIL WITH WATER							
E1	82.6	150.3	125.5	66.0	51.3	54.1	7,740	70.8	66.5	529	29.6	11.1
E2	115	138.7	118.7	68.0	51.6	54.7	8,580	59.5	87.8	698	37.7	12.0
E3	164	130.5	113.9	70.0	51.4	55.3	10,200	50.8	122	970	50.4	12.7
E4	234	141.2	124.2	79.2	53.0	58.1	14,800	51.3	175	1390	79.7	11.6
E5	253	210.0	179.8	115.4	68.9	78.1	30,900	75.2	252	2000	144	7.5
E6	316	197.6	173.3	122.9	64.9	75.9	31,800	58.2	332	2640	167	8.0
E7	334	132.3	119.4	82.1	53.6	58.3	16,200	41.5	237	1880	107	12.3
E8	335	191.1	168.4	116.3	64.7	73.8	30,100	59.1	309	2460	170	8.25
E9	413	194.4	173.0	121.6	65.3	75.6	35,400	57.1	379	3020	215	8.1
E10	492	132.5	122.1	89.5	55.7	61.2	19,200	35.1	333	2650	160	12.1
E11	562	200.2	182.4	139.4	69.8	82.3	40,400	46.2	534	4240	311	7.7
E12	587	188.6	171.9	127.7	67.8	79.3	39,100	47.1	507	4030	298	8.25
E13	672	190.0	175.1	140.7	69.7	81.9	40,000	36.3	671	5340	350	8.05
E14	682	191.8	176.4	139.5	70.1	82.7	42,100	38.7	663	5270	356	8.1
E15	739	132.6	124.6	97.2	58.1	64.8	22,100	28.3	477	3790	242	12.0
					SERIES F—RUNS COOLING STRAW OIL WITH WATER							
F1	85.1	149.8	141.8	46.1	38.6	39.9	2,520	99.4	15.5	123	10.7	31.1
F2	123	155.8	142.2	52.4	40.5	42.6	6,180	95.8	39.4	313	16.0	30.0
F3	141	362.3	296.3	139.8	82.8	91.0	42,100	183.8	145	1150	93.0	7.25
F4	143	477.6	385.7	194.8	104.1	116.2	65,600	228.0	183	1450	166	4.55
F5	157	568.1	454.9	208.7	90.4	107.0	95,500	289.8	206	1640	211	4.2
F6	160	486.7	396.6	176.4	84.4	97.5	72,800	255.4	174	1380	160	5.3
F7	161	413.2	342.4	157.4	79.0	88.8	54,000	213.1	155	1230	117	6.85
F8	165	138.9	130.3	52.4	42.7	43.7	5,190	81.5	38.8	308	15.5	40.9
F9	165	201.3	180.1	69.9	46.5	49.5	13,700	118.9	70.4	559	31.1	21.8
F10	165	317.8	270.0	116.9	66.9	73.0	34,600	172.3	123	978	73.5	10.3
F11	172	163.7	148.2	60.2	43.2	46.0	10,000	94.4	64.6	514	24.5	27.7
F12	252	140.5	130.1	62.9	44.5	46.0	9,560	71.1	82.0	651	26.9	36.0
F13	292	142.3	131.5	66.9	45.6	47.3	11,500	68.4	103	819	31.8	35.4
F14	394	133.0	124.6	69.6	46.3	48.5	12,000	57.5	127	1010	38.2	39.4
F15	437	244.9	218.7	141.4	67.1	75.5	46,700	84.1	338	2680	141	13.3
F16	474	130.6	123.1	71.7	46.6	49.1	12,900	53.5	147	1170	44.1	40.9
F17	474	376.1	330.6	232.9	106.9	125.4	100,000	106.9	592	4710	365	6.35
F18	485	181.1	166.5	102.3	57.9	63.2	27,000	67.8	243	1930	86.4	22.6
F19	505	134.9	126.8	75.4	47.0	49.8	14,800	53.5	169	1340	50.5	38.2
F20	556	171.9	159.5	99.8	56.7	61.9	26,200	62.3	257	2040	90.4	24.6
F21	572	137.9	129.6	80.6	49.2	52.2	17,200	50.9	206	1640	59.6	36.6
F22	618	310.8	281.6	217.0	95.5	111.2	79,000	68.5	704	5590	327	8.7
F23	633	244.1	222.8	160.4	74.5	84.7	55,100	65.6	512	4070	206	13.2
F24	679	162.4	152.0	99.3	56.1	61.3	26,400	54.3	296	2360	97.9	27.4
F25	744	196.6	182.7	129.1	63.8	71.1	40,100	55.1	443	3520	158	19.2
F26	761	155.4	146.0	97.6	53.8	59.1	26,700	49.4	328	2590	102	29.4

Table III—Data and Calculations (*Concluded*)

Run	V	t_1	t_2	t_p	T_1	T_2	Q/θ	Δt	h	$\frac{hD}{k}$	$\frac{DV}{z}$	$\frac{cz}{k}$
				SERIES G—RUNS COOLING LIGHT MOTOR OIL WITH WATER								
G1	55.5	242.6	210.1	58.5	43.8	45.0	7,090	166.9	26.0	206	9.30	25.5
G2	95.0	179.5	171.2	45.5			2,920	129.5	13.8	110	7.65	49
G3	96.1	179.0	179.0	46.0			3,100	128.2	14.7	117	7.60	50
G4	101	176.0	167.9	46.5			3,020	125.1	14.7	117	7.64	52
G5	108	199.4	183.9	53.7			6,300	137.1	28.0	222	11.2	39
G6	111	185.4	174.6	48.1			4,490	131.3	20.9	166	9.62	46
G7	111	185.4	175.3	48.4			4,200	131.4	19.5	155	9.69	46
G8	112	185.5	176.4	48.6			3,820	131.9	17.7	141	9.85	45
G9	112	186.5	176.4	49.0			4,280	131.9	19.8	157	9.92	44.5
G10	157	196.6	182.7	56.8			8,250	131.8	38.2	304	15.7	40
G11	159	196.6	182.6	57.1			8,400	131.4	39.0	310	15.9	40
G12	222	138.8	135.9	43.4	39.5	39.6	2,300	93.6	15.0	119	8.8	94
G13	225	195.3	182.9	64.0	47.5	49.8	10,500	123.7	51.9	412	22.5	40
G14	234	187.4	176.1	59.8			9,900	120.7	50.1	398	20.7	44.5
G15	322	200.4	187.6	75.6	51.5	55.0	15,600	116.3	81.8	650	34.4	37.5
G16	323	150.9	145.3	53.9	43.2	44.0	6,490	93.3	42.5	338	16.0	76.5
G17	455	203.5	191.5	89.1	57.0	61.3	20,800	105.6	120	956	51.3	36
G18	485	163.2	156.5	67.4	48.2	50.4	11,900	90.9	80	635	30.0	62.5
G19	616	197.6	186.6	94.8	58.6	63.1	25,700	93.8	167	1330	64.2	38.5
G20	767	193.1	183.4	99.8	60.8	65.9	28,100	84.7	202	1610	75.5	40.5
G21	800	158.3	152.3	77.0	51.6	55.0	17,400	75.9	140	1110	45.5	68

approximations to determine the relationship between the three variables. Starting with a set of runs where one variable is reasonably constant, the function connecting the other two is derived graphically. This tentative relation can then be applied to other data in order to bring out the influence of the first variable. By familiar processes of trial and error a repetition of similar steps leads to successive expressions which are each more accurate and more generally applicable than those preceding.

For the sake of brevity, let the modulus $hD/k = M$, $Du\rho/z$ or $DV/z = N$, and $cz/k = P$. The Nusselt equation then becomes

$$M = \phi(N)\psi(P)$$

Since the equation was derived for turbulent flow conditions, only those runs having N greater than 15 were considered in determining the functions. This value is the mean of several given in the literature as the critical. All plotting was done on logarithmic paper on which functions of the type $y = ax^m$ are straight lines having the slope m.

P is made up of physical properties and varies only with the temperature for a given oil. Therefore, runs were selected from each group having about the same temperature (so that P was constant) and M was plotted against N. The average slope of the lines thus found was about 1.02, showing that M is proportional to $N^{1.02}$.

$M/N^{1.02}$ was then plotted against P for all runs, giving a line with a slope about 0.5. This was tentatively assumed to be the relation between M and P, and $M/P^{0.5}$ was plotted against N for all data.

It was found that the data, including water runs, lined up fairly well on this basis, but the line was not straight. Several forms of equation were tried on the curve, the most successful having the form

$$\frac{M}{P^{0.5}} = AN^3 + BN^2 + CN + D$$

This equation was rearranged and $M/AN^3 + BN^2 + CN + D$ was plotted against P.

The process was repeated until it became cyclic—that is, until $M/\phi(N)$ plotted against P gave the same function for $\psi(P)$ as had been used for finding $\phi(N)$. The final equation was

$$M = (0.000016\ N^3 - 0.017\ N^2 + 10.8\ N - 53)P^{0.37}$$

It must be emphasized that this equation is not suggested for general design purposes. It merely lines up this particular set of data for values above $N = 15$. Below that value and, indeed, above $N = 400$ the equation gives absurd results.

Figure 3 shows a plot of $M/(0.000016\ N^3 - 0.017\ N^2 + 10.8\ N - 53)$ vs. P, for all runs having N greater than 15. It is seen that there is little justification for other than a straight line. It passes through the point (1,1) and has a slope of 0.37.

In Figure 4 $M/P^{0.37}$ is plotted against N for all runs. The runs having N less than 15 are included for convenience. There has been published no satisfactory analysis of heat transfer for liquids in laminar flow. It is known, however, that under isothermal conditions the type of flow depends on N, and it may be assumed that when heat is flowing N will be an important, though perhaps not the sole governing factor. An inspection of the plot shows no sharp break in the trend of the data at the isothermal critical point, indicating that the transfer of heat induces turbulent flow at velocities considerably below the isothermal critical.

About twenty runs were made at very low velocities, but these are not shown on the plot. Below $N = 5$ the scattering of points is so great as to show conclusively that the Nusselt relation is not valid in this region. At $N = 1$ there is a tenfold variation in values of $M/P^{0.37}$. Since no satisfactory correlation of these data has been made, they are omitted from this paper though some weight was given to them in drawing the lower end of the curve shown. It is hoped that at some future time these data can be amplified and correlated for presentation.

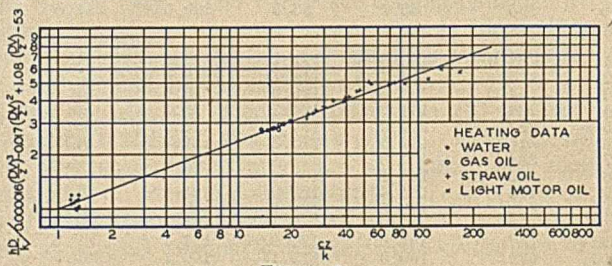


Figure 3

Cooling Runs—Less precision is to be expected in the cooling data than in the heating. The external coefficients for cooling water are smaller, relative to the oil, than the steam coefficients. Therefore, end effects in the external coefficients become more important and though their magnitude at the ends can be estimated from the external pipe temperatures, there is no way of knowing how far the disturbances extend toward the center. It was assumed in the calculations that the disturbances were local and had little effect on the calculated internal coefficients; that is, the pipe temperature at the center was used as an average pipe temperature. An alternate method of giving the end temperature half the weight of the central was tried on typical runs, but the data showed no greater consistency than when the end temperatures were disregarded. The difference between the coefficients calculated by the two methods seldom exceeded 10 per cent and since the first

was thought to give results nearer the truth it was adopted in the computation as recorded.

A plot of the cooling data similar to Figure 3 shows considerable scattering of points. A line may be drawn with a slope anywhere from one-third to one-half with about equal precision. For convenient comparison with the heating data, the exponent of cz/k is taken as 0.37 and $\frac{hD/k}{(cz/k)^{0.37}}$ is shown plotted against DV/z in Figure 5.

In drawing a line through the data, the shape of the heating curve was retained, since the heating data are the more reliable and it seems logical to expect the same general type

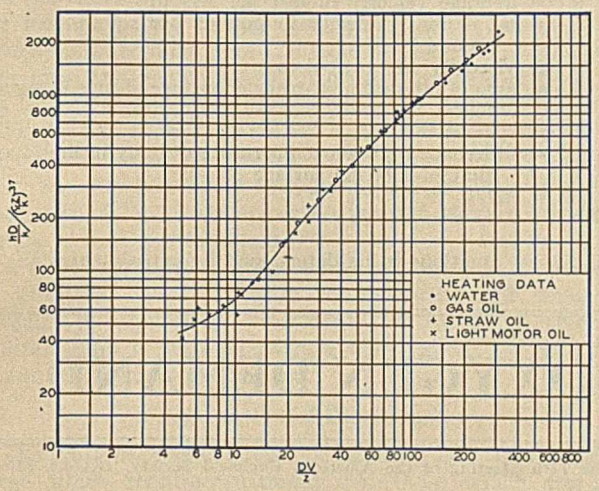


Figure 4

of function for the two cases. This is especially important in the region of low DV/z values where the cooling data considered alone indicate a very rapid falling off in coefficient with decreasing DV/z. A few runs at lower velocities, while widely scattered, indicate that the sloping of the curve toward the horizontal is justified.

The curve as drawn is 25 per cent below the heating line. *Hence in design work only one curve is needed, the calculated* h *for a liquid being cooled having 75 per cent of the value of* h *for a liquid being heated under the same body conditions.*

Comparison with Results of Others

As mentioned before, the short series of runs heating water was made in order to compare the results with those correlated by McAdams and Frost. Since the original data on which their work is based are not at hand, the comparison cannot be made using the method employed in this paper. This makes it necessary to adopt their method, although it is thought to be less precise than the more general one adaptable to both water and oils.

The principal points of divergence between the methods are these: (1) McAdams and Frost neglect any variation in cz/k, since they dealt only with water; (2) they use the properties of the film rather than those of the main stream; (3) they take a constant value of 0.329 for the thermal conductivity of water; and (4) they employ the arithmetic mean temperature difference in calculating h. The water data of series A were recalculated using their method throughout. $hD/0.329$ was plotted against DV/z_f, giving a line with the equation

$$\frac{hD}{0.329} = 18.2\left(\frac{DV}{z_f}\right)^{0.83}$$

The equation given by McAdams and Frost is

$$\frac{hD}{0.329} = 15.4\left(1 + \frac{50}{r}\right)\left(\frac{DV}{z_f}\right)^{0.80}$$

where r is the ratio of length of pipe to diameter.

It is evident from inspection of these equations that the water data of series A agrees with theirs in expressing the effect of DV/z_f as practically an 0.8-power function. The comparison of actual coefficients at equal values of DV/z_f is not so simple, however, owing to the uncertainty introduced by their end correction term.

At $DV/z_f = 100$ the coefficient h in our data is 442. If the "length" of the tube is taken as the length of the heating surface (as seems indicated by their paper), McAdams and Frost's equation predicts a coefficient of 408 for our tube when $DV/z_f = 100$. The observed value is only 9 per cent higher, and this should be regarded as an excellent check.

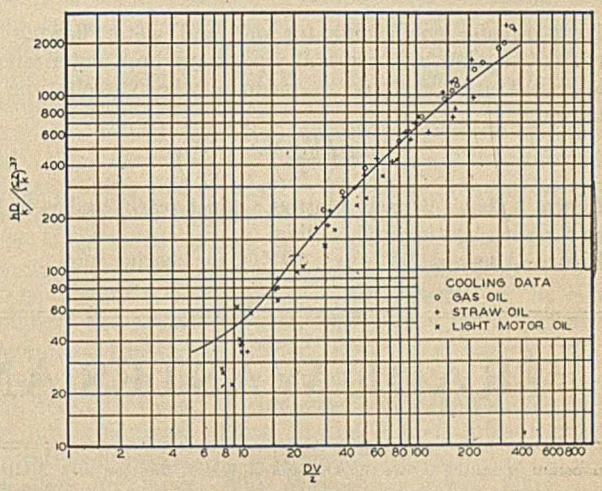


Figure 5

If, however, our tube is considered to be free from end effects —i. e., of infinite length—owing to its extension well beyond the heated surface, their equation would predict that $h = 325$.

Since experiments on one tube give no light on the subject of end effects and since the tube here used was particularly designed to avoid them as far as possible, it seems preferable to offer the coefficients here obtained as applying to pipes of infinite length. The designer of equipment can then apply such corrections for end effects as he deems advisable.

Use of Data

For use in design Figure 3 can be considered as a plot of $\psi(cz/k)$ vs. (cz/k) and Figures 4 and 5 as plots of $\phi(DV/z)$ vs. (DV/z). The process of estimating h for a given set of conditions will be as follows:

Calculate $\frac{cz}{k}$ and $\frac{DV}{z}$. Read $\psi\left(\frac{cz}{k}\right)$ and $\phi\left(\frac{DV}{z}\right)$ from the plots. Then $\frac{hD}{k} = \phi\left(\frac{DV}{z}\right) \cdot \psi\left(\frac{cz}{k}\right)$ and h is readily found.

For instance, suppose a crude oil is being heated in a long 3-inch pipe. The oil is at 150° F., and at that temperature its density is 50 pounds per cubic foot, its viscosity 1.5 centipoises, and its specific heat 0.51. It is flowing with an average linear velocity of 2 feet per second. Then

$$\frac{DV}{z} = \frac{Du\rho}{z} = \frac{3.07 \times 2 \times 50}{1.5} = 205$$

$$\frac{cz}{k} = \frac{0.51 \times 1.5}{0.078} = 9.8$$

From Figure 4, $\phi\left(\frac{DV}{z}\right) = 1600$

From Figure 3, $\psi\left(\frac{cz}{k}\right) = 2.3$

$$\frac{hD}{k} = \phi\left(\frac{DV}{z}\right)\psi\left(\frac{cz}{k}\right) = 3700$$

$$h = \frac{3700 \times 0.078}{3.07} = 94$$

It must again be emphasized that this is an instantaneous coefficient. If the oil changes greatly in temperature flowing through a pipe, it is not permissible to take its average temperature and from it calculate an average coefficient.

In designing a piece of apparatus in which a liquid changes enough in temperature to have a great effect on its viscosity, it is suggested that the pipe be broken up into sections in which the viscosity does not change more than, say, threefold. An alternate and more precise method would be to integrate graphically an equation obtained from a heat balance on a differential length of pipe.

Conclusion

Heat-transfer coefficients for oils and water flowing in turbulent motion in horizontal pipes have been determined. The results are correlated by means of the Nusselt type of equation.

$$\frac{hD}{k} = \phi\left(\frac{DV}{z}\right) \cdot \psi\left(\frac{cz}{k}\right)$$

Figure 3 shows $\psi(cz/k)$ plotted against (cz/k) and is to be used for both heating and cooling.

Figure 4 shows $\phi(DV/z)$ vs. (DV/z) for heating runs.

Figure 5 shows $\phi(DV/z)$ vs. (DV/z) for cooling runs. The line drawn gives values of $\phi(DV/z)$, which are 75 per cent of those given by the heating line of Figure 4.

All properties of the liquid are to be taken at the temperature of the main body of the liquid.

Nomenclature

D = diameter of pipe in inches
h = film coefficient of heat transfer in B. t. u. per hour per square foot per degree Fahrenheit
k = thermal conductivity in B. t. u. per hour per square foot per degree Fahrenheit per foot of thickness
Q/Θ = total heat transferred in B. t. u. per hour
ρ = density of liquid in pounds per cubic foot
u = average velocity in feet per second
V = $u\rho$ = mass velocity in pounds per square foot per second
z = viscosity in centipoises
A = area of internal heat-transfer surface of pipe in square feet
c = specific heat
Δt = difference between temperature of body of liquid and that of internal surface of pipe
M = hD/k
N = $Du\rho/z = DV/z$
P = cz/k
ϕ and ψ = functions to be determined by experiment

TRADE WASTES AND OXYGEN DEMAND

Symposium presented before the Division of Water, Sewage, and Sanitation at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927

Chemical Treatment of Trade Waste

IV—Wastes from Organic Ester Synthesis

Foster D. Snell and Cornelia T. Snell

Pratt Institute, Brooklyn, N. Y.

The waste to be treated consists of a calcium sulfate sludge produced in the manufacture of organic esters. This sludge is highly contaminated and strongly acid, varying in acidity with time of discharge. Neutralization with lime followed by vacuum filtration offers the best method of treatment. The use of 240 pounds of lime per thousand gallons of effluent is required. The lime is to be fed as a 20 per cent slurry at a rate to correspond to the flow and the variable acidity of the effluent, necessitating a flexible control of the feeding system.

THE plant whose waste problems are under discussion is located in the Passaic Valley in New Jersey and has in the past used the Passaic River as a natural sewer for its trade waste. This practice is now prohibited by law. A trunk sewer has been constructed into which the plant may deliver all sanitary waste and 10 per cent by volume of its trade waste. The remaining liquid discharges may go to the river, but only in a purified condition such as not to be injurious to fish and plant life. The part of the plant under discussion is so located as to be unable to take advantage of the 10 per cent trade-waste allotment.

Nature of Wastes

Two trade-waste sewers were already in use in this part of the plant, the first concrete and the second an open earthen ditch. At the time of this investigation the former carried a stream of condenser water and the discharge from one set of stills in which organic esters were synthesized. It led to a large receiving basin which remained from a previous method of treatment that had proved impractical. The earthen drain carried the discharge from a second set of ester stills, that from a drowning tank, and wash water from the nitrating department. It led directly to the river. The sanitary waste was handled by a separate system and does not enter into this problem.

The flow of condenser water in the first sewer was fairly constant, about 1.5 cubic feet of practically pure water per minute. The discharge from the stills to this sewer takes place for about 45 minutes during the day, during which a maximum flow of over 11 cubic feet per minute is reached. The stills are then washed with water. The total volume of still discharge and washings was calculated from measurements of flow to be about 4500 gallons per day. While the waste is being drawn off from the stills the sludge is very highly acid with sulfuric and acetic acids, attaining a maximum normality of approximately 2.4. The washings are also acid to a lesser degree. This waste is highly contaminated, is a dark brown, and carries a large amount of solid calcium sulfate. Tarry discharges from ethyl acetate stills occur about once a day. The sediment fails to settle to under 30 per cent on standing overnight. Total solids determined on the effluent neutralized with lime were found to be as great as 300,000 p. p. m. during the period of still discharge, but at other times were relatively very low. In the determination of solids the samples were neutralized with measured volumes of approximately 0.8 N potassium hydroxide and evaporated to dryness at 110° C.

A correction was applied in each case to give the corresponding amount of solid if lime were used for neutralization. The loss on ignition was roughly 10 per cent of the total solids, largely from water of hydration of the calcium sulfate, except at the time of tar discharge. At that time a very high content of organic matter was indicated. The curves (not reproduced here) representing the variability with time of the three factors—acidity, total solids, and loss on ignition—correspond closely in form except at the time of tar discharge.

The rate of flow in the second sewer fluctuates greatly, the data showing a range from less than 2 to about 25 cubic feet per minute, and a variation from 8.5 to 18.5 cubic feet per minute within 5 minutes. About 7000 gallons were estimated as coming from the stills during 1 hour. During this time the acidity of the sludge increases from about 0.2 to 1.7 *N* and then diminishes. The amounts of total solids parallel closely the change in acidity during the period of still discharge, reaching a maximum of about 190,000 p. p. m., but decreasing continuously after the end of the discharge. The change in loss on ignition corresponds very closely to that of total solids.

A wash water from the cleaning of drums is discharged at intervals. As it is little contaminated and small in volume, it requires no treatment. A 300-gallon calcium chloride tank is emptied twice a week, giving an acid discharge which should be treated.

Segregation of Discharges

The various wastes may be divided into two classes, those which require treatment and those which are not objectionable. All those in the first class are to be diverted to the concrete sewer leading to the storage basin; all those in the second, to the earthen sewer leading directly to the river. The wastes which belong in the first class include the discharges and wash water from the two sets of stills and the calcium chloride tank. In the second class are the condenser water originally sent through the concrete sewer, and wash water from the nitrating plant which is neutralized with soda ash in that department.

Neutralization

The mixed waste for treatment amounts to about 11,500 gallons a day. This waste is first to be neutralized with lime, requiring about 2800 pounds per day. This estimate is based on the known charges to the stills and on the known acidity of samples of the waste as determined by titrations with allowance for some excess as lime. The lime is best fed as a 20 per cent slurry introduced at a convenient point into the open concrete sewer. Since it must be supplied within a period of about 2 hours, a storage tank having a capacity for 2000 gallons of slurry with means of keeping the lime in suspension is required.

The method for feeding the lime must be very elastic to allow for rapid change in the rate of flow of the waste and its change in acidity. Equipment for determination of the hydrogen-ion concentration of the waste which would offer a means of automatic control of neutralization has been recommended. Manual control is both clumsy and expensive. The equipment recommended consists of a tungsten electrode with suitable recorder and operation by a solenoid, as a motor-controlled valve is not suitable with lime. It is planned to put the plant in operation with manual control and to install this automatic control later.

Treatment after Neutralization

Precipitation tests with lime and copperas on the neutralized effluent failed to diminish the color of the liquid, even with excessive amounts of the chemicals. Carbon used either before or after filtration showed good results in removal of color from the effluent.

Vacuum filtration was tried and gave a quick separation of a somewhat granular sludge cake. The best hydrogen-ion concentration for filtration is near the phenolphthalein end point, although the degree of alkalinity is not critical.

Practical filtration tests were made with an Oliver filter. The cake-forming solids were 28 per cent, the forming period 20 seconds, the drying period 30 seconds, and the filter cycle 65 seconds. A $^3/_8$-inch cake was formed and discharged with a moisture of 31 per cent. The vacuum maintained on both the form and the dry was 17 inches. As a result of these tests a 12 by 3-foot Oliver continuous filter, drum type, was recommended. This is not of non-corrosive construction as the effluent is alkaline before reaching it. It provides about 15 per cent excess capacity based on operation for an 8-hour day.

As mentioned before, the concrete drain leads to a large tank. This tank is to be utilized for storage of the neutralized effluent, which will be kept in suspension by air agitation from pipes in the bottom of the tank. An overflow to the river is provided in case of emergency. From the tank the waste will be pumped to the vacuum filter.

The filtrate is not suitable to go directly to the river, although the worst features, the high acidity and large amount of suspended matter, have been removed. The filtrate will flow into the earthen drain, be diluted there with about two parts of condenser water, and subsequently run into the river. Tests on the diluted filtrate showed a total color reading in a Lovibond tintometer of 15 units per 50.8-mm. layer. The oxygen consumed, taken as a rough measure of tendency to putrefaction was 6000 p. p. m. Further dilution in the river will quickly reduce these values.

The filter cake will discharge from the filter into an automatic conveyor which carries it to storage or to a waiting truck. The weight of moist solids to be disposed of is about 28,000 pounds per day.

Cost of Treatment

The estimated cost of treatment is based on the use of 2800 pounds of lime per day. At the current market price for lime (June, 1927) this amounts to about $29.50 per day. At a cost of about $500 equipment for automatic control of the process of neutralization can be installed to replace manual operation. This must wait for some further stages in the development of mechanical features of the feeding device.

Discussion

The nature of the effluent to be emptied into the river from the filter is objectionable from the standpoint of color and contamination. Such procedure is recommended however, for the following reasons:

1—The volume of diluted discharge is relatively small, about 35,000 gallons daily.

2—The color and contamination cannot be removed by the usual coagulating agents, copperas and lime or alum and lime.

3—Purification by activated carbon or other means is so expensive as to amount to an unreasonable burden, requiring an entirely separate installation.

4—Treatment as recommended removes the most serious objections, the high acidity and large amount of suspended solids, and constitutes all that can be done at a reasonable cost.

Acknowledgment

The results given in this paper were obtained in coöperation with Gerald W. Knight, consulting sanitary engineer of Passaic, N. J. Publication is by permission of Maas and Waldstein, Inc.

Technic and Significance of the Biochemical Oxygen Demand Determination

F. W. Mohlman, G. P. Edwards, and Gladys Swope

SANITARY DISTRICT OF CHICAGO, CHICAGO, ILL.

DURING the past fifteen years much of the scientific work of the laboratories of the Sanitary District of Chicago has been based on the biochemical oxygen demand determination. The value of such an analytical method was first appreciated by Langdon Pearse, sanitary engineer for the District, as a basis for the study of the unique conditions that obtain at Chicago with regard to disposal of sewage by dilution. The principles of oxygen balance so frequently discussed by Phelps[1] have a particular bearing on the problems encountered at Chicago.

The importance of the B. O. D. determination as a fundamental basis for the past, present, and future oxygen requirements of the District has stimulated continuous research on the technic of the method and interpretation of the results.

METHODS FOR DETERMINING BIOCHEMICAL OXYGEN DEMAND

The B. O. D. determination has been in use in several forms for many years.[2] Three methods of analysis have been in general use:

RELATIVE STABILITY METHOD—This method[3] was used only to a limited extent. It consisted in making dilutions of the sample with water of known oxygen content, adding methylene blue, and incubating until the methylene blue was decolorized. The initial oxygen was multiplied by the dilution factor, then this oxygen value divided by the relative stability, giving the complete demand. This method was very inaccurate owing to toxic effect of the methylene blue, doubt as to whether the relative stability curve was applicable, and impossibility of observing intermediate stages of oxygen demand. The method was included in the 1917 edition of Standard Methods of Water Analysis, but was dropped from the 1920 edition.

NITRATE METHOD—This method[4] was developed in the laboratories of the Sanitary District of Chicago by Arthur Lederer, former chief chemist. A solution of sodium nitrate is added to the undiluted sewage in a 250-cc. bottle, the treated sample is incubated for the desired period, and residual nitrite and nitrate nitrogen are determined. The oxygen equivalent of the residual nitrogen is subtracted from the oxygen equivalent of the nitrate added, on the basis that nitrite nitrogen is equivalent to 1.71 oxygen (2N:30) and nitrate nitrogen to 2.86 oxygen (2N:50). This method has the advantage that samples can be taken and prepared for incubation by inexperienced samplers who are not chemists, a number of individual samples can be composited after incubation, and absorption of oxygen during incubation introduces very little error since the sample is not diluted. These advantages do not warrant the use of the method, however, if the results do not check with the dilution method, as now revised.

DILUTION METHOD[4]—This is now so well known that no extended description of its technic is necessary. The sample is diluted with stored water, the initial dissolved oxygen determined, and after incubation the residual oxygen is determined. A blank of the dilution water is also incubated. The loss in the sample, corrected by the loss in the blank, multiplied by the dilution factor, gives the oxygen demand.

This brief description of the dilution method gives no idea of the many precautions that must be observed in using it, or the many details of technic that are necessary to get accurate and satisfactory results. These details form part of the subject matter of this paper.

[1] *Am. J. Pub. Health*, **3**, 324 (1913).

[2] A complete bibliography of the development of the method has been compiled by E. J. Theriault, of the U. S. Public Health Service, who has been foremost in the United States in research on the dilution method. A monograph including this bibliography may soon appear; consequently this paper will contain little reference to the historical basis for the determination.

[3] Standard Methods for Examination of Water and Sewage, p. 71 (1917).

[4] *Ibid.*, p. 76 (1925).

Nitrate Method

The dilution method was used by Hoover[5] at Columbus in 1911, but mainly as a rough measure of plant operation, with incubation at 37° C. for 1 day. Other investigators attempted to use the English method, with incubation for 5 days at 18° to 20° C., but found it impossible to obtain check results in different dilutions. Lederer[6] compiled the results obtained under his direction by a number of investigators selected from the laboratory section of the American Public Health Association. The conclusions were that the oxygen demand varied with the dilution, and that the discrepancies were so great as to cast doubt on the advisability of the use of the dilution method. Lederer[7] had been working on the nitrate method since 1913, and suggested that it might be preferable to the dilution method.

Lederer concluded that when proper dilutions were used the two methods did not differ greatly, but a study of his results indicates that those by the dilution method were consistently higher than those obtained by the nitrate method. The values obtained by the dilution method were erratic, and he assumed that the variations were due to inaccuracies in the method. The errors were probably due to the use of unsatisfactory dilution water. In 1918 Theriault and Hommon[8] explained the source of difficulty in the dilution method and suggested an improved technic. Since then the dilution method has become far more accurate.

In 1925 this laboratory again compared the two methods. Over a period of 6 months daily samples of raw 39th Street sewage were incubated at 20° C. The results (Table I) show that for 5-day incubations the dilution results were 13 per cent higher than the nitrate ones, and for a 10-day period 28.4 per cent higher. Fifteen-day incubations did not materially increase the nitrate demand. The dilution method results seemed to follow the stability curve, but the nitrate results followed a consistently lower rate of reaction.

Table I—Comparison of Dilution and Nitrate Methods

39th Street Sewage

(Monthly averages, p. p. m. at 20° C.)

1925	Dilution Method 5-Day	Dilution Method 10-Day	Nitrate Method 5-Day	Nitrate Method 10-Day
January	136	185	121	133
February	108	144	99	117
March	127	160	100	121
April	110	145	95	115
June	102	132	92	109
July	99	128	96	102
Average	113	149	100	116

Lederer claimed that for practical purposes the total demand was completely satisfied in 10 days. An experiment was made to determine the effect of the dilution method after a nitrate incubation. When an initial 10-day nitrate incubation was completed, some samples were diluted with aerated water and replaced in the 20° C. room for 10 days. Table II shows that the dilution method added about 28 per cent to the 10-day nitrate demand.

[5] *Eng. News*, **65**, 311 (1911).

[6] *Ind. Eng. Chem.*, **6**, 882 (1914).

[7] *J. Infectious Diseases*, **14**, 482 (1914).

[8] *U. S. Pub. Health Service, Bull.* **97**, 71 (1918).

Table II—10-Day Dilution Demand after an Initial 10-Day Nitrate Demand

39th Street Sewage

Sample	10-Day Demand Nitrate Method	Additional 10-Day Demand Dilution Method	Increase	Total Demand
	P. p. m. at 20° C.		*Per cent*	*P. p. m.*
1	117	16.5	14.1	133
2	75	12.0	16.1	87
3	98	43.2	44.1	141
4	151	40.0	26.5	191
5	88	19.5	22.1	109
6	114	23.6	20.7	138
7	55	16.0	29.1	71
8	61	20.5	33.6	82
9	94	40.0	42.5	134
10	94	34.0	36.1	128
		Average	28.5	

Since our results have indicated that the nitrate method gives low results, and as it is desirable to use dissolved oxygen rather than nitrate, provided accurate results can be obtained, the B. O. D. work in the Sanitary District laboratories for the past five years has been directed toward improvement of the technic of the method and toward a study of the factors that determine the course of the reaction. We now feel that the method is reliable when the proper precautions are observed.

The Dilution Method

The essential equipment required for B. O. D. determinations is (1) cylinders and siphons for making dilutions, (2) bottles and seals, (3) suitable dilution water, and (4) an incubator.

Cylinders and Siphons—The procedure in the Sanitary District laboratories involves diluting in 500-, 1000-, or 2000-cc. graduated cylinders. The diluting water is siphoned into the cylinder until partly full, then the sample is added below the surface from a pipet, and the dilution water is again siphoned to fill to the desired concentration. The diluted sample is then siphoned into the 250-cc. bottles. It is essential that the sample be thoroughly mixed while siphoning, especially with raw sewage. Our practice is to stir the sample with a perforated, cone-shaped copper disk attached to a metal rod, one of the perforations being large enough to allow one end of the siphon to pass through in order that stirring may be continued during transfer of the sample.

Bottles and Seals—For incubation of the samples 250-cc. tincture bottles, with ground-glass stoppers, are used. These bottles must be scrupulously clean, sterilized if possible, or they may be washed in dichromate cleaning solution, then thoroughly rinsed with tap water.

It has been found practically impossible to prevent air bubbles from appearing in the bottles during a 5-day incubation period unless some type of water seal is used. The incubators contain fans for circulation of air and this circulation quickly evaporates any water which seeps around the glass stopper. Small fluctuations in incubator temperature are bound to occur. If water is drawn in instead of air the amount of oxygen introduced is decreased by about 95 per cent.

In our routine work we maintain water seals by means of rubber collars, which are cut in 1.5-inch sections from radiator hose of the proper diameter to fit snugly over the lip of the bottle. After the sample is siphoned into the bottle and the stopper inserted, the collar is filled to the top with the sample. Circulation of air in the incubator may evaporate all this water in less than 5 days; consequently distilled water is added to the seals daily during incubation.

An all-glass seal which is blown from the lip of the bottle in the form of a cup has recently been found quite satisfactory, but it is very expensive.

In one of our laboratories, where approximately the same number of bottles are removed from the incubator each day, no seals are used, but the bottles are inverted in galvanized-iron trays partly filled with water.

Greenfield, Elder, and McMurray[9] used a water bath maintained at a constant temperature, in which the bottles were completely immersed. This is quite satisfactory for special studies, but the capacity is too limited for a large amount of routine work.

Dilution Water—The preparation of satisfactory standard, duplicable dilution water is the most important requirement for accurate B. O. D. determinations. Standard Methods of Water Analysis does not specify what kind of dilution water should be used, except that it must be "free from iron, not containing more than 0.01 p. p. m. of nitrogen as ammonia, nitrite, and nitrate, and carrying between 8.0 and 9.2 p. p. m. dissolved oxygen after 8 to 10 days' storage at 20° C. or at room temperature." Few tap waters could meet these specifications and the inference is that distilled water would be suitable provided it is low in ammonia. Theriault recommends stored tap water, and has found the Cincinnati water, after filtration and chlorination, to be quite satisfactory.

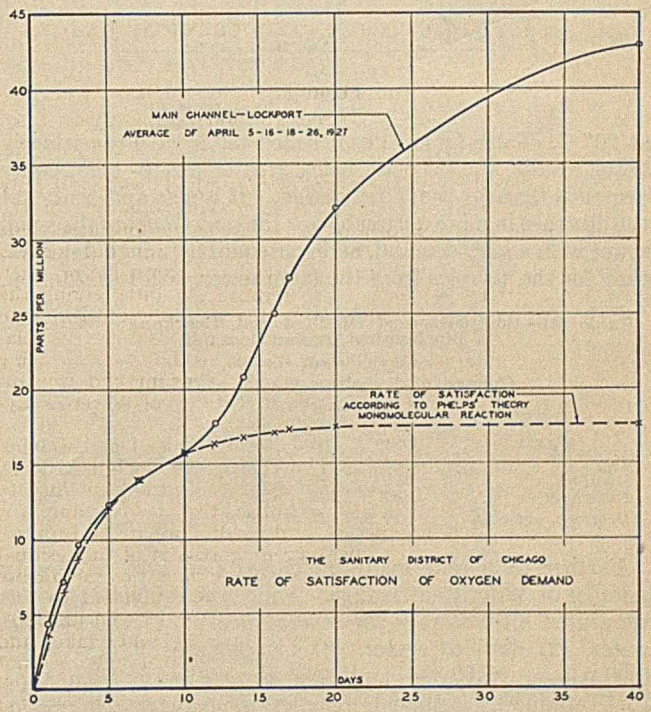


Figure 1

Suitable tap water is not always available, and as no two waters are exactly alike, distilled water would seem to be preferable in the interests of uniformity. We used distilled water several years ago, but suspected the results of being low. We accordingly ran a long series of comparative tests using various waters. There are nine varieties of tap water available in the control and field laboratories of the Sanitary District. We compared some of these with distilled water. We also included a synthetic water of the simplest possible composition, which in theory seemed to obviate the objectionable characteristics of distilled water, but at the same time was easily prepared and similar to natural waters. This water was distilled water containing 500 p. p. m. sodium bicarbonate. The bicarbonate acts as a buffer, and also furnishes the salt content necessary in high dilution. The pH is fairly high (7.8 to 8.2) at equilibrium, but the alkalinity may decrease as carbon dioxide is given off.

[9] *Ind. Eng. Chem.*, **18**, 1276 (1926).

The first tests which confirmed our suspicion that distilled water gives low results were run on corn-products wastes having a 5-day demand between 200 and 300 p. p. m. Distilled and bicarbonate water were used on identical samples for twenty-six tests with 5-, 10-, and 20-day incubations

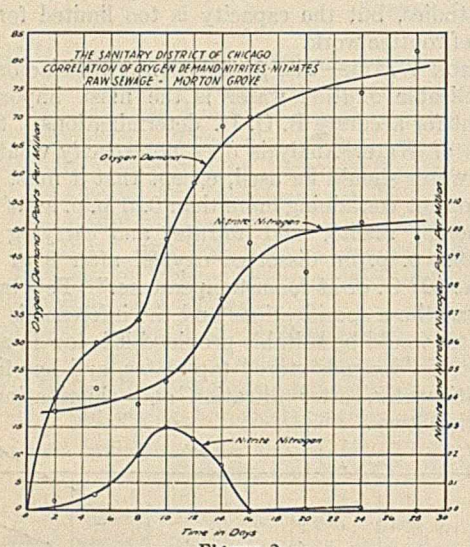


Figure 2

at 20° C. (Table III). The distilled water gave consistently lower results, the decrease being greater for 10- and 20-day demands than for the 5-day period. It is also apparent that the decrease in more noticeable for the samples from the small sewer with a high demand, and consequently a high dulution, than for the samples from the large sewer with less dilution.

Table III—Comparison of Distilled and Bicarbonate Water—Biochemical Oxygen Demand

Corn-Products Wastes

(Average of 26 analyses, p. p. m. at 20° C.)

	Small Sewer			Large Sewer		
Water	5-Day	10-Day	20-Day	5-Day	10-Day	20-Day
Tap	363	598	753	81	123	141
Distilled	299	376	482	71	98	115
Difference	64	222	271	10	25	26
Decrease, per cent	17.6	37.2	36.0	12.4	20.3	18.4

Further tests were made by Hurwitz in 1926 on twenty samples of 39th Street sewage. Four types of diluting water were used after storage for several weeks: (1) Chicago tap water, (2) distilled water, (3) bicarbonate distilled water (500 p. p. m. $NaHCO_3$), and (4) a deep-well water from Argo, Ill. (Table IV). Although there are some anomalous results, the conclusion is quite evident that distilled water gives low results, Chicago tap water high results, and deep-well or bicarbonate water intermediate.

Table IV—Comparison of Four Types of Dilution Water—Biochemical Oxygen Demand

39th Street Sewage

(Average of 20 analyses, p. p. m. at 20° C.)

Water Used	2-Day	5-Day	10-Day	20-Day
Chicago tap water	53.2	64.1	80.5	98.8
Argo well water	39.6	58.3	72.1	81.9
Bicarbonate distilled water	38.3	63.4	71.5	77.1
Distilled water	32.7	56.6	63.3	75.7

In view of these results bicarbonate distilled water has been adopted for all laboratories of the Sanitary District. It may not be the ideal type of water because of the high pH and the lack of variety of cations, but it is an improvement on distilled water or tap waters of widely varying composition.

Greenfield, Elder, and McMurray[9] used a more complex synthetic water containing $CaCl_2$, 165; $MgSO_4.7H_2O$, 285; KCl, 10; and $NaHCO_3$, 336. p. p. m. They obtained even higher results than when using bicarbonate or distilled water.

Gaunt and Abbott[10] have claimed that filtered, chlorinated Shanghai tap water gives low results, even if stored for many days after all residual chlorine has disappeared. Our results with Chicago tap water do not confirm these conclusions, although we did not make direct comparisons of the same water before and after chlorination. We are now carrying on such comparisons. We also expect to make further studies of synthetic waters.

Incubator—Incubation at 20° C. is decidedly preferable to 37° C. Most laboratories, including that at Baltimore, have now adopted the lower temperature, and at Columbus Maguire[11] has made comparisons of 1-day 37° C. results with 5 days at 20° C. Streeter and Theriault[12] have developed an exponential equation for expressing rate of reaction at temperatures other than 20° C. which holds for the first stage, but Theriault claims that the limit of the first stage varies with temperature and has given an equation for computing the total first stage at various temperatures.

Dissolved Oxygen—Dissolved oxygen is determined in the Sanitary District laboratories by the unmodified Winkler method, unless nitrites are present above 0.10 p. p. m., or the sample contains sulfite, sulfide, ferrous iron, or other reducing agents, in which case the Rideal-Stewart modification is used, as given in Standard Methods of Water Analysis. It is not necessary to oxidize organic matter in diluted samples for B. O. D., and it is our belief that the use of oxalate may give low results. The other interfering substances are usually not present in sufficient concentration to warrant the use of the modified method.

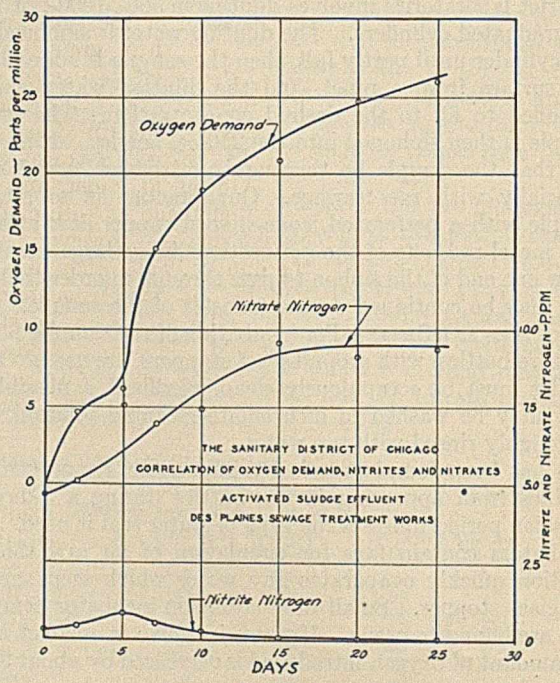


Figure 3

Initial dissolved oxygen in dilutions is always computed from the dissolved oxygen of the sample when taken and from the dissolved oxygen of the diluting water, as this method includes any initial demand or any loss of dissolved oxygen in the sample between the time of collection and dilution. When immediate demands are desired the initial dissolved oxygen is determined. Comparisons are frequently made of calculated and determined initial dissolved oxygen.

[10] *J. Soc. Chem. Ind.*, **45**, 323T (1926).

[11] 18th Annual Report Division of Sewage Disposal, 1925, Columbus, Ohio, *City Bull.* **43** (1925).

[12] *U. S. Pub. Health Service, Pub. Health Reports* **41**, 207 (1926).

INTERPRETATION AND SIGNIFICANCE OF B. O. D. RESULTS

Theory of Two-Stage Curve

Figure 1 shows a typical curve obtained from samples collected in the Drainage Canal of the Sanitary District of Chicago at Lockport, Ill. This curve clearly indicates two stages, the first one being completed in 10 days, and the other continuing from that point. During this first stage it coincides with the one derived from Phelps' theory of monomolecular reaction, but from this point there is

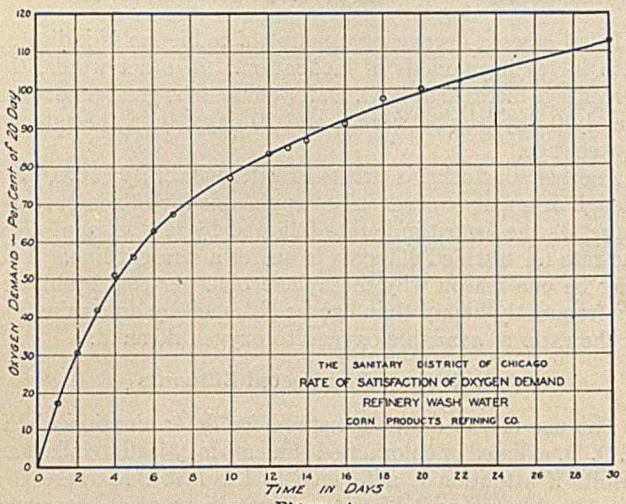


Figure 4

a marked deviation. Phelps' curve follows the logarithmic rate, while the rate of deoxygenation of the canal water accelerates again for 10 days and then gradually diminishes. Theriault[12] has stated that these two stages may represent two stages of oxidation—the first being that of carbonaceous material, and the second nitrification. His theory is in accordance with English theories concerning the biological oxidation of sewage. Greenfield, Elder, and McMurray[9] reported that dilute sewage made up with distilled water uniformly gave single-stage curves. However, on the addition of bicarbonate to the dilution water they obtained a two-stage curve. Further addition of non-carbonate magnesium, calcium, and potassium salts amplified the effect.

Although Theriault and Greenfield, Elder, and McMurray have discussed the second stage as being one of nitrification, they have advanced no data showing the change in nitrate during the reaction. In support of this two-stage theory, Figures 2 and 3 illustrate the relationship between the oxygen demand and the nitrates, and nitrites in a raw sewage and an activated sludge effluent. In the raw sewage (Figure 2) the two stages are clearly defined, the first being complete in about 7 days. During this period the nitrite increased slightly, while the nitrate remained nearly constant. In the second period, after a slight lag in nitrification, the nitrates increased rapidly. The nitrites decreased and practically disappeared. The activated sludge effluent (Figure 3) also gave a second stage, but the time required for completion of the first stage was shorter. As was the case with the raw sewage, the nitrates increased rapidly at the beginning of the second stage. The nitrites again approached the vanishing point, having been converted to nitrate. Tables V and VI give the analyses for these curves.

According to the theory of two-stage oxidation, we should obtain a curve with a single rise when using a sample high in carbonaceous material but low in nitrogen. Figure 4 represents the average of a number of determinations using a refinery wash water from the Corn Products Refinery Co., at Argo, Ill. This waste is very high in carbohydrates, but comparatively low in nitrogenous material. The incubations carried out for 30 days show no secondary rise. The fact that the nitrate method, as previously discussed, shows only one stage strengthens the theory that the carbonaceous oxidation is complete in from 10 to 12 days.

Rates of B. O. D., Illinois River

During the past two years the Sanitary District has been making very comprehensive studies of the oxygen relations of the Desplaines-Illinois Rivers, from Lockport to the mouth. Special oxygen demands are run each week on samples collected at fourteen stations. In 1926, and through July, 1927, from four to six samples collected throughout one 24-hour period were set up each week, with incubation at 20° C. for 1, 2, 3, 5, 10, and 20 days. This gave twenty or thirty runs per month, which were averaged for each station. Results were computed and plotted as per cent of the 20-day demand. A large number of such curves have been drawn, of which those shown in Figure 5 are typical. The Lockport curve follows the usual logarithmic rate fairly well up to 11 days, then comes the transition period, and after 12 days the secondary rise appears. The curve for the Morris sample has a slower rate for the first 5 days and the break comes at about the ninth day. The rate for the Chillicothe samples is even slower than for Morris during the first 5 days and the break comes at about the seventh day.

Table V—Comparison of B. O. D., Nitrites, and Nitrates
Raw Sewage—Morton Grove (Concentration, 5 Per Cent)
(Series set up on April 28, 1926)

Time Incubated	Dissolved Oxygen	B. O. D.	Nitrate (N_2O_5)	Nitrite (N_2O_3)
Days	*P. p. m.*	*P. p. m.*	*P. p. m.*	*P. p. m.*
2	5.2	20.0	0.357	0.03
5	5.2	30.0	0.424	0.06
8	5.2	34.0	0.390	0.20
10	5.2	48.0	0.460	0.30
12	5.2	58.0	...	0.25
14	5.2	68.0	0.744	0.16
16	5.2	70.0	0.950	0.00
20	5.2	..	0.850	0.001
24	5.2	74.0	1.029	0.01
28	5.2	82.0	0.970	0.00

Table VI—Comparison of B. O. D., Nitrites, and Nitrates
Activated Sludge Effluent—Desplaines Treatment Works
(Series set up on January 10, 1927)

Time Incubated	Dissolved Oxygen	B. O. D.	Concentration	Nitrite (N_2O_3)[b]	Nitrate (N_2O_5)[b]
Days	*P. p. m.*	*P. p. m.*	*Per cent*	*P. p. m.*	*P. p. m.*
0	5.5	..	..	0.240	4.72
2	5.5	4.6	50	0.480	5.04
5	5.5	6.1	50	0.800	7.56
7	5.5	15.2	25	0.560	6.96
10	5.5	19.0	25	0.280	7.48
15	5.5	21.0[a]	25	0.080	9.64
20	5.5	24.8	12.5	0.013	9.22
25	5.5	26.0	12.5	0.005	9.44

[a] Estimated from curve.
[b] Corrected to 100 per cent.

Many similar series of curves have been obtained. Intermediate stations usually give curves which fit in between those shown, although at times downstream stations revert to

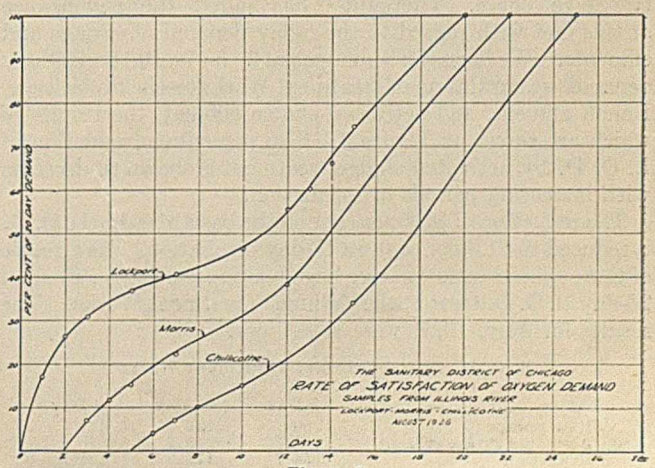


Figure 5

the Lockport type. However, at Beardstown, some 200 miles below Lockport, the curve is frequently a straight line.

From these curves it is concluded that the shape of the B. O. D. curve depends upon the state of oxidation or nitrification of the sample, and that in the secondary stage, when nitrification is established, the rate may be nearly a straight line rather than logarithmic. In fact we have fitted the down-river curves on the Lockport curves with fair success for the first stage, but the slope varies so much for the second stage that we have not been able to formulate any single equation with fixed constants that will express this part of the curve. We are now running weekly samples, in duplicate, with incubation periods of 1, 2, 3, 5, 7, 10, 12, 14, 16, 18, 20, and 40 days in order to define the shape of the curve more accurately.

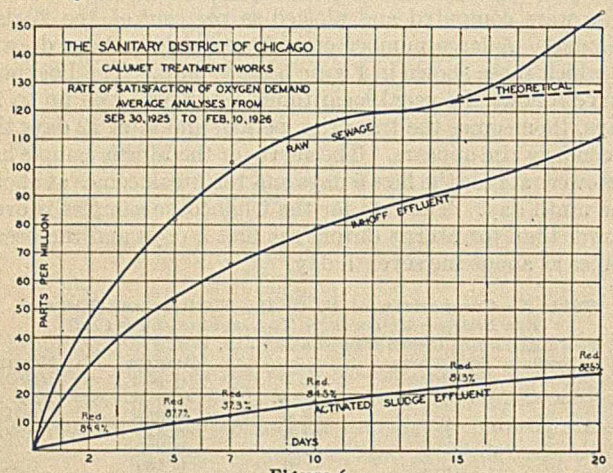


Figure 6

The significance of these results, which we have confirmed many times, is that in a stream undergoing self-purification the B. O. D. curve determined on the freshly polluted water is followed progressively downstream, even through the secondary stage, and consequently the ratio of the 5-day demand to longer time demands is constantly changing, although approaching a fairly constant ratio for a number of days when in the secondary state, which we believe is the stage of active nitrification. Fairly constant ratios during the first 10 days have also been obtained many times on samples of fresh sewage, even though quite dilute, but the ratios have been quite variable for stages intermediate between the first and second stages.

Significance of B. O. D. in Sewage Treatment

The logical conclusion from our Illinois River results is that sewage undergoing biological oxidation also follows the two-stage curve. Theriault[12] has noted the significance of this fact with regard to the 5-day demand of sewage and effluents. We have run some special 2-, 5-, 7-, 10-, and 20-day demands at our Calumet Treatment Works on the raw sewage, Imhoff effluent, and activated sludge effluent, the results of which are shown in Figure 6. The percentage reduction of B. O. D. by activated sludge treatment is shown to decrease with increasing periods of incubation.

The reduction of 87.7 per cent on the basis of 5-day B. O. D. is reduced to 81.3 per cent on 15-day incubation. As a result of these special tests we have been making routine 5-, 10-, and 20-day B. O. D. tests at the Calumet Treatment Works. The results for July, 1927, were as follows:

B. O. D. Tests—Calumet Treatment Works
(P. p. m. at 20° C.)

	5-Day	10-Day	20-Day
Raw sewage	80	122	174
Activated sludge effluent	5.3	8.2	16.1
Reduction	74.7	113.8	157.9
Per cent reduction	93.4	93.2	90.6

A series of twenty special samples of raw sewage and effluent from our Desplaines Treatment Works, collected at intervals between February 24 and July 20, 1927, gave the following results:

B. O. D. Tests—Desplaines Treatment Works
(P. p. m. at 20° C.)

	2-Day	5-Day	7-Day	10-Day	15-Day	20-Day
Raw	76.1	116.2	134.1	150.0	168.8	185.0
Activated sludge effluent	1.8	3.2	4.2	4.9	6.1	8.3
Reduction	74.3	113.0	129.9	145.1	162.7	176.7
Per cent reduction	97.6	97.3	96.9	96.7	96.3	95.5

In all cases a decreasing amount of reduction is indicated with increasing periods of incubation. In other words, the percentage increase of B. O. D. for effluents is greater between 5 and 10 days, or between 5 and 20 days, than the rate for raw sewage.

Another conclusion is that the relative-stability curve, even though originally considered as applicable for effluents, really expresses the logarithmic rate followed by raw sewage, while the rate for nitrified effluents is nearer a straight line. This may be one reason why methylene blue per cent stabilities are frequently higher than can be obtained by determination of the ratio of available oxygen to oxygen demand.

B. O. D. of Disinfected Effluents

The use of the dilution method for determination of the B. O. D. of limed or chlorinated effluents may lead to fallacious results if attention is not given to the fact that there is a considerable lag period before active consumption of oxygen takes place. It is obvious that oxygen is required only when bacterial growth is progressing. Neutralization and seeding may shorten the lag period somewhat but will not eliminate it.

Some work has been done in the Sanitary District laboratories on the effect of chlorination on the B. O. D. of settled and activated sludge effluents, but not enough data are yet available to warrant publication. We have learned that a study of rates of demand over a 20-day period is more enlightening than an expression of percentage reduction of 2-day, 5-day, or 10-day demand.

Conclusions

1—The nitrate method gives lower results than the dilution method, and does not indicate the demand during the stage of nitrification.

2—The dilution method is satisfactory when proper precautions in technic are observed.

3—Results vary, depending on the type of dilution water used. A standard water is desirable, preferably a synthetic water made up of inorganic salts added to distilled water. At present the Sanitary District uses distilled water containing 500 p. p. m. sodium bicarbonate.

4—The rate of satisfaction of demand in polluted river waters follows the two-stage curve as self-purification progresses, with nearly a straight-line rate when the stage of nitrification is reached.

5—The rate of satisfaction of demand varies in sewage treatment in the same way as in progressive self-purification of polluted streams. The rate for nitrified activated-sludge effluents is more nearly a straight line than logarithmic. As a result of this change in shape of the curves, the percentage reduction of B. O. D. is less for longer periods of incubation at 20° C. than it is when based on the 5-day demand.

6—Methylene blue stabilities, expressed in per cent, are not applicable for nitrified effluents but only for diluted freshly polluted waters.

7—The reduction of B. O. D. of effluents by disinfection should be studied by rates of demand up to 20 days at 20° C., in order to eliminate the effect of the initial lag phase.

A New Method for Determining Biochemical Oxygen Demand[1]

F. Sierp

RUHRVERBAND, ESSEN, GERMANY

"STANDARD Methods for the Examination of Water and Sewage" specifies two methods for determining biochemical oxygen demand. According to the one method a quantity of sewage, predetermined in each case, is diluted with oxygen-saturated water and the oxygen demand measured by the decrease in dissolved oxygen of the diluted mixture. In the second method a nitrate solution is added as a source of readily available oxygen. In both methods, apart from other difficulties, the quantity of oxygen in the dilution water or the nitrate solution progressively decreases as the organic matter is broken down, without being replenished again. As a result the later stages of decomposition often have available only low oxygen concentrations; the organisms are in an increasingly unfavorable environment and will thus show a corresponding decrease in activity. In order to avoid these difficulties biochemical oxygen demand methods with undiluted sewage, as in the nitrate method, have been studied in this laboratory.[2]

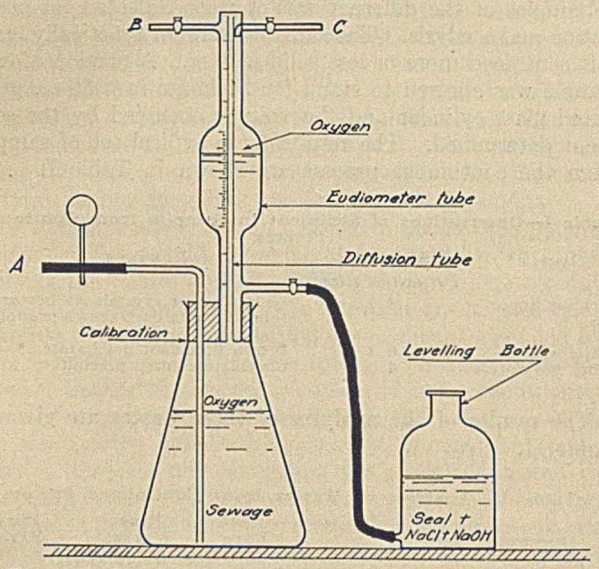


Figure 1—Apparatus for Determining Biochemical Oxygen Demand with Gaseous Oxygen

The best solution of the problem seemed to be the use of pure oxygen. With the coöperation of Mr. Fränsemeier, an apparatus was constructed to bring pure gaseous oxygen into contact with undiluted sewage. The volume of oxygen, corrected to 0° C. and 760 mm. pressure, which is absorbed in a given time at a constant temperature of 20° C., gives the biochemical oxygen demand.

Apparatus

The apparatus shown in Figure 1 consists of an Erlenmeyer or Florence flask of about 500 cc. capacity which holds the undiluted sewage. Supported on the flask by a well-fitting rubber stopper is a gas buret, the gas chamber of which is connected by a central diffusion tube to the space above the liquid in the flask. A leveling bulb, attached by rubber tubing to the gas buret, insures constant pressure. This bulb contains an alkaline sodium chloride solution, which absorbs carbon dioxide formed in the flask and prevents solution of gas in the confining liquid.

Procedure

The apparatus is weighed and then filled in the following manner: The Erlenmeyer flask, after careful cleaning with potassium dichromate–sulfuric acid mixture, is completely filled with the sample of sewage. The stopper carrying the gas buret is now forced into the neck of the flask to a predetermined mark (which controls the volume of the flask), the liquid meanwhile being forced up into the capillary tube until it is full and any excess allowed to escape through tube *A*. The leveling bulb is raised until the salt solution almost reaches the tip of the diffusion tube, and the fraction of a cubic centimeter of air remaining in the top of the buret is swept out by oxygen admitted at *C* and escaping at *B*. Tube *B* is now closed, *A* is opened, and from 100 to 200 cc. of sample are forced out by the oxygen into a measuring cylinder, leaving 300 to 400 cc. in the flask. *A* is closed and the gas buret filled with oxygen by lowering the leveling bulb, and then *C* also is closed. The quantity of sample retained is now determined by again weighing the apparatus.

In order to satisfy the immediate oxygen demand and to saturate the sewage with oxygen, the apparatus is well shaken; this requires 1 to 2 hours. It is then stored in a dark place at 20° C., the leveling bulb being raised enough to maintain a slight pressure. By shaking the apparatus daily, or, if possible, more frequently at the start, intimate contact is maintained between the oxygen and the sewage. Likewise, before each reading of the gas volume the apparatus must be shaken to insure a saturation of the liquid comparable to the initial reading.

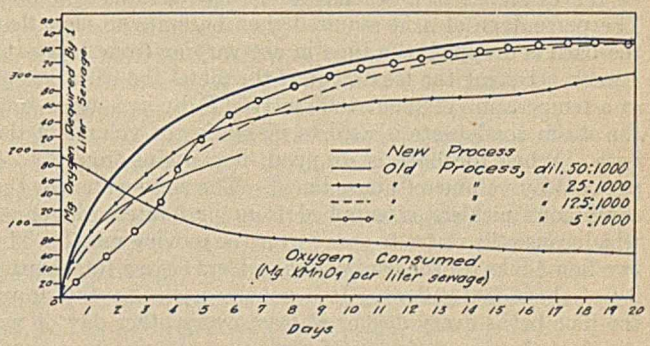


Figure 2—Comparison of Direct Absorption and Dilution Methods for Determination of Biochemical Oxygen Demand

In accordance with American practice, oxygen absorptions have been determined over periods of 5 to 20 days. Figure 2 shows a comparison between the direct absorption method and the dilution method; the direct process, since carbon dioxide is continuously removed, gives somewhat higher, but always comparable, results while the values for the dilutions vary widely.

This apparatus enables one to read off the oxygen demand hourly or daily, while with the old method this necessitated a large number of bottles.

[1] Translated by S. L. NEAVE, Illinois State Water Survey, Urbana, Ill.

[2] Great Britain, Sewage Disposal, Report **5**, App. VI, addendum to Sec. 1, p. 438 (908). Ed.

Disposal of Acid-Iron Wastes from a Steel Mill

Stuart E. Coburn

METCALF & EDDY, ENGINEERS, BOSTON, MASS.

THE presence of acid-iron wastes is often a serious handicap in the purification of polluted streams or in the treatment of sewage. The discharge of these wastes into a stream or other body of water tends to kill the fish and to render the water turbid and discolored by the precipitation of iron hydroxide on oxidation of the ferrous sulfate. This oxidation also tends to deplete the dissolved oxygen in the waters of the stream. If the acid-iron wastes are discharged into a sewer system, they may seriously affect the treatment of the sewage. The disposal of such wastes is an important problem.

In a recent investigation conducted by the writer at a steel mill, the pickling wastes were being discharged into a concrete sewer of the city and had caused serious disintegration of the concrete. The city authorities had notified the concern that the wastes must be either kept out of the sewer or treated so as to render them harmless before discharge into the sewer.

Source of Wastes

These wastes consist of spent acid liquor from pickling steel, rinse waters from washing the metal after pickling, and spent lime solution from neutralizing the small amount of acid adhering to the metal after rinsing. Two processes of pickling are in use at this plant. In one process the metal is passed continuously through the acid bath, rinsing arrangement, and lime bath; and in the other process it is allowed to remain in the acid bath as long as necessary, after which it is transferred to the rinse bath and then to the lime bath.

There are two continuous picklers. The acid-bath tanks have a working capacity of about 1000 gallons each. When the acid bath is first made up, it contains about 8 per cent by volume of sulfuric acid. The bath is tested each day and reënforced with additional acid as found necessary until the dissolved iron reaches about 0.5 pound per gallon. The percentage of acid required then becomes so high that the bath is dropped, the time in use varying from 2 days to 1 week. During the treatment of the metal the bath is kept at a temperature of about 180° to 190° F. by live steam, and the steam condensate is used to maintain the volume of the bath. When the bath is dropped, it contains from 3 to 5 per cent by volume of unused acid. The rinse water for the continuous picklers is supplied from perforated pipe lines which cause the water to spray over the moving metal. The two lime tanks for the continuous picklers have a total capacity of about 500 gallons. It is usually necessary to "drop" the lime baths every day or at least every other day on account of the accumulation of dirt.

In the tub process used for products that are not suited for the continuous process, there are four acid-bath tanks having a total working capacity of about 1500 gallons. As previously stated, the metal is allowed to remain in the acid bath as long as necessary, after which it is transferred to the rinse bath and then to the lime bath. In this process it is possible to work the free-acid content of the pickling liquor down to about 1 per cent by volume.

Volume of Wastes

The wastes from the acid baths of each of the continuous picklers amount to about 1000 gallons every time the bath is dropped. With both baths dropped on the average of twice a week, this is equivalent to approximately 4000 gallons per week or an average of about 700 gallons per working day. The discharges from the acid baths of the tub process average about 300 gallons per day, making the total average volume of acid-bath wastes about 1000 gallons per working day.

The volume of rinse-water wastes from the two processes is estimated at 7500 gallons per working day. The volume of lime-bath wastes from the two processes averages about 550 gallons per working day.

Composition of Wastes

Samples of the different wastes were collected for observation and analysis. The samples were all practically clear, but contained more or less solid matter. A portion of each sample was allowed to stand for 24 hours in a 50-cc. graduated glass cylinder and the volume occupied by the sediment determined. The results for a typical set of samples from the continuous process are shown in Table I.

Table I—Observations of Sediment in Samples from Continuous Process

Sample	Sediment	Remarks
	Per cent by volume	
Pickling liquor	4.4	1/2-inch green crystals at bottom of bottle, with dark brown precipitate above
Rinse waters	0.4	Brown flocculent precipitate
Lime wastes	4.0	Chocolate colored precipitate

The results of the analyses of these wastes are given in Table II.

Table II—Analyses of Wastes from Continuous Process

Determination	Acid Bath	Rinse Waters	Lime Bath
	Per cent by weight		
Sulfuric acid (H_2SO_4):			
Total[a]	19.60	0.85	Neutral[c]
Free acid[b]	8.17	0.50	...
Iron (Fe):			
Total	5.250	0.242	0.0125
Ferrous	5.180	0.162	0.0007
Ferric	0.070	0.080	0.0118
Total solids	33.21	1.483	0.183
Specific gravity	1.220	1.010	1.000
Hydrogen-ion concentration, pH index	1–	1.4	6.5

[a] By phenolphthalein at boiling temperature.
[b] Computed by deducting from total acidity the sulfuric acid equivalent of the ferrous iron.
[c] By methyl orange.

Possible Methods of Disposal of Wastes

The analyses show that the lime-bath wastes may be discharged into the sewer without harmful effects. They contain considerable suspended matter, but this is light in weight and not enough in amount to cause objectionable deposits in the sewer. The rinse waters are distinctly corrosive and require treatment before discharge into the sewer. There is no question that the acid-bath wastes must either be taken out of the sewer or treated to remove their corrosive action before discharge into the sewer.

The following methods of disposal were considered: (1) dilution with water, and discharge into the sewer; (2) neutralization with lime and discharge into the sewer; (3) treatment with lime in separate tanks and disposal of resulting sludge; (4) disposal by cesspool method; (5) recovery of ferrous sulfate.

Dilution

If the acid wastes were sufficiently diluted with water before discharge into the sewer, no harm would result. It would be necessary, however, to mix the water thoroughly with the wastes prior to discharge.

In the laboratory all the samples of wastes received were mixed together in approximate proportion to the average volumes produced, and it was found that one volume of the mixture would require at least 100 volumes of water to reduce the hydrogen-ion concentration to a pH index of about 4, which, although slightly acid, would have no serious effect upon the sewer.

The volume of water required for such dilution would be nearly 1 million gallons per day, and under conditions existing at this plant this would involve a large expenditure for water. It is also questionable whether the city authorities would approve of putting such a large volume of water into the sewer.

Neutralization with Lime

Experiments were made to determine the amount of lime required to neutralize the acid wastes. The amounts of lime required were determined on two bases: first, to neutralize the acidity indicated by methyl orange, and second, to neutralize the acidity indicated by phenolphthalein. Methyl orange indicates the most aggressive part of the acidity including the free sulfuric acid, while phenolphthalein indicates the total acidity including the ferrous sulfate acidity.

The tests indicated that an average of about 1600 pounds of lime per day would be required to neutralize the total acidity of the wastes and about 500 pounds of lime per day to neutralize the most aggressive portion of the acidity.

The use of lime for neutralizing the acidity is attended by the precipitation of the iron in solution forming hydroxide of iron. Undiluted samples of the acid-bath wastes after lime treatment became thick sludges in the case of neutralizing the acidity indicated by methyl orange, and pasty masses in the case of neutralizing the acidity indicated by phenolphthalein. The lime treatment could not be properly controlled in practice without pumping the wastes to separate treatment tanks and utilizing rinse waters for dilution. Even then, the proportion of sludge produced would be so large that it would be likely to form troublesome deposits in the sewer.

Treatment with Lime in Separate Tanks and Disposal of Sludge

All the wastes could be pumped to a suitable lime-treatment plant including storage tanks, the effluent discharged into the sewers, and the sludge disposed of by other means. The tanks would have to be large enough to hold 2 or 3 days' storage of wastes in order to secure proper mixing before treatment. The sludge could be discharged into lagoons if suitable low areas could be found or be dewatered on beds of porous material like sand or by filter presses or vacuum filters and the dewatered sludge hauled away to a suitable dumping ground. It would be practically worthless.

The amount of lime required and the percentages of sludge produced were as follows:

To Neutralize Acidity by:	Lime	Sludge Produced on Standing: 2 Hours	24 Hours
	Lbs./1000 gallons	*Per cent*	*Per cent*
Methyl orange	100	45	42
Phenolphthalein	192	66	58

Assuming that the sludge in practice would be concentrated to one-half of the above percentages after 24 hours' standing, the sludge from neutralizing the methyl orange acidity would amount to about 20 per cent of the volume of wastes or, say, 1800 gallons per day. There would be large expense involved in dewatering and disposal of this sludge, in addition to the cost of the lime treatment. No further consideration was given to this method because of the possibility of other much less expensive methods.

Disposal by Cesspool Method

It would be difficult to dispose of all the wastes by the cesspool method even with the sandy, porous soil available. As previously stated, the lime-bath wastes can be discharged directly into the sewer without any treatment, and the rinse waters can be so discharged after the addition of moderate amounts of lime sufficient to neutralize the acidity indicated by methyl orange. The acid-bath wastes could then be discharged into leaching cesspools, the liquid passing away into the soil. A more effective method of disposal would be by means of subsurface drains laid in porous soil with open joints properly surrounded with graded gravel. However, these wastes contain considerable amounts of suspended matter which would tend to clog the soil. Furthermore, as the wastes passed into the soil and became partially neutralized and oxidized, hydroxide of iron would be precipitated, tending to clog the soil and render the system inoperative.

This method of disposal is also open to the objection that the acid waters passing through the soil might come in contact with iron pipes for gas, water, etc., and cause serious corrosion. Furthermore, if the acid waters should get into wells or surface water supplies they would impair the quality of the water and might cause serious trouble. For these reasons this method of disposal was not considered satisfactory for permanent use.

Recovery of Sulfate of Iron

The acid-bath wastes contain large amounts of dissolved iron, as shown by the analysis. This iron is in the form of ferrous sulfate, which can be recovered and sold as copperas. In the recovery process the wastes are discharged into lead-lined tanks, the excess water is evaporated by steam coils, and the concentrated liquor, after sedimentation to remove suspended matters, is discharged into a lead-lined tank, where the copperas crystallizes out on cooling.

The free acid may be neutralized by addition of scrap iron before evaporation, thus increasing the amount of copperas produced and rendering the liquor suitable to discharge into the sewer with the addition of relatively small amounts of lime as may be required to neutralize any methyl orange acidity remaining. If scrap iron is not available, the mother liquor, after the copperas is crystallized out, will be strongly acid and can be returned to the acid tanks.

The analyses indicate that over 12,000 pounds of copperas per week could be recovered from the acid-bath wastes without the addition of scrap iron to neutralize the free acid, and over 20,000 pounds per week if the free acid were so neutralized.

While this recovery process may not be profitable at the present market price of copperas, it will prove in the long run to be the most satisfactory and most economical method of disposal of the acid-bath wastes.

[End of Symposium]

Some Economic Aspects of Chemical Production[1]

Williams Haynes[2]

CHEMICAL MARKETS, 25 SPRUCE ST., NEW YORK, N. Y.

ANY industrial consultant—a chemist, an attorney, a banker—will confirm the common belief of almost every industrial executive that his own business is "different"—that is, in some mysterious or singular way his manufacturing and sales problems are unique. The wider the experience of the consultant, the more promptly will he be able to define individual problems in the terms of broad, well-accepted classifications and apply to them generalizations of theory and practice, with a wealth of successful, practical experience to confirm his conclusions. Nevertheless although this egotistical conception of business is true to but a limited extent, it does justify itself in a special, fundamental sense in manufacturing that deals with chemical processes. Even this distinguishing mark, it should be noted, is common to all chemical-process industries. Throughout their activities, however, it is of paramount importance.

The Chemical Industry Unique

Chemical processes in any industry involve chemical reactions and result in chemical changes. It follows, therefore, that any industry built upon chemical foundations produces at every step in its operations an entirely new product with new and different materials as by-products. This unique, basic characteristic of chemical production creates peculiar industrial conditions. It gives rise to unparalleled problems of extreme practical importance in the successful conduct of chemical enterprise. These problems center about yields and wastes. They involve costs and by-products. They subject the chemical manufacturer in an extraordinary degree to unusual risks arising at once from competition with improved processes and with new products.

No such difficult conditions surround the fabricating industries. In the woodworking group, for example, from the standing tree in the forest to the ultimate consumer, the raw material is wood. Whether it comes to the final user as roof beam or a penholder, a table, a shingle, or an oar, it is—and throughout all its fabricating processes it has remained—wood. Although cherry may be stained to simulate mahogany, or beech may appear to be walnut, nevertheless, save for the curing and drying processes, the wood itself has been quite unchanged in its physical and chemical characteristics. Furthermore, throughout every step in all the multitudinous branches of woodworking, all of the by-products—scrap, slabs, sawdust, chips, and shavings—are wood.

Contrast this with what happens when the identical raw material enters the chemical industry. A cord of hardwood thrust into a retort and subjected to destructive distillation produces 50 bushels of charcoal, 12 gallons of crude pyroligneous acid, with varying quantities of wood-tar and gas. From a single raw material four distinct products, each differing widely in chemical and physical characteristics, have been produced. Each will go into widely different fields of consumption. The gas is used right at the wood-distillation plant as a source of heat. The charcoal finds its principal use in the production of certain grades of iron; for the manufacture of some grades of gunpowder; for removing impurities, colors, and odors in many chemical processes; in sugar- and oil-refining. Cresol, certain crude disinfectants, and wood preservatives are recovered from the tar, although the bulk of this material is used right at the plant for fuel, either directly or else as a binder to make briquets out of the waste charcoal dust. From the crude liquor is obtained methanol and acetate of lime. This by no means exhausts the products that are found in crude pyroligneous acid which include, besides these two chief commercial chemicals, formic, butyric, propionic, valeric, caproic, crotonic, pyromucic and angelic acids, allyl alcohol, acetaldehyde, furfural, methylethylketone, ethylpropylketone, methylamine, dimethylacetal, methylal, valeroctane, pyrocatechol, and ammonia. The tar is also a highly complex compound containing chiefly creosote, terpenes, benzene, xylene, cumene, cymen, chrysene, retene, and paraffin.

The inherent distinction between even such a technically simple chemical process as wood distillation and the fabrication of a floor board or chair is obvious; but this multiplicity of new materials produced by chemical processes is not the sole economic feature distinguishing the two types of industry. The percentage yields of the different products of a chemical operation may vary according to the process used, or even according to the conditions surrounding one or more steps in a given process.

It has become a proverb that the tailor must cut his suit according to his cloth. He may elect to make his goods up into overcoats or into boy's suits. He may change the styles so as to use more or less material. But of a given kind and style it will take just so much cloth to make so many units; and he may rest quite secure in the knowledge that no competitor of his will be able to make up more out of the materials. The analogy goes back further. The textile manufacturer, in whose mills the cloth was made, knows with fractional accuracy how many spools of yarn will weave so many yards of cloth of a given texture. Further still, he can accurately determine how many pounds of wool will make so much yarn of a given weight. Just so much iron is required to make so many kegs of tenpenny nails, so many hides to make this many pairs of shoes, so many gallons of paint will cover so many square yards of surface; materials may be sophisticated, workmanship may be deceptive—but only at the expense of quality.

Throughout the various fabricating industries, therefore, the costs of raw materials are, within sharply defined and well-understood limits, almost fixed. Except for variations of buying power due to different degrees of bargaining skill, of market knowledge, of experience and foresight, or of larger consuming capacity and stronger credit which command discounts, these competitors are upon an even basis at this pivotal point of cost.

Chemical-process industries have no such known and sure foundation. Inherent in chemical operations are variables much more serious than those arising from differences in purchasing skill or financial strength. When a given quantity of raw material produces a varying amount of finished products, there is immediately introduced a variation in cost that gives a great competitive advantage to the manufacturer with the most efficient plant process. He may sell his finished product at the same price and enjoy extra profits. He may sell at a lower price and still have equal profits. He may even sell at a price which will represent a small profit, or cost, to him but a loss to his less favorably situated competitor. Accordingly, owing directly to those variations

[1] Received January 21, 1928.

[2] Publisher of *Chemical Markets*.

in yields, common to most chemical industrial processes, a highly competitive element is injected into the very heart of chemical production. The variations of cost which result quite obviously affect chemical prices. As we shall see when we consider the distribution problems of the industry, they often define sales functions and determine sales policies. Moreover, consideration of them very often forces changes in the production program of a chemical plant.

Shifting of Yields to Meet Competition

Because yields vary, it is frequently possible to shift the percentages of the different products made by chemical operations. As new demands raise the price of one chemical or when new competition forces down the price of another, the chemical manufacturer who is alert to economic conditions and well armed with research is able by such means as these to adjust himself to these changing market conditions.

Again the wood-chemical industry will serve as a vivid example both of competition from new processes and of adjustments to this competition by shifting the proportion of yields. Wood-distilling is one of the oldest branches of our chemical industry, and long enjoyed a monopoly of two important commercial chemicals, methanol and acetate of lime. The U. S. Census of Manufactures records the mounting value of their products: 1880, $275,000; 1900, $3,685,000; 1914, $10,284,000; 1923, $29,695,000. The passage of the Tax-Free Alcohol Act of 1906, which specified methanol as the denaturing agent and the use of formaldehyde in the rubber and plastics industries, constantly increased methanol consumption. The demands of the new cellulose industries, both for acetone as a solvent and for acetic acid in the production of acetates, played a similar role in the market for acetate of lime. During the earlier stages of our post-war chemical developments every indication pointed to a brilliant future for the wood-chemical distillers.

After the war the acetone, produced willy-nilly in the butyl alcohol fermentation process, quickly became a by-product, and as the production of butanol was increased to keep pace with the sensational rise of lacquers, this by-product became a drug on the market which the manufacturer was literally forced to move out of his storage tanks. Produced direct, of high purity, and at by-product cost, this fermentation acetone cut seriously into the market for acetate of lime, which, however, continued to find a big chemical use in the manufacture of acetic acid. In the meantime the carbide process for the manufacture of acetic acid was perfected, threatening acetate of lime for the production of this increasingly important acid.

With the consumption for acetate of lime, one of their two main products, thus crippled, the wood distillers were suddenly attacked by synthetic methanol. The immediate commercial results of this new competition were sensational. In 1924 our imports of methanol had been 48 gallons at an average price of 60 cents a gallon. The 1925 imports totaled 508,409 gallons at a price of 45 cents. After this savage thrust President Coolidge invoked the flexible provision of the tariff law, and then last year synthetic methanol, produced in the United States and exempt from tariff duties, appeared on the market, with the result that the price dropped within six weeks from 70 cents to 55 cents.

In all the annals of industry is there a more striking instance of devastating competition from new processes than that which the American wood-chemical industry faced during the five short years between 1922 and 1927? Even their market for charcoal—long thought to be impregnable—is now undermined by new iron alloys, and they are left in control of but a single market outlet, the denaturing use of the 95 per cent grade of methanol. In hardwood distillation it is impossible to produce pure-grade methanol without producing about 20 per cent of the denaturing grade. Nevertheless it is possible so to control this process that as high as 75 per cent of the crude will come from the refining stills in this so-called denaturing grade. Since synthetic methanol, produced only in the pure grade which is not authorized for use in denaturing, has appeared on the market, the refiners of natural methanol have made this shift in order to produce as large a proportion as possible of the denaturing grade and the smallest possible gallonage of the pure grade which is in direct competition with the more cheaply produced synthetic material.

Thus a shifting of yields is used sometimes with deliberate intent, and most advantageously, to adjust new factors in chemical competition or to satisfy changing demands. It is more common, however, and infinitely more significant, as the chief element determining the production costs among individual companies competing with the same chemical product.

Selling Price Determined by Marginal Cost

Chemical selling prices must eventually be based upon costs of production. Says Edie,

> If prices soar far above the cost of production, the profits will be so high that business men will flock to that branch of activity and by their increased production and increased competition will tend to force prices down to normal levels, i. e., levels approximating the cost of production. If prices fall below the cost of production, men will be losing money and will retire from that branch of business in such numbers that the supply will fall off; and under the scarcity, prices will rise to the normal level, i. e., the cost of production. Selling prices cannot long stay below the cost of production without ruining the branch of industry concerned. * * * Hence the cost of production sets the minimum level below which prices must not fall for any considerable period of time.

Now the cost of production, which sets the base line of prices, varies greatly between different individual producers. In the chemical industry this variation is marked, and it is caused chiefly by variations in yield. Maximum yield is therefore of prime importance in chemical enterprise; more essential to profitable operation than low labor costs, or advantageous supply of raw materials, or economical plant design, any one of which may determine the vital difference between profit or loss in the fabricating-process industries. None of these elements of production cost may be neglected with impunity in these times of severe competition; but in by far the majority of chemical operations the factor of yield is the one that fixes what the economists call the marginal cost.

For in the industrial world the base line of cost upon which prices are predicated is not set by the most efficient, fortunately located, brilliantly managed plant. Rather, prices are set by the high-cost producers, for without their production supply would be inadequate. Marginal costs are the costs of those concerns which are just on the margin of profit and loss, of business life and death. They are the costs of the marginal producer, just able to produce at a profit. Since what he produces is indispensable for the demands of society, we must pay prices for his goods sufficiently high to cover their comparatively high cost. This marginal cost will, in the long run, set the standard of prices.

Meanwhile, the producers with costs below this margin reap a royal reward in additional profits. The classic example of production by two sugar-beet factories shows vividly the dollars and cents results of such variations in costs and emphasizes the effect, in chemical processes, of varying yields. In factory A the average extraction of sugar increased from 51.52 per cent in 1891 to 88.98 per cent in 1924, while in the

larger and more efficient factory B the extraction percentage increased from 82.49 in 1899 to 97.43 in 1924. As Zitkowski pointed out:

> Factory B, during several operating seasons, has introduced more than 100,000,000 pounds of sugar; a difference in 1 per cent in the extraction means 1,000,000 pounds of sugar at 5 cents per pound, worth $50,000 for each per cent. The extraction of factory B during the recent year has been more than 10 per cent above the results of the early years of its life, and 10 per cent means $500,000 worth of additional sugar recovered each season.

By-Products and Wastes

Parallel to yield, in their effects upon costs, are by-products and wastes. From the economic point of view a by-product is any material, produced in chemical operations, not the direct object of the operation but which has a commercial value. A waste, on the other hand, is any product so produced for which there is no market.

This distinction is important. Obviously, a by-product may either have a direct market, or it may be used within the plant as a raw material for further operations. The by-product problem, therefore, resolves itself into finding the most profitable market for the material. The waste problem is not so simple. Most chemical industrialists agree that if a waste product may be disposed of without committing an unlawful nuisance it is best to regard it simply and solely as waste. It is distinctly uneconomic to store waste in the hope that future generations will find a use for it. It is as unsound to work it up into a salable product at a cost greater than the same material can be made by other methods. No possible opportunity should be overlooked to find a profitable use for any waste material produced in considerable quantities and ofttimes the laws against nuisance or pollution will remove the whole waste problem from the realm of profitable operation; but management should scrupulously weigh wastes by commercial standards. It is foolish not to turn waste into a profitable product, if practical; but it is more foolish to waste more money over waste utilization which is impractical—that is, unprofitable.

The competitive advantage of better-than-marginal cost is obvious, and its secret, in chemical processes, lies largely in yields. Accordingly, a maximum yield is the measure of chemical-plant efficiency. Increased yield is the proper objective of all operating policy, and far-sighted management will not hesitate in this cause to scrap equipment, or even to install an entirely new process. Chemical manufacturing deals constantly with changes in chemical composition, which may usually be wrought only by applying or removing energy at some stage of the process; and since control and maximum utilization of heat and power thus affect yields directly, they are a prime concern of the chemical-plant executive. In like manner research applied to industrial problems will always be largely concerned with this basic problem of yield. The tangible results are those new and improved processes, or the commercial use of by-products or waste, which by lowering costs give the company undertaking such research an initial advantage over competitors.

New Products

Such new processes are not, however, the only disturbing competitive element in chemical production. There is also the competition from new products. Since a century ago, when Marcelin Berthelot turned analysis inside out and directed the attention of chemists to the possibilities of synthesis, literally hundreds of thousands of chemical compounds have been put together; many of them old products made in new ways, but many of them quite new chemical combinations. From this scientific storehouse of synthesis the chemical industries are drawing a constantly increasing number of commercial products. Sometimes these new products supply, or even create, new needs; but far more often they replace existing commodities.

In 1894, when synthetic indigo was introduced, it destroyed the great and profitable trade of the Indian plantations. It was able to do this only because it supplied at less cost a more pure, absolutely uniform dyestuff of greater brilliancy and fastness; and while for a short period it caused havoc in the existing agricultural economics of India, the land once devoted to growing dye now raises foodstuffs. This substitution of a chemical for a natural product has been a distinct economic gain to the world, and in studying economic causes, or judging economic effects we must deal broadly, often over a period of many years, not with what is for the individual's advantage, but with what is for the ultimate benefit to mankind. This substitution of chemical for natural products is, as we shall see, but the natural outworking of inevitable, irresistible economic forces. If a new product accomplishes this fundamental economic purpose, it succeeds; if it has not this inherent soundness, no genius of invention nor skill in production, no financial backing, no patent protection, no salesmanship will make it a commercial success.

Such substitutions fall into two economic classes: (a) one chemical for another; (*b*) a chemical for a natural product. We have vanillin for vanilla beans; rayon for silk; sodium silicate for dextrin and glue; lacquers for varnish; synthetic menthol for camphor; aspirin replacing quinine; phenolphthalein in place of buchu, cascara, aloes, and a score of other cathartic drugs; ammonia, methanol, and acetic acid produced from chemical raw materials by chemical processes. Among the first group we find lithopone and zinc oxide used for white lead in paint-mixing; chlorine taking the place of bleaching powder; new chemical accelerators for rubber vulcanization following each other with bewildering rapidity; butyl acetate for amyl acetate in lacquer-making; ethylene glycol for glycerol as an antifreeze; sulfur dioxide as an antichlor; calcium phosphate used as an abrasive in tooth pastes. Despite their diversity, all these substitutions have a common characteristic—each new product is produced from cheaper, more available raw materials.

The economic activities of mankind have always been directed towards satisfying human wants. Whatever has brought goods to the consumer more quickly and at less cost has been economic progress. That progress, since the Industrial Revolution, has been so accelerated that we are today housed better, clothed better, fed better than were any people ever before, while we enjoy hundreds of material advantages of which even our grandfathers never dreamed. As a result we have made unprecedented demands upon the world's stock of basic raw materials. It is estimated that each of us consumes in a life time seven times as much material as did the Englishman of Queen Elizabeth's day, while the population of the world has already exceeded the limit which a century and a half ago Malthus set for the beginning of a period of slow starvation.

We have been able to perform these economic miracles, flying in the face of Malthus' carefully calculated prophecies, chiefly because of the improved technic of production. Population will continue to increase and our demands for material goods will grow. Already we are calling upon the last, most modern technic of production, chemical production, to help supply our wants.

In the case where chemica products replace natural products the gain is naturally greatest. For years the supply of varnish gums has been dwindling in the face of a constantly increasing demand. The price has naturally risen. In time we should have been forced to devote great acreage, years

of growing time, and considerable human labor to gum-tree plantations in tropical countries. Before that time has really arrived, lacquers using cellulose from comparatively cheap and quickly replaceable sources appear and, quite contrary to the natural products, the greater their production the lower the cost will fall. Eventually, when the problem of feeding the human race becomes more pressing (as it most surely will) any chemical substitution which frees land and labor for foodstuffs will be a capital economic consideration.

The Goal—Lower Prices

So throughout the chemical industries we see the natural tendency to employ in chemical production the cheapest, most available, more abundant, most easily replaceable raw materials. Much of our industrial technical advance is based on discoveries that enable us to wrest necessary elements from the commonest sources and by recombining them to increase their form utility. The immediate incentive is, as it has always been, the gain of the individual. Chemical production is made more profitable. Yields are increased; wastes are utilized; costs are lowered. The margin of profit is increased. But always the tendency is towards lower prices; and success in chemical production is to be won only by chemical vision, supported by chemical control of plant operations, and led by chemical research to improved processes and new products.

Computation Methods in Countercurrent Absorption Systems[1]

W. K. Lewis and W. H. McAdams

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Mass.

The research work of recent years on the interaction between gases and liquid solvents has thrown a flood of light on the mechanism of such reactions and has apparently resulted in substantially universal acceptance of the so-called two-film theory of diffusion. However, these research results have rendered obsolete the methods of computation hitherto accepted as standard in the design of commercial absorption units, except for certain special cases. This article presents graphical methods of design, based on present-day theories, which are generally applicable. Furthermore, these methods are advantageous in that they lessen the labor of computation and make possible a clear visualization of the operating conditions in the unit and the influence of various important factors upon them.

During the last decade a great deal of work has been done in studying the mechanism of absorption of gases by liquids. The results were well summarized in the Absorption Symposium held at the Ithaca Meeting of the American Chemical Society in September, 1924.[2] It is now generally agreed that the controlling factor in rate of absorption is diffusion of the absorbed material through two films in series—namely, the films of gas and of liquid on the two sides of the interface between the phases. Sometimes the problem is simplified by the fact that the diffusional resistance of one of these films is negligible compared with that of the other, but often both films are important. The work cited above has made clear the methods of computation for those cases in which during the process of absorption the changes in concentration in the gaseous and liquid phases are small, but in commercial practice this situation is seldom met. Thus, in continuous countercurrent absorption concentrations are normally very low at one end of the absorption unit and high at the other. Since rate of absorption is profoundly influenced by both concentrations and concentration differences, computation methods become correspondingly involved. The problem becomes even more difficult where the equilibria are complicated. The purpose of this article is to outline simple, exact, graphical methods of solution for this general case of steady, countercurrent operation of absorption and desorption units.

Countercurrent Absorption Unit

Figure 1 represents a countercurrent absorption unit. The incoming gas is indicated entering at the bottom and leaving at the top and the liquid absorbent is flowing in the opposite direction. The entering gas carries the material to be absorbed, which dissolves as solute in the liquid absorbent. The exit gas carries only the residual solute not dissolved in the absorbent liquid flowing from the bottom. It is advisable to express the concentrations of material being absorbed—i. e., of solute—as parts of solute per part of solute-free gas for the gas phase and parts of solute per part of solute-free absorbent for the liquid phase. One may use any suitable units.

Operating Equation

Call the pounds of incoming, solute-free gas per unit time, G, and the pounds of liquid absorbent, L. The concentration of solute in the liquid, expressed as pounds per pound of absorbent liquid, is x. This has the value x_1 at the bottom of the tower in the effluent liquid and x_0 at the top of the tower in the incoming liquid. y is the concentration of solute in the gas, expressed as pounds of solute per pound of solute-free gas. Its value is y_1 in the incoming gas and y_0 in the outgoing. Consider any section in the middle of the tower, taken at right angles to its axis. At this section the concentrations are x and y, the numerical values of these quantities differing, of course, with the point at which the section is taken. Consider a second section at a differential distance dl below the first, at which point the corresponding concentrations are $x + dx$ and $y + dy$. Since equality of input and output demands that any solute removed from the gas in this section be taken up by the liquid, it follows that $Gdy = Ldx$. Furthermore, since continuity of operation is assumed, L and G are constants for any fixed conditions of operation. It is therefore possible to integrate this equation directly, obtaining $Gy = Lx +$ constant. This equality may also be written

$$G(y - y_0) = L(x - x_0) \qquad (1)$$

Inspection of this equation shows that in any such continuous, countercurrent system y must be linear in x. Be-

[1] Received September 27, 1927.

[2] *Ind. Eng. Chem.*, **16**, 1215 (1924).

cause this relation was derived solely from an equality of input and output, it must hold whatever the character of the equilibria between the phases, the type of apparatus, the intimacy of contact, the relative velocities of flow, or any other similar relationships however important from other points of view. It does, however, postulate steady rates of flow of both gas and liquid. It also neglects any solubility of the gas or volatility of the absorbing liquid.

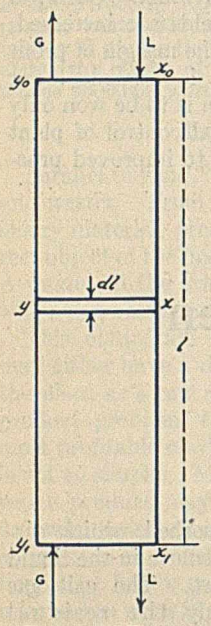


Figure 1—Countercurrent Absorption Unit

This equation reminds one strongly of the similar relationships existing in rectifying columns and now so generally used in their design.[3] Since this expression gives the relation which must exist between the composition of liquid and vapor phases at any point in a steady, countercurrent absorption operation, it may be called the operating equation and the line corresponding to it the operating line.

Drying of Air by Sulfuric Acid

As a specific case consider the drying of air by sulfuric acid. The equilibrium relationship between air and sulfuric acid is given by the curve *OABC* in Figure 2.[4] Obviously, sulfuric acid can absorb water only from air containing more than corresponds to this equilibrium—i. e., any air being dried by sulfuric must correspond to points to the left of this curve. Furthermore, if one assume air entering such a system with a moisture content $y_1 = 0.016$ (Figure 2) being treated with sulfuric acid with an initial moisture content $x_0 = 0.60$, the moisture in the air being ultimately reduced to $y_0 = 0.006$ and the water content of the acid rising to $x_1 = 1.4$, it follows from the preceding paragraphs that the concentrations of moisture in both the air and the acid throughout the apparatus must be represented by the line *EF*. Such a line must always lie to the left of the equilibrium curve and, furthermore, it can never cross that curve although, theoretically at least, it can touch it. However, if it touches the equilibrium curve, tangentially or otherwise, at that point, gas and liquid are at equilibrium or only differentially separated from it, so that transfer of solute from gas to liquid in the neighborhood of that point is indefinitely slow, requiring, therefore, indefinitely large surface of contact, which is equivalent to a negligible capacity for any apparatus of finite size

Inspection of equation (1) shows that the slope of the line *EF* is the ratio of liquid absorbent to gas treated—in this case 0.0125 pound of sulfuric acid per pound of bone-dry air. Since in general it is desirable to use as little absorbent as practicable, it is important to keep this slope low. Assume, for example, that it is required to dry air down to a moisture content $y_0 = 0.006$ with acid entering the system with a concentration $x_0 = 0.6$. This corresponds to point *F* on Figure 2. The flattest line which can be drawn through *F* and reach the high water content $y_1 = 0.016$ without crossing the equilibrium curve is obviously the line *FH*, tangent to the equilibrium curve at *J*. The slope of this line, $(0.016-0.006)/(2.26-0.6) = 0.006$ pound of sulfuric acid per pound of bone-dry air, therefore represents the smallest ratio of acid to air which it is theoretically possible to employ in drying air of high moisture content y_1 to the low moisture content y_0 by the use of acid with initial water content of x_0. Furthermore, since in such a system one would of necessity approach equilibrium in the middle of the absorber, it follows that the air-treating capacity of the absorber would be negligibly small or else the size of the absorber infinitely great. It is, however, interesting to note that in such a case the air is not, and can never be, in equilibrium with the absorbent at either its entrance or exit.

If the initial air to be treated contains less moisture than corresponds to point *J*, it becomes possible to draw flatter lines—i. e., to use less acid per pound of air—and still stay on the left of the equilibrium curve. This diagram therefore makes it possible for one to determine directly the theoretically minimum amount of liquid absorbent necessary for any particular case. It is obvious that the amount actually employed will exceed this minimum by a margin sufficient to furnish reasonable capacity.

Absorption Rate

The instantaneous rate of transfer of material from the one phase to the other is proportional to the surface of contact between the phases and to the concentration gradient through each of the two surface films on the two sides of the interface, the two phases being at equilibrium at the interface itself. It therefore follows that in Figure 2 the equilibrium curve *OABC* represents the interfacial conditions; i. e., at each point in the apparatus the concentrations there existing at the interface must fall somewhere on this curve. Calling k_G and k_L the individual or film coefficients of the gas and liquid films, respectively, *A* the area of cross section of the apparatus, *a* the interfacial surface of contact between the gas and the liquid per unit volume of the apparatus (obviously *S*, the total interfacial surface, equals $aA1$), and x_e and y_e the liquid and gaseous concentrations at equilibrium and therefore also at the interface, the rate of transfer of material can be expressed as follows:

$$\frac{dW}{d\theta} = Ldx = k_L aA(x_e - x)dl = Gdy = k_G aA\,(y - y_e)dl \quad (2)$$

Obviously, the numerical values of the absorption coefficients k_L and k_G will depend on the materials treated, the type of apparatus, and the units employed.

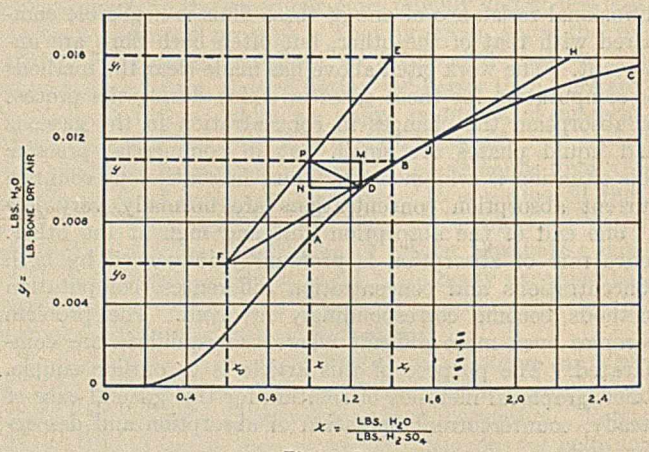


Figure 2

LIQUID-FILM CONTROLLING—In Figure 2 the point *P* on the line *FE* represents the conditions in liquid and gas at a certain point in the absorber, where the liquid and gas concentrations are *x* and *y*, respectively. Assume for the instant that in this case the diffusional resistance is mainly in the liquid film and that the gas-film resistance is negligible. This is equivalent to saying that the concentration

[3] McCabe and Thiele, *Ind. Eng. Chem.*, **17**, 605 (1925).
[4] Based on data by Wilson, *Ibid.*, **13**, 326 (1921).

gradient through the gas film is negligible, or that the gas concentration at the interface is essentially identical with the concentration in the bulk of the gas y. It therefore follows that the interfacial conditions are represented by point B in Figure 2, at which the concentration in the gas film at the interface is equal to that in the main body of the gas, while the concentration in the liquid film at the interface has the value x_e. Therefore, the driving force causing diffusion in equation (2) is numerically equal to $x_e - x$ corresponding to the length of the line PB.

Rewriting equation (2) in the form

$$\frac{dx}{x_e - x} = \frac{k_L a A dl}{L} \qquad (2a)$$

it is seen that, granting a knowledge of the constants $k_L a$, A, and L, one can calculate the length, l, of absorber necessary by evaluating the integral, $dx/(x_e - x)$. (A, the cross section of the apparatus, is determined by the gas handled per unit time and by the gas velocity to be employed.) This may be done by plotting the reciprocal of $(x_e - x)$ vs. x. In this way it is possible to determine the volume of absorber necessary for any desired operation, once the constants of the equipment are known for the case in question.

Gas-Film Controlling—Assume, on the other hand, that this is a case in which the resistance of the gas film is considerable and that of the liquid film negligible. Since the concentration in the liquid film will be substantially equal to that in the main body of the liquid x, it follows that the interfacial conditions will correspond to the point A (Figure 2). Furthermore, the driving force causing diffusion through the gas film is $y - y_e$, corresponding to the line PA in Figure 2. It is obvious that equation (2) can be graphically integrated for this case by a method entirely analogous to that given above—i. e., by plotting $1/(y - y_e)$ vs. y, the area under the curve being equal to $k_G aAl/G$.

General Case—In those important cases in which both gas and liquid film resistances must be taken into account, the graphical method of computation is of especial value. It is clear from inspection of equation (2) that $k_L/k_G = (y - y_e)/(x_e - x) = \Delta y/\Delta x$. Granting that the ratio of the liquid and gas-film coefficients is known, by drawing through point P a line PD (Figure 2), the slope of which equals k_L/k_G, it will be clear that the intersection D of this line with the equilibrium curve $OABC$ is the only point on the equilibrium curve which can possibly fulfil this last relationship. Therefore, for such a case the concentration gradient, $y - y_e$, through the gas film is equal to the line DM or PN, and the gradient, $x_e - x$, through the liquid film is equal to the line DN or PM. In such a case the area curve is obtained by using these lines instead of one of the lines PA or PB, as before. From inspection it is obvious that PN is always less than PA, and PM less than PB; i. e., the areas under the reciprocal curves are always greater. In other words, the rate of transfer through two films in series is less than if one film alone were present.

The preceding discussion has been based on the assumption that the driving forces Δy and Δx are proportional to the differences in potential Δp and Δc. It can readily be shown that where concentrations are low this is substantially true, but where concentrations are high it is not true. In the latter case the diagram of Figure 2 should be constructed, not in terms of y and x, but in terms of partial pressures and concentrations p and c, or of whatever units of concentration must be chosen such that differences in concentrations expressed in these units are proportional to diffusion rates. On this diagram of p vs. c, the equilibrium curve should be drawn. The actual curve, corresponding to the line FE, can be drawn by computation, most conveniently by constructing first an auxiliary $x - y$ diagram and transferring the corresponding points from this diagram to the $p - c$ plane. The FE line will not be straight in the $p - c$ plane.

If the equilibrium between phases corresponds to Henry's law, at least in the form $y = kx$, the equilibrium curve becomes a straight line. Since the operating line is also straight, study of the diagram will show that, if the ratio of gas-film to liquid-film resistance remains constant, the ratio of the driving forces through the two films will also remain constant. Consequently, the true driving force through either film is proportional to what would be the driving force through that film were the resistance of the other negligible. That is, it is allowable in such a case to assume a single film resistance; for, while the coefficient thus computed will differ from the true one, it will be constant for these operating conditions and can be employed without hesitation. Further study will also make it clear that the average driving force will be the logarithmic mean of the driving forces at the two ends of the unit.

If the gas being treated in a countercurrent absorption system contains a component which it is not desired to dissolve, but which is appreciably soluble in the solvent employed, one should use an absorption column designed to give the most efficient possible countercurrent contact between absorbent and gas and strictly limit the amount of absorbent used per unit of gas treated to the lowest possible quantity adequate to dissolve the desired constituents.

Unfortunately, the gas treated is often subject to variations both in composition and quantity. Whenever the solubility of the constituent to be absorbed follows Henry's law, the minimum adequate ratio of absorbent to gas treated is independent of the composition. Thus, assume a certain composition and a corresponding ratio of absorbent to gas; if, now, one double the concentration of the desired constituent in the entering gas, since its solubility in the absorbing medium is proportional to its concentration, the absorbing capacity of the menstruum is doubled. Therefore, there need be no increase in the quantity of the absorbing medium per unit quantity of gas treated in order to dissolve the increased amount of the solute. This can be summarized in the following rule:

For a given material to be dissolved from a gas in a given absorbing liquid in which the solubility of the material follows Henry's law, the minimum adequate quantity of absorbent per unit quantity of gas treated is independent of the concentration of the material absorbed.

From the above it follows that, to get best results, the ratio of absorbent to gas treated should be kept constant.

Materials Obeying Raoult's Law

In the case of a volatile liquid dissolved in an essentially non-volatile liquid, in the presence of a substantially insoluble gas, the partial pressure of the dissolved vapor following Raoult's law, the equilibrium relationships are greatly simplified. Although the following discussion will be general, it will perhaps be clearer to illustrate by the case of benzene vapor dissolved from an inert gas, such as flue gas, by absorbent oil, the oil being later denuded by distillation with steam. It is assumed that both the absorption and stripping are conducted by countercurrent flow, under steady conditions of operation. Call x the mols of benzene per mol of oil, in the liquid phase, and y the mols of benzene per mol of gas (flue gas or steam as the case may be), L the mols of absorbent oil, and G the mols of gas employed per unit time. Hence, as before,

$$L(x_0 - x) = G(y_0 - y) \qquad (3)$$

represents the actual operating conditions in the unit. Granting constancy of temperature in the tower, calling P

the pressure of pure benzene at this temperature and π the total pressure on the unit, the partial pressure, p, of benzene over the liquid is given by the expression, $p = Px/(1 + x)$, while the partial pressure of benzene in the gas is $p_g = \pi y/(1 + y)$. At equilibrium these two are equal—i. e.,

$$y = \frac{Px}{\pi - (P - \pi)x} \qquad (4)$$

This equation represents a rectangular hyperbola with axes parallel to the major axes.

Special Cases—(I) $P > \pi$. When stripping a volatile component from a non-volatile absorbent by steam, it is advantageous to have the temperature as high and the pressure as low as possible. Generally, therefore, the operating conditions are such that $P > \pi$. In this case inspection of the equilibrium, equation (4), shows that y becomes infinite when the denominator on the right-hand side is zero, when $x_a = \pi/(P - \pi)$, where x_a is the asymptotic concentration above which the dissolved constituent cannot exist in the absorbent liquid. If the absorbent enters the stripping column richer than this, the excess of dissolved vapor boils out spontaneously, reducing the concentration to the asymptotic value. The equilibrium curve is represented by Figure 3.

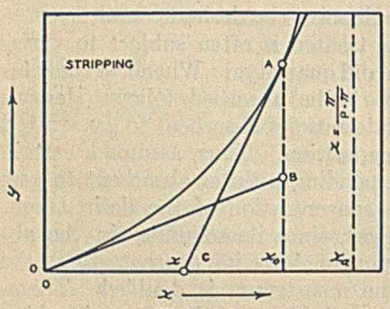


Figure 3

If, in this figure, x_0 represents the concentration of the incoming rich absorber stock, inspection will make it clear that, if one wishes to secure complete stripping—i. e., to have the operating line go through the origin—the steepest line which can be drawn is one tangent to the equilibrium curve at the origin, cutting the vertical line through x_0 at the point B, this point corresponding to the highest possible degree of saturation of the steam leaving the stripping column under these conditions. Inspection of the equilibrium, equation (4), shows that its slope is given by the expression

$$\frac{dy}{dx} = \frac{P\pi}{[\pi - (P - \pi)x]^2} \qquad (5)$$

Therefore, for complete stripping the operating line has for its slope the value of this expression at $x = 0$; i. e., $dy/dx = P/\pi$ or $dx/dy = \pi/P = G/L$, where G/L is the mols of steam required per mol of oil. Furthermore, it is obvious in this case that the equation of the operating line is $y = (P/\pi)x$ and that the steam consumption is proportional to the total pressure on the system and inversely proportional to the pressure of the pure solute at the operating temperature. In other words, the lower the total pressure the less the steam consumption necessary for complete stripping, and also the lower the volatility of the absorbed component the greater the steam necessary to do the work. Inspection, both of the diagram and of these equations, shows that the steam consumption for complete stripping is independent of the initial concentration of the rich absorber stock. From this it follows that if one is stripping from the oil a mixture of a number of dissolved components, since the more volatile strip out first, the steam necessary for complete stripping is that computed for the least volatile component, just as though the others were not present.

If one wishes to saturate the steam leaving the stripper—i. e., to bring it into equilibrium with the incoming rich stock—the steepest operating line attainable is a tangent to the equilibrium curve at a point A, cutting the horizontal axis at point C, corresponding to the best possible stripping compatible with the assumption made. The equation of this line can be calculated from its slope,

$$\frac{dx}{dy} = \frac{G}{L} = \frac{[\pi - (P - \pi)x_0]^2}{P\pi}$$

whence,

$$x_0 - x = \frac{[\pi - (P - \pi)x_0]^2\,(y_0 - y)}{P\pi}$$

Hence at the bottom of the apparatus, where $y = 0$,

$$x = x_0 - y_0\,\frac{[\pi - (P - \pi)x_0]^2}{P\pi}$$

This value of x represents the lowest attainable concentration of the stripped oil compatible with steam saturation at the top.

If $x_0 = x_a$, inspection of the diagram makes it clear that it is impossible to strip at all and at the same time have the vapors leaving the still at equilibrium with the absorber stock entering it. This is true because, under these conditions, the partial pressure of the entering absorber stock is equal to the total pressure on the still, so that the presence of any steam whatever would lessen the partial pressure of the solute and therefore destroy the equilibrium.

If, as is usually the case, a large fraction but not all of the benzene in the feed is to be removed, then x_1 is small but finite. The minimum steam consumption would then correspond to equilibrium at some value of x intermediate between x_0 and x_1, the operating line being tangent to the equilibrium curve at

$$x_t = \sqrt{\frac{\pi\, x_1}{P - \pi}}$$

Obviously this value of x is independent of x_0 and depends only on x_1, π, and P. Since the values of y_1, x_t, and x_0 are known, y_0 is computed by proportion:

$$y_0 = y_t\,(x_0 - x_1)/(x_t - x_1)$$

(II) $P < \pi$. Absorption should take place at the highest practicable total pressure and the lowest possible temperature—i. e., at high values of π and low of P. In other words, the conditions of this case ($P < \pi$) are those normally existing in absorption processes but not in stripping.

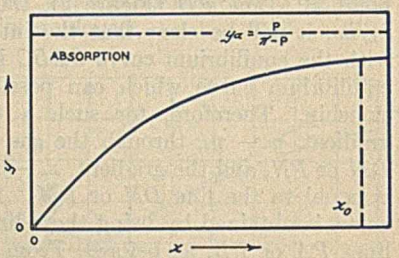


Figure 4

Inspection of the equilibrium equation makes it clear that it corresponds to the curve of Figure 4, being asymptotic to the horizontal line, $y = P/(\pi - P)$.

It is obvious that if one desires to denude the gas completely, the operating line must go through the origin and cannot possibly have a slope less than that corresponding to tangency there. Since at $x = 0$, $dy/dx = P/\pi$, the corresponding operating line is $y = Px/\pi$ and the amount of absorbent required per mol of inert gas treated, $L/G = P/\pi$. It will be noted that the absorbent required for a given amount of gas is proportional to the volatility of the solute absorbed and inversely proportional to the total pressure of the system. Here, too, the absorbent needed is independent of the initial concentration in the other phase at the other end of the unit. Since $y = Px/\pi$, it is obvious that $x_0 = \pi y_0/P$ = the maximum saturation of oil compatible with complete denuding of the gas treated.

To saturate oil up to equilibrium with the gas entering the absorber,

$$y_1 = y_0 - \frac{P\pi x_0}{[\pi + (\pi - P)x_0]^2}$$

This gives the lowest value to which the concentration of solute vapor in the exit gas can be reduced if the oil is brought up to equilibrium with the entering gas.

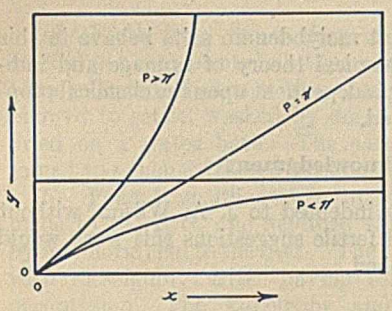


Figure 5

(III) $P = \pi$. For this case at equilibrium $y = x$, and it is therefore theoretically possible to have equilibrium at all points in the system, provided the capacity of the equipment is sufficient to carry out the absorption under a negligible driving force.

The conditions for the three cases are given in Figure 5, the upper curve corresponding to stripping, the lower to absorption, and the straight line between them to the special case of $P = \pi$. It is worth noting that in both stripping and absorption one normally operates on the unfavorable side of the equilibrium curve—i. e., it is theoretically impossible to secure equilibrium at both ends of the operating line. Were one absorbing under conditions corresponding to the upper curve or stripping under those of the lower, the reverse would be true. However, this disadvantage is more apparent than real, because the height of the equilibrium curve corresponding to stripping conditions, secured by raising the temperature and lowering the pressure, far more than compensates for its unfavorable shape, and the same is true of the advantages gained by lowering the equilibrium curve for absorption, through decreased temperature and increased pressure.

While for many cases of absorption Raoult's law does not apply, there are important instances, notably the absorption of hydrocarbons in oil, where it is a satisfactory approximation. Furthermore, even in those cases where the deviations are too wide to justify its quantitative use, it none the less gives a clear visualization of the qualitative effects of various factors upon operating results.

Molybdenum Tannage[1]

Joseph G. Niedercorn

A. F. Gallun & Sons Co., Milwaukee, Wis.

THE analogy between the compounds of chromium and those of molybdenum seemingly becomes more firmly established as the true character of molybdenum is better understood. This consideration gives rise to the conception that salts of tervalent molybdenum should form, with hide substance, unhydrolyzable compounds very similar to those formed in chrome tannage.

There are two sulfates of tervalent molybdenum, the purple-red and the green. The green sulfate has been assigned the formula $Mo_2O(SO_4)_2$;[2,3] the constitution of the red salt is as yet undetermined. Both salts are best obtained by the electrolytic reduction of a solution of molybdic anhydride in sulfuric acid, using a diaphragm cell and smooth platinum electrodes.[4]

In hydrochloric acid solution molybdic acid is reduced as follows:[5]

$$\underset{\text{colorless}}{Mo^{VI}} \longrightarrow \underset{\text{emerald-green}}{Mo^{V}} \longrightarrow \underset{\text{purple-red}}{Mo^{III}} \longrightarrow \underset{\text{olive-green}}{Mo^{III}}$$

In sulfuric acid solution the emerald-green salt was not obtained unless the solution was more strongly acid than was desirable for tanning purposes, inasmuch as it would become loaded with sodium sulfate in adjusting the acidity; instead, molybdenum blue, Mo_3O_8(?), was formed as intermediate product. In solutions nearly neutral the reduction did not proceed beyond molybdenum blue; in strongly acid solution it sometimes stopped at the red stage. No vivid green solutions, such as those that appear in the reduction of molybdenum salts with zinc in an atmosphere of hydrogen, were obtained.

An attempt was made to determine the acidity of the solutions potentiometrically, but this method proved uncertain because of the oxidation-reduction potentials which made the hydrogen-ion concentration seem much greater than it really was, especially in the case of the red solution.[5,6] According to Chilesotti,[7] platinum black exerts a catalytic influence upon molybdenum solutions, causing them to be reduced in the presence of hydrogen and then causing them to be oxidized. Because of the strong reducing action of the solution, indicators could not be effectively used, and therefore the acidities were controlled very inaccurately with the hydrogen electrode, making no allowance for oxidation-reduction potentials. *Apparent* acidities could be duplicated without difficulty.

Note—Oxidation with the evolution of hydrogen takes place immediately upon the reduction of all the metal to what is apparently the tervalent state, and occurs even in an atmosphere of hydrogen.

The green solution turned red upon standing, even if kept in a tightly stoppered bottle; it had no sharp precipitation point, but noticeable amounts of hydroxide appeared at pH 3 and kept increasing. At pH 9 complete precipitation had not taken place. The solution tanned calfskin well at apparent pH 2 to 2.5.

Probably because of the greater oxidation-reduction potential, the red solution showed a greater acidity than the green (the opposite is true of the corresponding chromium salts), and precipitated sharply at pH 2.5. It tanned very rapidly at pH 1–1.5, but at pH 2 it no longer penetrated into the skin.

Both salts yielded a dark brown leather that could be boiled without altering its condition. However, upon standing in the air it gradually lost this property; even then no hydroxide was removed by boiling—the skin merely shrank and hardened.

Experimental

A solution was made up by dissolving 40 grams of molybdic anhydride in 54 cc. of boiling sulfuric acid (sp. gr. 1.84)

[1] Presented before the Division of Leather and Gelatin Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

[2] Wardlaw, Nicholls, and Sylvester, *J. Chem. Soc.* (*London*), **125**, 1910 (1924).

[3] Chilesotti, *Gazz. chim. ital.*, **2**, 33 (1903).

[4] Wardlaw, Law, and Sylvester, *J. Chem. Soc.* (*London*), **123**, 969 (1923).

[5] Chilesotti, *Z. Elektrochem.*, **12**, 173 (1906).

[6] Clark, "The Determination of Hydrogen Ions," p. 242, Williams & Wilkins Co., Baltimore, Md., 1922.

[7] *Z. Elektrochem.*, **12**, 146 (1906).

to which had been added a few drops of nitric acid, and then diluting to 1 liter. The solution was then electrolyzed in a diaphragm cell, using a current density of 8 amperes per square decimeter at 15 volts.

When it had assumed a deep purple-red color, the solution was removed and showed an apparent pH < 0. This was not compatible with the quantity of acid added originally.

If the reduction were allowed to proceed to the green stage, the solution would show an apparent pH 0.5, which obviously was not its true acidity, although the figure is somewhat more reasonable than the one preceding.

To reduce the acidity, 1 *M* sodium carbonate solution was slowly added to the green molybdenum solution until apparent pH 2 was reached; in like manner the red solution was brought to pH 1–1.5.

No further neutralization was necessary during tannage; the pieces of skin were simply immersed in the solution and in about 24 hours tannage was complete.

Conclusion

The fact that tervalent molybdenum salts behave in this manner supports the chemical theory of tannage and indicates that tanning power is dependent upon the chemical properties of the salts involved.

Acknowledgment

The author is greatly indebted to J. A. Wilson, without whose kind interest and fertile suggestions this work would not have been accomplished.

Migration of Cane-Wax Complex through Stations of a Refinery[1]

C. F. Bardorf

St. Lawrence Sugar Refineries, Ltd., Montreal, Canada

Waxlike substances are extracted from refinery sugar liquors, raw sugar, blackstrap, etc., and by comparing the composition of the extracts it is endeavored to show that they pass through all stations of a refinery. The methods of gathering the wax complex are described and tables show how the composition of the extracts may vary when passing from the raw sugar to the final products, and to what extent the complex may be retained by Filter-Cel, paper pulp, etc. Finally, in a brief discussion of the significance of the data presented, it is pointed out that certain constituents of the complex, rather than the whole complex, should be considered as influencing refinery products.

In his "Report (No. 13) on a Preliminary Investigation of the Colloids of Cane Juice and Molasses," R. G. W. Farnell gives thirty-three references which convey a fair idea of the general interest and wide field of research that colloidal matter in sugar products of different origins has aroused in recent years. In the closing paragraph of the report four lines of investigation are indicated, and it is to the third of these—viz., "the examination of the wax present in juice, sirups, and molasses and its effect on manufacture"—that the data presented herein refer. Indeed, the nature of non-dialyzable substances in raw sugar is, no doubt, directly traceable to methods of defecation and subsequent operations in its manufacture; and in this respect not only is the quantity but also the composition of this wax complex of significance as a factor influencing refinery processes.

Through the recognition that this wax complex appears at different stages of refining operations, a series of preliminary experiments was undertaken. These experiments are necessarily but the "raw material" upon which subsequent investigations may be based. Most of the examinations were made with a view of explaining certain phenomena observed during the refining of the raw sugars listed in Table I. All these sugars were "centrifugals" of approximately 96 degrees polarization, but they exhibited very different qualities, irrespective of color or grain structure, in affination and press and char filtration.

Methods of Isolating Wax Complex

For the purpose of isolating the waxlike material in these sugars, and also the sirups and liquors produced from them, three methods were tried.[2]

Solution—Little need be said upon the possibility of extracting waxlike material by the solvent action of alcohol, ether, benzene (C_6H_6), carbon tetrachloride, or ethyl acetate. None of these solvents are of value when acting on the whole raw sugar; most of them dissolve an appreciable quantity of sugar, which cannot be separated readily from the extract. Furthermore, with the exception of hot acetone and hot alcohol (denatured 96.0 per cent) they are poor solvents of the cane-wax complex. Acetone and alcohol are, however, valuable for fractional separation of the constituents of the wax complex.

Trapping—This method consists of trapping the finer suspended matter by means of the flocculent precipitates of zinc or aluminum hydroxide or that caused by trisodium phosphate. In this work zinc hydroxide was used. The zinc precipitate settles rapidly, carrying down with it most of the suspended matter at the first addition of the precipitate. This can be washed by decantation, so that after the first three washings the precipitate is fairly free of sugar. The washed zinc hydroxide is then dissolved with a minimum of hydrochloric or sulfuric acid. The suspended matter so separated is treated for further examination.

Dialysis—This method has proved most satisfactory in that the sugar can be completely diffused and all the colloidal and suspended matter conveniently gathered for subsequent treatment and examination. The diffusion bags were made in 100-cc. test tubes and the collodion was prepared as prescribed by Holmes.[3]

The dialysis of a lot of sugar, in from 20 to 25 bags, each holding about 50 cc. of sirup (30° to 40° Brix), required from 24 to 36 hours. The bags were hung in a trough through which a current of hot water (80° to 85° C.) was flowing at the rate of about 10 liters per hour. At the end of this time the contents of the bags were free of sugar.

Sacks of fish membrane are not very satisfactory. If

[1] Presented before the Division of Sugar Chemistry at the 72nd Meeting of the American Chemical Society, Philadelphia, Pa., September 5 to 11, 1926. Received September 27, 1927.

[2] Farnell, *Intern. Sugar J.*, **26**, 420 (1924).

[3] "Laboratory Manual of Colloidal Chemistry."

heated they contract and become impermeable. In the cold, dialysis is so slow that the membrane tends to rot before completion of the process.

FOAM FROM SUGAR LIQUORS

(*a*) Froth from the surface of char-filtered liquors (85 to 88.0 per cent purity) and foam adhering to sides of tanks were collected, shaken with water, and diluted to 12° Brix; allowed to settle, washed by decantation, and the sediment dried on a water bath. The earthy-gray material so obtained was then extracted with acetone in a Wiley apparatus.

(*b*) Foam from affination sirup (greens) was also gathered, made to 12° Brix, and acidified with 20 cc. of concentrated hydrochloric acid to the liter. The acidified liquor was shaken with kieselguhr. After having settled it was washed by decantation. The kieselguhr and the trapped sediment were dried and the mixture was extracted with acetone. The results were practically the same as obtained under (*a*).

In each case the extract was of a fatty consistency as described under Properties of Fractional Extracts, Acetone Extract. The extract from the greens (*b*) was a little darker, tending to a brownish shade.

EXTRACTION OF WAX COMPLEX FROM RAW SUGAR BY DIALYSIS

Although other methods were investigated, dialysis proved the most satisfactory in all respects. The wax complex was obtained in a comparatively pure form, and could be easily collected from the bags and brought to dryness for subsequent examination. With due precaution this method should be fairly quantitative; indeed, it did give very valuable information in this respect, considering that there was little time to develop details of the method.

The dialysis was made upon the affination sirup of the respective sugars by repeatedly shaking the whole sugar with ice-cold water, and the sirup so obtained was dialyzed at 30° Brix, as already indicated. The liquid remaining in the collodion bags was collected, concentrated on a steam bath, and finally dried at 100° C. for 4 hours to constant weight.

Table I—Extracts from Raw Sugars Obtained by Dialysis

	Raw Sugar	Wax Complex in Whole Sugar
		Per cent
B. W. I.	Composite sample of 12 marks	0.24
I	San Domingo	0.38
II	Cuban	0.25
III	Cuban	0.25
IV	San Domingo	0.15
V	Cuban	0.18

It is not pretended that the percentages in Table I represent the true amount of the wax complex, but they are comparative, as all determinations were made along identical lines.

If, however, the ash content of the different extracts (Table III) is considered, and the total ash in the extract is calculated from these data, a nearer approximation of the true percentage of wax can be obtained. In illustration: B. W. I. extract, 0.24 per cent contains 17.25 per cent ash; I San Domingo extract, 14.87 per cent ash; therefore,

$$\text{B. W. I. } 0.24 - \left(\frac{0.24 \times 17.25}{100}\right) = 0.198 \text{ per cent wax complex}$$

$$\text{I San Domingo } 0.38 - \left(\frac{0.38 \times 14.87}{100}\right) = 0.3236 \text{ per cent wax complex}$$

Assuming that the extracts contain an average of 15 per cent of ash, then the content of the wax complex is as follows:

		Per cent
II	Cuban	0.213
III	Cuban	0.213
IV	San Domingo	0.128
V	Cuban	0.153

Again, if we regard the insoluble residue (Table III) of the B. W. I. and I San Domingo as containing little or no wax (and qualitative examination suggests this opinion), the true percentage on the whole sugar of these marks will be B. W. I., 0.197, and I San Domingo, 0.286.

PARTIAL INVESTIGATION OF EXTRACTS

The most interesting feature of the investigation so far undertaken lies in the data collected under this heading, and with reference to the migration of some of the constituents of the extracts passing through the different stations of a refinery. The composition of the extracts[4] from blackstrap and molasses, and extracts retained by Filter-Cel, etc.,[5] are to be considered.

The complex nature of the extracts is well illustrated by what may be termed "fractional extraction" of the material obtained by dialysis of raw sugars, refinery liquors and sweetwaters, and finally, blackstrap. The various extracts from the sugars listed in Table I were submitted to fractional extraction.

The composition of extracts from the B. W. I., I San Domingo, and II Cuban only (as representing extreme types) is given in Table II. As acetone, alcohol, and water were used as solvents, three fractions and a residue were obtained.

Table II—Fractional Extracts Obtained from Non-dialyzable Material

Solvent	I San Domingo	B. W. I.[a]	II Cuban
	Per cent	*Per cent*	*Per cent*
Acetone	14.95	13.14	27.20
Alcohol	33.68	10.80	34.29
Water	26.73	58.50	Not detd.
Insoluble residue	24.64	17.55	Not detd.

[a] If acetone and alcohol extracts only are considered as approximating true waxlike material, then B. W. I. contains 0.057, I San Domingo 0.185, and II Cuban 0.152 per cent. (See Table I.)

Table III—Ash Content of Extracts

Extract	I San Domingo	B. W. I.
	Per cent	*Per cent*
Acetone	0.63	1.55
Alcohol	3.64	19.07
Water	29.87	18.00
Residue	32.37	38.78

Table IV—Content of Ash from Residue

Constituent	I San Domingo	B. W. I.
	Per cent	*Per cent*
SiO_2	34.75	11.12[a]
CaO and MgO	24.03	19.19
Fe and Al oxides	15.74	8.34

[a] This was not pure silica but contained what is believed to be a complex phosphate. At any rate this had a decidedly different appearance from the silica obtained from I San Domingo.

Properties of Fractional Extracts

Acetone Extract—A greenish, buttery substance. Melts at 52° C. Not readily attacked by cold concentrated sulfuric acid.

Alcohol Extract—Separated into oily globules during evaporation, then settled to a brown, opaque, gumlike mass. Melts at 82° C. Not readily attacked by cold concentrated sulfuric acid.

Water Extract—Does not melt. Burns direct, leaving a fused crystalline ash.

Residue—Dirty dark brown, somewhat gritty. Humuslike and contains nitrogenous substances.

The properties of the alcohol extract are in accordance with those given by Thorpe:[6]

> It (sugar-cane wax) is a dull yellow, hard and can be powdered; it is insoluble in water, cold alcohol, and cold ether; hot ether dissolves it to some slight extent, and deposits it on cooling in small crystalline grains; boiling alcohol dissolves it completely, and the solution on cooling becomes semisolid just as does alcoholic soap solution. It melts at 82° C.

[4] Paine, Badollet, and Keane, *Ind. Eng. Chem.*, **16**, 1252 (1924).

[5] Paine and Walton, *Intern. Sugar J.*, **23**, 700 (1921); Wilnberg, *Ibid.*, **17**, 73 (1915).

[6] Dictionary of Applied Chemistry, Vol. V, p. 745.

As a matter of direct practical interest, another set of experiments was made upon the wax complex from II Cuban. The material collected for this experiment was separated by the trapping method and the product ground and treated with acetone and alcohol, giving three fractions, the third being the insoluble residue. The three fractions were evaporated to dryness in separate test tubes and then heated with 50 cc. of white sugar liquid (58° Brix) for 2 hours at 80° C. It was then noted that the sugar liquors had been considerably darkened—i. e., they had dissolved some of the extracts. The residue fraction gave a distinctly brown color to the liquid, while the acetone and alcohol extracts were both of a clean yellow tint. Although the acetone extract yielded little color to the liquor, it did give a decided indication of colloidal suspensions—a visible turbidity.

Migration of Colloidal Matter

In the preceding sections it has been shown that the colloidal matter extracted from raw sugars and the foam from char filtrates obtained from such sugars contains a wax complex yielding fractional extracts that always exhibit similar physical properties, especially marked in the acetone and alcohol extracts. In the sweet-waters from the char filters the presence of the wax complex was also observed. It therefore follows that correlated information on the migration of colloidal matter should be sought in intermediate and end products and the materials with which liquors carrying the colloids had come in contact. With this end in view blackstrap, greens, Filter-Cel, paper pulp, and press filter cloth were examined.

Extraction and Separation of Wax Complex from Blackstrap—*Preliminary Treatment of Blackstrap.* Blackstrap was diluted to 40° Brix and allowed to stand in a hydrometer jar for 24 hours at 50° C. At the end of that time a copious sediment had settled to the bottom of the jar. This sediment was drawn up through a pipet. The supernatant liquor was clear but not brilliant.

Dialysis of Sediment. The sediment, containing some of the liquid, was dialyzed in a fish-membrane sack. The nondialyzable material was a thick, muddy-looking fluid. On evaporating to dryness on a plate, a tough, buff-gray, earthy scale about $^1/_{16}$ inch (1.5 mm.) thick was obtained. On the surface of this scale a dark brown, waxlike coating had formed. This was the same as that obtained by dialysis of the liquid (see below).

Fractional extraction of this scale (from which the wax coating had been removed) yielded to acetone 6.41 per cent and to alcohol 10.42 per cent. The residue contained 23.80 per cent of ash insoluble in hydrochloric acid and 18.20 per cent of ash soluble in hydrochloric acid.

One gram of the dried scale (wax coating removed) was incinerated and gave 50.47 per cent ash, 24.41 per cent insoluble in hydrochloric acid and 26.04 per cent soluble in hydrochloric acid. The soluble ash contained 5.75 per cent silica.

Dialysis of Liquid. 280 cc. of the clear liquid were dialyzed in two fish-membrane sacks for 70 hours at 40° C. The contents of the sacks evaporated to dryness yielded a dark brown, lustrous, brittle, waxlike material. The 3.7 grams so collected were approximately 2.7 per cent of the blackstrap solids, exclusive of the sediment.

Two grams of this material submitted to fractional extraction showed acetone 6.23, alcohol 5.80, water 67.80, and residue 20.10 per cent. The insoluble residue was hard and gritty, and no doubt contained a large percentage of nitrogenous matter, as on heating on a platinum foil a disagreeable odor of burning bones was very noticeable.

Color Tests—Since the acetone, alcohol, and water extracts from this dialyzed blackstrap were similar to those obtained from raw sugars, it was a matter of practical interest to determine whether these extracts would yield a similar color to that from the white sugar liquor.

About 50 mg. of each of the extracts were heated with 50 cc. of white sugar liquor (58° Brix) at 84° C. for 90 minutes, and the liquors then examined for the color adsorbed. The Lovibond tintometer (1-inch cell used) showed the original liquor to contain 0.36 yellow tint. The colors found in the liquor after heating with the extracts were:

Extract	Yellow	Red	Blue	Total
Acetone	0.70	..	..	0.70
Alcohol	9.80	2.2	..	12.00
Water	36.00	16.5	2.50	55.00

The white liquor had not increased in color during the heating—viz., remained at 0.36 yellow.

In 1917 the writer made a tintometric determination of color adsorbed from raw sugar by diatomaceous earth.[7] It was observed that a good grade of earth as then used by refiners, shaken with a raw sugar solution (52.0° Brix) and agitated for 10 minutes at 85° C., had adsorbed 61.2 per cent of the color from the sugar solution. Ten grams of earth to 100 grams of solids in the sugar solution were used.

Color	Original Solution	Solution after Earth Treatment
Yellow	18.00	6.60
Red	3.80	1.60
Blue	0.15	..
Total	21.95	8.20

Consideration of this fact led to the examination of Filter-Cel, filter cloth, and paper pulp relative to their power of retaining colloids.

Wax Complex Retained by Filter-Cel—A Filter-Cel slurry from a Sweetland that had filtered its normal quota of washed sugar was put through a plate-and-frame press. The cake eventually formed (about 2 inches thick) was washed with hot water (90° C.) to practical exhaustion of the sugar, and dried and extracted with acetone and then alcohol.

Extract	*Per cent*
Acetone	1.796
Alcohol	1.792
Total	3.588

Wax Complex in Tissue of Filter Cloth—A piece of filter cloth cut from leaf of a Sweetland that had been used for filtering refinery greens (80 to 83 per cent purity) was extracted with acetone and then alcohol.

Extract	*Per cent*
Acetone	0.953
Alcohol	0.414
Total	1.367

Although this particular cloth was worn out and the leaf had to be redressed, the leaf and cloth were nevertheless washed and scrubbed in the refinery apparatus for that purpose. The extraction was then made on the dry cloth.

Wax Complex Retained by Paper Pulp—If the wax complex is retained, as indicated in the two preceding paragraphs, especially after the materials had been submitted to such thorough washing with hot water, then any paper pulp used in a Vallez press for the clarification of greens should also retain acetone- and alcohol-extractable matter.

Paper pulp was therefore prepared by pressing refinery greens (about 72 per cent purity) through an experimental Vallez press, washing the pulp to exhaustion of sugar, and then drying. Two lots were prepared, but one (*a*) was washed with water at 64° C. and the other (*b*) with water at 88° C.

[7] *Sugar*, **19**, 141 (1917).

A third lot (*c*) had been taken from Vallez filtering greens under the usual refinery practice. In these three instances similar retention of wax complex was found.

Extract	(*a*) 64° C.	(*b*) 88° C.	(*c*) 88° C.
	Per cent	*Per cent*	*Per cent*
Acetone	2.726	2.740	3.920
Alcohol	1.540	0.940	2.110
Total	4.266	3.680	6.030

Pulps (*a*) and (*b*) were washed at different temperatures because it was expected that by keeping the wash water a little below the melting point of the acetone extract more of this and also more of the alcohol-extractable portion would be retained by the pulp. This seems to be borne out by the determinations cited and also by a second set of extractions made upon another portion of pulp, which yielded to acetone (*a*) 3.034 per cent and (*b*) 2.828 per cent, showing that 7 per cent more of the fatlike extract had been retained in (*a*) over that of (*b*).

Trisodium Phosphate as a Trapping Agent—Although zinc and aluminum hydroxide precipitates were used for trapping suspensoids of a coarser type, a means was sought to remove some of the colloidal matter known to be left in liquors and greens after these had been clarified in the usual manner by Filter-Cel and pressing through Sweetlands. Superphosphate of lime (paste), phosphoric acid, and milk of lime and trisodium phosphate were tried, and the sodium salt was found to be the most efficient for this purpose.

Not only can satisfactory investigations be conducted by this reagent, but it can be applied with considerable advantage in connection with Filter-Cel in the clarification of greens, when these tend to be unusually charged with colloids after filter-pressing.

The efficiency of trisodium phosphate is well illustrated by the following experiment: One liter of greens was defecated with Filter-Cel and pressed, and the clear liquor (no visible turbidity) treated with 3 grams of trisodium phosphate, heated, and the precipitated calcium phosphate allowed to settle. (There are usually sufficient calcium salts in the liquor, but a little limewater may be added if necessary.) The precipitate and some of the liquid were then placed in a collodion sack and the non-dialyzable residue was dried and extracted with acetone and alcohol, yielding to acetone 0.147 and to alcohol 0.1605 gram. Both of these extracts possess all the properties described under Properties of Fractional Extracts.

The greens so treated had a purity of 85 per cent and therefore contained about 10 per cent of non-sucrose, excluding invert sugar and ash. A liter of greens of 52° Brix will contain 64.6 grams non-sucrose, 15 grams of which will be colloidal matter, so that the sodium salt had removed 2 per cent of the total colloidal matter.

Problems for Future Investigation

Among other migrations of the wax complex there are to be considered the adsorption by bone black and the difficulty of washing out the acetone extractable and other constituents. The rate and thoroughness of destruction of the complex in the chars passing through the retorts of the kilns must also receive attention and are in the program for future investigation.

Conclusions

It is somewhat hazardous to draw conclusions from the few data so far collected, but some speculation may be allowed. Although it may be admitted that the cane-wax complex from raw sugar, greens, and blackstrap is not uniform in composition, the fact that all the fractional extracts so far examined are exceedingly similar, at least in physical properties, leads to the conclusion that an approximation of uniformity of the wax in the cane itself may be more pronounced. Variation due to climate and soil, supplemented by different methods of manufacture may account for the diversity of composition of the extracts from raw sugars, etc.

In view of these considerations, and also from refinery experience, it seems reasonable to conclude that the three fractions extracted migrate, accumulate, and disperse in different degrees and have diverse influences on the final products of a refinery.

Little has been said about the water-soluble extract, but this can be traced as passing in solution to the char filters without, or to a slight extent only, forming dispersoids which cannot be trapped by diatomaceous earths or by flocculent precipitates. It is strongly adsorbed by bone black, of course, but only a small portion is removed by preliminary operations. It stains the collodion sacks and in practice darkens filter cloths, etc. It is the color-producing agent in distinction to the acetone and alcohol extracts, which contribute, in their disperse phases, to dull and gray products.

A remarkably high percentage of the acetone and alcohol extracts is retained by Filter-Cel, paper pulp, and cloth tissue. Furthermore, the acetone extract, despite its low melting point, is more tenaciously retained than the alcohol extract. This is illustrated in Table V. In the average of the first five items, the proportion of acetone and alcohol extracts is 45 to 53, while in the second five the proportion is 64 to 36.

Table V—Relative Percentage of Acetone and Alcohol Extracts

Source	Acetone	Alcohol
	Per cent	*Per cent*
I San Domingo	30.74	69.26
B. W. I.	56.77	43.23
II Cuban	46.10	53.90
Blackstrap, from 280 cc. clear liquid	51.70	48.30
Precipitated by Na_3PO_4	47.8	52.20
Extract from:		
Filter-Cel	50.05	49.95
Cloth	69.71	30.29
Pulp (*a*)	63.90	36.10
(*b*)	74.40	25.60
(*c*)	65.00	35.00

It seems reasonable to conclude, therefore, that the acetone and alcohol extracts of the wax complex tend to be strongly retained by Filter-Cel and cloth tissue; flocculent precipitates in general adsorb them with avidity, especially the acetone extract.

The data presented seem to justify the conclusion that the total percentage of the complex found does not *per se* prognosticate refinery trouble, but rather that the composition of the complex must be considered. Indeed, the objectionable features of the cane-wax complex, or cane colloids in general, lie chiefly in the high percentage of the cane-wax complex extractable by acetone and alcohol, particularly acetone.

Acknowledgment

The author is indebted to J. W. Schlegel, of the National Sugar Refining Company, New York, N. Y., for the paper pulp prepared for these investigations; to J. A. B. Ball, chief chemist of the St. Lawrence Sugar Refineries, and to F. J. Toole, of McGill University, who collected the preliminary data.

Calendar of Meetings

American Chemical Society—75th Meeting, St. Louis, Mo., April 16 to 20, 1928.

Pacific Northwest Regional Meeting—Reed College, Portland, Ore., April 6 and 7, 1928.

8th Midwest Regional Meeting—Minneapolis, Minn., June 7 to 9, 1928.

Division of Colloid Chemistry—6th National Colloid Symposium, Toronto, Canada, June 14 to 16, 1928.

Institute of Chemistry—Northwestern University, Evanston, Ill., July 23 to August 18, 1928.

American Electrochemical Society—Hotel Stratfield, Bridgeport, Conn., April 26 to 28, 1928.

Influence of Phosphate and Colloid Contents of Cane Juice on Defecation[1]

H. S. Paine, J. C. Keane, and M. A. McCalip

CARBOHYDRATE DIVISION, BUREAU OF CHEMISTRY AND SOILS, WASHINGTON, D. C.

A series of large-scale laboratory defecation experiments made during the recent sugar season in Porto Rico showed many significant facts concerning cane-juice clarification. The phosphate content of the raw juice, an important constituent from the standpoint of clarification by simple lime defecation, showed an approximately linear relation to the colloid elimination as determined by the dye test. The increased colloid elimination at higher phosphate content was accompanied by an increase in the weight and volume of mud. With increasing phosphate content of the raw juice the rate of increase in volume was greater than the rate of increase in weight of mud. This is of significance in connection with defecation capacity. Increasing the pH to which the juice was limed increased the colloid elimination and also materially increased the content of lime salts in defecated juice. The content of lime salts per 100° Brix showed a definite relation to the content of reversible colloids in defecated juices. Excess of lime in defecation apparently has a peptizing effect on the gummy substances in the juice, as there is an increase in quantity of reversible colloids proportionate to the increase in lime salts, a portion of which is of a colloidal character. It is believed that lime compounds are more deterimental in raw cane-sugar manufacture than is generally recognized, as they adversely affect boiling-house operations.

The juice at this factory was deficient in phosphates. The raw juice was defecated with and without the addition of phosphate, the juice being limed to the same pH value in each case. A comparison of the two groups showed a decided increase in colloid elimination as determined by ultra-filtration, an average relative improvement of 70 per cent for irreversible colloids, 20 per cent for reversible colloids, and 28 per cent for total colloids in the case of addition of phosphate. A distinct reduction in lime compounds per 100° Brix was noted in juices which had been defecated after addition of phosphate. A number of samples of juice were defecated both by single and double defecation, the procedure being as nearly as possible that used in sugarhouse operations. The colloid elimination by dye test was distinctly greater in double defecation, which method also gave a larger rise in apparent purity as well as a slightly better general appearance. This is attributable, in a measure at least, to colloid elimination by acid defecation of the lower purity juices where the quantity of mud is proportionately large.

LIME has been used for centuries as the principal agent for defecating cane juice in raw-sugar manufacture. Its relative inefficiency has been recognized for some time, but the many attempts which have been made to find satisfactory and economical defecating agents to replace it have so far resulted in failure. Lacking satisfactory substitutes or supplementary reagents, and realizing the need of improving the defecation of cane juice, considerable research has been directed in recent years to a detailed study of the functions and proper use of lime. The investigation described in this paper[2] is a continuation of work begun in Porto Rican sugar factories during the season of 1926[3] with the object of studying additional factors that influence defecation, particularly the relation between pH values and clarification, and the effect of the phosphate content of raw juice on colloid elimination.

Procedure for Studying Defecation at Various pH Values

Samples of raw juice were taken at the juice scales, mixed thoroughly, and passed through a 250-mesh screen, after which the Brix, purity, hydrogen-ion concentration, phosphoric acid content, lime content, and colloid content as shown by the dye test were determined. The screened juice was divided into three portions, and each was limed to a different pH value.

By a suitably arranged copper steam coil the separate portions of juice were heated to the boiling point and kept at this temperature for 1 minute before being transferred to steam-jacketed glass experimental defecators 2 inches (5 cm.) in diameter and 36 inches (91 cm.) in height. The samples were allowed to settle under close observation for 1 hour and 15 minutes at a temperature of 90° to 98° C. At the end of the settling period the volume of mud was noted, and the supernatant defecated juice was siphoned off. A portion of this juice was cooled, and the following determinations were made: hydrogen-ion concentration, colloid content as determined by the dye test, purity, color, lime content, and phosphoric acid content. The mud from each defecator was transferred to the container in which the limed juice was heated, mixed with a weighed quantity of specially prepared diatomaceous earth, and filtered through paper on a Büchner funnel. After being washed sugar-free, the mud was removed from the paper, transferred to a silica dish, and dried to constant weight at 80° C. under reduced pressure (25 inches or 635 mm. vacuum). The mud was then ashed at a low temperature; the loss in weight was expressed as percentage of organic matter.

Methods of Analysis

The quinhydrone electrode method[4] was used for determining pH values. The phosphoric acid and lime contents were determined in the ash from a 100-cc. portion of juice of known specific gravity; the lime was estimated by the oxalate method[5] (titrating with 0.1 *N* potassium permanganate), and the phosphoric acid by the volumetric molybdate method.[6] The colloid content of all samples was determined by the dye method.[7] This method consists in the mutual electrical neutralization and flocculation of the dye and the colloids of the juice; the end point of the reaction—namely, the exact neutralization of the electric charges on

[1] Presented before the Division of Sugar Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

[2] The authors wish to express their appreciation of the coöperation extended by the operating staff of Central Fajardo, Fajardo Sugar Co., Fajardo, Porto Rico.

[3] Paine and Keane, *Planter Sugar Mfr.*, **78**, 168 (1927).

[4] Dawson, *Sugar*, **28**, 211, 262, 310, 369 (1926).

[5] Assocn. Official Agr. Chemists, Methods, 1925, p. 41.

[6] *Ibid.*, p. 3.

[7] Badollet and Paine, *Intern. Sugar J.*, **28**, 23, 97, 137, 497 (1926); *Planter Sugar Mfr.*, **79**, 121 (1927).

Table I—Defecation of Dilute Juice at Various pH Values

Date	No.	Density (20° C.)	Apparent Purity	pH Before defecation	pH After defecation	Dye Value	Colloid Elimination by Dye Test	P_2O_5 Per 100 cc.	P_2O_5 Per 100° Bx.	CaO Per 100 cc.	CaO Per 100° Bx.	Mud Total volume	Mud Per 1000 cc.	Mud Per 100° Bx.	Ash in Mud	Remarks
			%				%	Gram	Gram	Gram	Gram	%	Grams	Grams	%	
Jan. 24	0[a]	12.45	74.40	5.00	...	1147	...	0.0149	0.1140	0.0335	0.2563	...	...	...	...	
	1	12.65	...	8.05	7.36	915	20.22	0.0059	0.0444	0.0432	0.3250	...	3.4104	2.5656	25.31	Dark, slow settling
	2	12.65	...	8.44	7.74	878	23.45	0.0042	0.0316	0.0481	0.3619	...	3.3018	2.4839	25.42	Lighter, better settling
	3	12.65	...	9.08	7.88	805	29.82	0.0052	0.0391	0.0594	0.4469	...	3.4561	2.6000	25.60	Lightest, slight turbidity
Jan. 31	0	12.40	79.40	5.16	...	1153	...	0.0247	0.1898	0.0281	0.2173	...	...	...	...	
	1	12.85	...	7.94	6.95	962	16.57	0.0058	0.0429	0.0486	0.3596	...	3.3752	2.5928	33.14	Poor juice, slow settling
	2	12.85	...	8.44	7.63	888	22.98	0.0049	0.0363	0.0464	0.3460	...	3.8564	2.8536	32.50	Best juice of series
	3	12.80	...	8.86	8.00	817	29.14	0.0047	0.0349	0.0610	0.3655	...	3.2622	2.4238	33.95	Light color, but turbid
Feb. 5 Fine screen	0	12.15	79.55	...	...	1060	...	0.0411	0.3230	0.0199	0.1568	...	...	...	...	
	1	12.10	82.10	8.24	7.66	828	21.89	0.0030	0.0244	0.0356	0.2806	19.0	4.2107	3.3188	36.00	Very good defecated juice, light color and sparkling
Coarse screen	0	12.15	79.55	...	...	1060	...	0.0410	0.3221	0.0159	0.1250	...	...	...	...	
	1	12.25	81.95	8.12	7.86	817	22.92	0.0034	0.0269	0.0340	0.2650	15.38	4.8668	3.7867	32.05	Same quality as with fine screening
Feb. 8 Cane cut 4 days	0	13.30	79.80	4.60	...	1071	...	0.0315	0.2249	0.0265	0.1891	...	...	...	...	
	1	13.10	...	7.94	6.76	835	22.04	0.0043	0.0314	0.0405	0.2937	...	4.7437	3.4397	40.28	Fair juice, poor settling rate
	2	13.15	...	8.35	7.32	758	29.22	0.0040	0.0290	0.0448	0.3236	...	5.8618	4.2335	41.23	Clarified juice turbid
	3	13.10	...	8.90	7.54	725	32.31	0.0041	0.0300	0.0464	0.3365	...	4.9855	3.6151	42.48	About same quality as No. 2
Feb. 14	0	12.90	74.80	5.10	...	1142	...	0.0224	0.1653	0.0210	0.1552	...	...	...	...	
	1	13.35	76.20	7.84	6.84	818	28.37	0.0039	0.0302	0.0388	0.2969	7.85	3.9018	2.9857	31.86	Good juice
	2	13.10	76.40	8.48	7.36	689	39.67	0.0036	0.0265	0.0426	0.3093	9.49	3.7450	2.7156	34.35	Good juice, faster settling
	3	13.10	76.60	8.94	7.72	689	39.67	0.0034	0.0247	0.0486	0.3524	9.75	3.8520	2.7932	34.42	Clarification same as for No. 2
Mar. 17	0	14.45	85.60	4.92	...	1014	...	0.0086	0.0566	0.0232	0.1517	...	...	...	...	
	1	14.85	86.55	8.16	7.56	921	9.17	0.0043	0.0274	0.0454	0.2884	6.58	3.5084	2.2285	22.29	Poor juice; dark and turbid
	2	14.95	85.64	8.62	8.03	835	17.65	0.0037	0.0233	0.0502	0.3166	6.10	3.5262	2.2240	20.02	
	3	14.90	85.37	9.10	8.48	775	23.57	0.0034	0.0215	0.0551	0.3482	7.80	3.9113	2.4756	23.15	
Mar. 24	0	14.30	84.97	5.00	...	1454	...	0.0166	0.1098	0.0205	0.1355	...	...	...	...	
	1	14.65	86.01	7.94	7.18	1095	24.69	0.0049	0.0318	0.0594	0.3828	6.28	2.8871	1.8604	23.64	Poor juice, dark, slow settling
	2	14.65	86.15	8.40	7.70	967	33.49	0.0041	0.0267	0.0605	0.3900	7.49	3.1592	2.0315	23.92	Fair juice, reddisn, good settling
	3	14.70	85.51	9.10	8.35	963	33.36	0.0045	0.0290	0.0724	0.4649	9.00	3.3455	2.1480	25.97	About same as No. 2
Apr. 1	0	12.60	82.15	4.92	...	1134	...	0.0100	0.0756	0.0156	0.1183	...	...	...	...	
	1	12.85	82.73	7.84	7.48	961	15.26	0.0032	0.0237	0.0329	0.2437	6.08	3.1038	2.2967	22.82	Dark and turbid
	2	12.85	82.96	8.54	8.15	908	19.93	0.0029	0.0219	0.0383	0.2838	6.15	2.9416	2.1767	23.47	Best juice of series, but still poorly clarified
	3	12.85	82.57	9.20	8.50	896	20.99	0.0025	0.0192	0.0453	0.3357	7.00	3.0268	2.2397	24.40	Better than No. 1 and slightly worse than No. 2
Apr. 12	0	13.65	81.32	5.14	...	868	...	0.0110	0.0768	0.0194	0.1350	...	...	...	...	
	1	14.10	81.76	7.80	7.00	757	12.78	0.0039	0.0265	0.0367	0.2464	5.32	2.8765	1.9301	17.39	Good juice, rapid settling
	2	14.00	82.06	8.58	7.62	744	14.29	0.0035	0.0242	0.0383	0.2592	5.38	2.8200	1.9065	16.63	
	3	13.95	82.27	9.06	8.10	780	10.14	0.0032	0.0222	0.0448	0.3042	5.75	2.7375	1.8577	16.57	Good juice, slower settling
Apr. 21 Fine screen	0	16.40	86.76	5.10	...	972	...	0.0089	0.0512	0.0172	0.0988	...	...	...	...	
	1	16.55	87.61	8.20	7.48	722	25.72	0.0035	0.0203	0.0415	0.2354	5.82	3.5531	2.0113	27.09	Dark, poor settling
	2	16.60	87.15	8.66	8.05	733	24.59	0.0035	0.0202	0.0496	0.2803	5.64	3.4651	1.9551	28.01	Reddish, poor settling
Coarse screen	3	16.60	87.10	8.66	8.03	733	24.59	0.0032	0.0185	0.0486	0.2742	6.25	4.1795	2.3580	23.65	About same as No. 2
May 3 Burned cane	0	12.50	82.80	5.16	...	1372	...	0.0152	0.1158	0.0140	0.1069	...	...	...	...	
	1	12.70	85.69	7.84	7.19	1274	7.14	0.0063	0.0472	0.0394	0.2952	5.32	3.1752	2.3787	31.87	Poor juice, poor settling
	2	12.70	86.72	8.34	7.94	1274	7.14	0.0060	0.0450	0.0454	0.3401	6.05	3.3882	2.5383	31.79	
	3	12.70	85.93	8.90	8.50	1236	9.92	0.0059	0.0442	0.0535	0.4008	7.25	3.2365	2.4246	30.76	Reddish, best of series
May 12 Heated to 97° C. Regular Superheated	0	14.40	83.96	5.06	...	1083	...	0.0291	0.1910	0.0346	0.2271	...	...	...	...	
	1	14.45	84.51	8.44	7.16	787	27.33	0.0042	0.0275	0.0529	0.3459	16.46	3.9669	2.5806	34.80	Slow settling, fair juice
	2	14.45	85.36	8.44	7.40	780	27.97	0.0041	0.0268	0.0535	0.3498	16.15	3.9857	2.6060	34.74	
	3	14.35	85.52	8.44	7.50	727	32.87	0.0045	0.0297	0.0524	0.3451	13.75	3.5809	2.3585	35.49	Rapid settling, darker
Apr. 7	0	14.40	80.90	5.20	...	1099	...	0.0189	0.1254	0.0210	0.1382	...	...	...	...	
	1	14.70	82.58	7.54	6.76	1024	6.83	0.0054	0.0349	0.0345	0.2219	8.35	3.3696	2.1635	20.60	Good juice, light
	2	14.65	81.15	8.20	7.44	1027	6.56	0.0043	0.0279	0.0396	0.2558	9.23	3.8831	2.5022	21.32	Good juice, light, rapid settling
	3	14.70	81.28	8.60	7.96	909	17.29	0.0044	0.0286	0.0448	0.2878	8.50	3.6155	2.3214	21.08	

[a] 0 indicates raw juice.

the colloid particles—is determined by means of an ultramicroscopic cataphoresis apparatus. In several samples, after the finely suspended non-colloidal material was separated approximately by filtration, the colloids were separated, and their quantity was determined, by ultrafiltration through standardized collodion membranes.[8]

[8] The preparation of standardized collodion membranes will be the subject of a publication by L. E. Dawson to be issued in the near future.

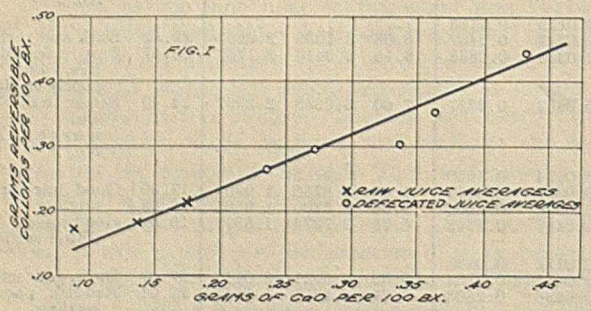
Relation between pH and Colloid Elimination

In considering the first series of experiments from the standpoint of pH and colloid elimination, some interesting correlations were obtained. These data are presented in Table I. The experiments were made at intervals during the season and represent tests on raw juices which varied considerably in composition, particularly as to their phosphate

content, the importance of which in cane-juice defecation has been well established.[9,3]

The different experimental lots of raw juice varied somewhat in composition, but as each lot of juice was limed to three pH values, the averages in the three groups equalize these variations in juice to a great extent and show principally the effect of increasing the quantity of lime. The samples limed the least gave defecated juices with an average pH of 7.18. The average colloid elimination in this group (limed to the lowest pH) was 18.3 per cent, and the average CaO content was 0.2899 gram per 100° Brix. The average pH value in the second group of defecated juices was 7.71, and the average colloid elimination was 22.3 per cent, which is a distinct increase over the group of lowest pH. The lime content, however, was increased to 0.3163 gram per 100° Brix. The defecated juices of group 3 (average pH value 8.05) gave the greatest average colloid elimination—namely, 25.3 per cent—but the CaO content was again increased, averaging 0.3572 gram per 100° Brix. The average apparent purity of the three groups of defecated juices was approximately the same.

From these data it is concluded that colloid elimination is unquestionably greater at the higher pH values. Increase in the quantity of lime increases the colloid elimination and likewise the volume and weight of mud. In addition, it also increases the lime-salts content of the clarified juice. In the opinion of the authors these lime salts have a distinctly detrimental action, and means of preventing their formation in excessive quantity should receive attention in every raw-sugar factory. The question as to whether the benefit derived from increasing the colloid elimination from 18.3 per cent to 25.3 per cent by increasing the quantity of lime is sufficient to offset the detrimental effect of increasing the CaO content from 0.2899 gram to 0.3571 gram per 100° Brix should be considered carefully.



During the course of these experiments many of the samples were ultra-filtered in order to determine the colloid content by this method and also to ascertain the relative quantities of colloids of reversible and irreversible types.[10] These data are compiled in Table II. As there is a considerable quantity of suspended material (of greater than colloid dimensions) in raw juice, even after screening, the best procedure for preparing the juice for the determination of colloids by ultra-filtration presents a difficult problem. Even though there is evidence that some colloidal material is removed when filtering cold raw juice with large quantities of diatomaceous earth, this procedure, followed by ultra-filtration, was adopted because it was thought to give a fairly correct value for the quantity of colloids present (particularly those of reversible type). The ultra-filtration data, however, have not been used as a basis for calculating colloid elimination, and it has been considered preferable, in interpreting the present data, to base colloid elimination on the dye values.

[9] Bond, *Ind. Eng. Chem.*, **17**, 492 (1925); Smith, Rept. of Raw Sugar Technical Committee, 1924, Hawaiian Sugar Planters' Assocn.

[10] Paine, *Reference Book of Sugar Industry of World*, **5**, No. 5, 53 (1927).

Although a small quantity of diatomaceous earth was used in filtering the hot defecated juice (to remove unsedimented particles of mud), filtration was rapid and there was no evidence that colloids were removed by this procedure.

Table II—CaO, Dye Value, and Colloids by Ultra-Filtration in Defecated Juice

Lot	pH	Dye Value	CaO (per 100° Bx.)	Colloids: Irreversible	Colloids: Reversible	Colloids: Total
			Gram	*Gram per 100° Brix*		
1	7.48	960	0.2437	0.030	0.414	0.444
	8.15	907	0.2837	0.037	0.400	0.437
2	6.76	1024	0.2219	0.034	0.307	0.341
	7.44	1027	0.2558	0.031	0.333	0.364
	7.96	909	0.2878	0.022	0.347	0.369
3	7.00	650	0.2463	0.012	0.244	0.256
	7.62	671	0.2592	0.008	0.236	0.244
	8.10	638	0.3042	0.020	0.207	0.227
4	7.48	654	0.2354	0.012	0.163	0.175
	8.05	658	0.2803	0.031	0.227	0.259
	8.03	665	0.2742	0.010	0.229	0.239
5	7.19	1054	0.2952	0.041	0.338	0.379
	7.94	1129	0.3402	0.065	0.372	0.437
	8.50	1054	0.4009	0.053	...	...
6	7.16	752	0.3473	0.012	0.263	0.275
	7.40	714	0.3478	0.015	0.278	0.293
	7.50	724	0.3463	0.016	0.296	0.312

A significant correlation between the CaO content and the reversible colloids of defecated juice (and also a few samples of raw juice) derived from the ultra-filtration data is shown in Figure 1. It may be noted that the correlation holds to some extent in normal raw juice but does not apply to the raw juice of deteriorated cane, in which case the reversible colloid fraction is greatly increased. The points on this curve represent averages obtained as follows: All lots of juice having a calcium oxide content between 0.05 and 0.10 gram per 100° Brix, those having a calcium oxide content between 0.10 and 0.15 gram, etc., were grouped together and the data on each group were averaged, both as to calcium oxide and reversible colloid contents.

Figure I shows that the calcium oxide content of defecated juice bears an approximately linear relation to the content of colloids of reversible type. This relation is of considerable significance. It indicates a detrimental effect of a high content of lime salts on certain phases of the raw-sugar process and the importance of avoiding the addition of lime in excess of a quantity which can be utilized profitably during defecation. Excessive liming in defecation has generally been considered principally from the standpoint of scale formation on heating surfaces, but a consideration of at least equal importance is its adverse effect on boiling-house operations owing to an increased quantity of viscous colloidal material in addition to lime salts.

The increase in the quantity of colloidal material of distinctly gummy character (reversible type) is possibly caused by the peptizing action of excess lime on the pectinous material in the cane juice, and possibly also by the liberation and dispersal of colloidal material flocculated or adsorbed by the lime precipitate; another possible explanation is the conversion of unflocculated irreversible colloids into those of reversible type. This dispersing effect seems to be more pronounced in cases where the quantity of lime added is in material excess of that which can be combined with the constituents of the juice and precipitated as insoluble compounds in the mud. It is possible that the relation shown in Figure I is due in considerable degree to chemical combination between calcium oxide and colloidal substances of reversible type. In other words, a considerable proportion of the "lime salts" present may consist of colloidal lime compounds. This possibility will be investigated.

In factory practice local overliming, which is caused by insufficient mixing of the lime with the juice before it is heated,

no doubt contributes to the effect discussed. The importance of producing a homogeneous mixture of the lime and juice before heating is quite generally recognized, but the data presented indicate a detrimental effect of poor lime distribution which is not generally considered.

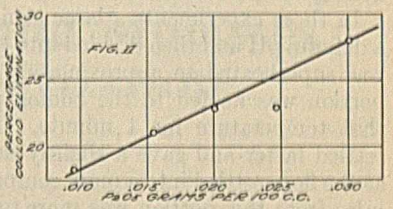
Effect of Phosphate Content on Colloid Elimination

In studying the data from this series of experiments, as recorded in Table I, a wide variation in the phosphate content of individual raw juice samples is noted. This variation furnishes the basis for other significant correlations. The weight of mud, for instance, was found to bear a definite relation to the phosphate content of the juice. This is to be expected since, with increasing phosphate content, a greater quantity of lime must be added to bring the juice to a given pH value and the weight of calcium phosphate precipitated is likewise increased.

The volume of mud in the defecators increased with the increasing phosphate content of the raw juice, but not proportionately to the weight of the mud. When comparing results obtained by using 40- and 250-mesh screens, it was noted that the weight of mud from raw juice which was passed through a fine screen was less, but the volume was greater, than that from juice which was passed through a coarse screen and similarly defecated. These are important considerations from an operating standpoint, since a juice which has a high phosphate content or which has been finely screened will require increased defecator capacity because it is impossible to thicken the mud in the usual length of time. Here again, juice from badly deteriorated cane constitutes an exception.

Data on the effect of the phosphate content of raw juice on colloid elimination as determined by the dye test are shown in Figure II. The points on this curve also represent averages. The various lots of raw juice are grouped according to their P_2O_5 content, and the average per cent elimination and P_2O_5 content of each group are compared. The effect that the pH value may have on percentage of colloid elimination is largely equalized by averaging the eliminations obtained at the three different pH values in each group. The data show that, up to a certain point at least, the quantity of colloidal material eliminated increases approximately in proportion to the P_2O_5 content of the juice. This is to be expected in a general way, when it is considered that juice of high phosphate content requires an increased quantity of lime and yields an increased quantity of precipitated calcium phosphate. However, the fact that even an approximate ratio exists between percentage colloid elimination and the P_2O_5 content of the juice raises a strong presumption that the elimination of colloids from cane juice by lime defecation is accomplished *primarily* through adsorption of colloids by the precipitated calcium phosphate.

In order to improve the quality of defecated juice it has been proposed recently to add phosphate to juices which are deficient therein. For the purpose of ascertaining the specific effect of the added phosphate on the removal of colloids, a series of experiments was conducted in which a number of samples of raw juice were defecated with and without the addition of phosphate. The samples were divided into two portions. One was defecated in the usual manner and to the other a small quantity of phosphate was added. Both portions were limed to approximately the same pH and the defecated juices were ultra-filtered. The results are presented in Table III, which shows also the average percentage increase in colloid elimination obtained by increasing the phosphate content of raw juice.



In addition to the increase in colloid elimination there was a relative decrease in lime salts in the portions to which phosphate was added. As in the natural cane juice, the weight and volume of mud increased with increased phosphate content. However, the volume of mud is so much increased at higher phosphate content that caution must be exercised in adding phosphate so as not to decrease materially the defecation capacity. When sufficient phosphate is added to the juice to bring the total to 0.035 gram of P_2O_5 per 100 cc. of dilute raw juice, it is questionable whether the benefit derived from further addition of phosphate is sufficient to offset the decrease in defecation capacity caused by the increased volume of mud and the cost of the additional materials required.

There appear to be two alternative methods of increasing the phosphate content of cane juices on a practical basis: (1) addition of phosphate to the juice as already indicated, which is the most direct method and at present the one that appears most feasible, or (2) application to the soil of certain combinations of fertilizers of high phosphate content. Application of a suitable type of phosphate fertilizer to the soil might serve the twofold purpose of increasing the tonnage and sugar yield per acre and at the same time increasing the phosphate content of the juice, thereby improving its "work-

Table III—Effect of Adding Phosphate to Raw Juice

No.	Density (20° C.)	Apparent Purity	pH Before defecation	pH After defecation	P_2O_5 (per 100 cc.)	CaO (per 100° Bx.)	Mud in Total Volume	Wt. of Mud (per 100° Bx.)	Dye Value	Colloids Irreversible	Colloids Reversible	Colloids Total	Remarks
		%			*Gram*	*Gram*	%	*Grams*		*Gram per 100° Brix*			
0[a]	15.50	82.97	4.82	...	0.0209	0.1803	...	...	...	...	...	...	
1	15.50	86.52	8.10	7.03	0.0042	0.3606	16.98	2.9680	781	0.008	0.223	0.231	P_2O_5 of raw juice adjusted to 0.0391 gm. per 100 cc.
2	15.65	85.20	8.42	7.68	0.0035	0.3739	8.50	2.4458	1074	0.023	0.329	0.352	No P_2O_5 added to raw juice
3	15.50	86.52	8.44	7.50	0.0040	0.3606	19.23	2.9346	781	0.006	0.191	0.197	P_2O_5 of raw juice adjusted to 0.0391 gm. per 100 cc.
0	13.25	79.24	5.02	...	0.0184	0.1316	...	...	...	...	...	...	
1	13.15	84.00	8.22	7.63	0.0044	0.4185	7.09	4.1706	1372	0.267	0.498	0.765	No P_2O_5 added
2	13.10	83.74	8.78	7.90	0.0041	0.4112	6.92	4.2769	1378	0.124	0.589	0.713	No P_2O_5 added
3	13.00	83.70	8.28	7.76	0.0028	0.3789	23.50	4.9744	1243	0.043	0.544	0.587	P_2O_5 of raw juice adjusted to 0.0464 gm. per 100 cc.
0	14.00	83.57	5.28	...	0.0090	0.0767	...	...	...	...	...	...	
1	14.35	84.05	8.48	7.76	0.0057	0.3561	...	...	989	0.054	0.269	0.323	No P_2O_5 added
2	14.05	84.20	8.22	7.54	0.0030	0.3044	...	...	640	0.012	0.197	0.209	P_2O_5 of raw juice adjusted to 0.0595 gm. per 100 cc.
0	12.50	77.84	5.16	...	0.0126	0.1892	...	...	...	...	...	...	
1	12.60	80.96	8.44	7.78	0.C037	0.4627	5.82	...	1509	0.078	0.404	0.482	No P_2O_5 added
2	12.15	80.25	8.44	7.76	0.0046	0.4135	8.00	...	1491	0.071	0.475	0.546	No P_2O_5 added, juice superheated to 110° C.
3	12.65	80.87	8.38	7.72	0.0031	0.4237	11.03	...	1279	0.023	0.395	0.418	P_2O_5 of raw juice adjusted to 0.0350 gm. per 100 cc.
Average per cent increase in colloid elimination at same pH value due to phosphate added										76.52	15.47	28.87	

[a] 0 indicates raw juice.

ability" in the factory. A preliminary experiment,[11] which substantiates some experiments by Walker[12] in Hawaii, indicated that adding such phosphate combinations to the soil will increase the phosphate content of the juice, but further experimental work along this line is required in order to arrive at a more definite conclusion regarding the conditions for obtaining maximum utilization of phosphoric acid by the cane.

Superheating of Juices

Another consideration in defecation is the temperature to which the cold-limed juice is heated. In practice the method of heating and the temperature to which juice is heated at this stage of the process vary, but slight superheating of the cold-limed juice is common. A laboratory superheater was designed for the purpose of studying the effect of superheating as compared with heating only to the boiling temperature.

In these experiments a large sample of juice was limed to a definite pH and then divided into two portions, one of which was superheated to approximately 110° C. while the other portion was heated to the boiling point and maintained at that temperature for 1 minute. The superheated portion settled faster and gave a slightly decreased volume of mud, as the flocs settled into a more compact mass. The defecated juice from this portion was more turbid, however, and somewhat darker in color. In two experiments in which the defecated juices were ultra-filtered, the quantity of reversible colloids in the superheated portion showed a slight increase when compared with the same juice heated only to the boiling point. No doubt the effect of superheating varies with different juices, judging from the evidence presented by other investigators,[13] particularly in juice superheated before liming. Each operator should therefore determine for himself whether any advantages are to be gained by such practice.

Double Defecation[14]

Because of the adoption of a double-defecation process of juice clarification by a large number of factories, several samples of juice were clarified both by single and by double defecation in order to determine the relative merits of the two methods. The procedure followed as closely as possible that used in practice. The mill juices were divided into two portions; crusher and first mill juices constituted the primary juice and the remaining mill juices comprised the secondary juice. A large sample of each was collected during the grinding of one car of cane. A portion of the primary juice was limed and defecated in the usual manner; a portion of the secondary juice was limed to about 6.8 pH (in the cold), and about 15 per cent of mud from factory defecators was added. This was substituted for primary mud in the preliminary defecation. The juice from the first primary defecation was drawn off and discarded. The mud was retained to be added to the next secondary defecation. The juice from the secondary defecation was siphoned off, cooled, and added to the raw primary juice in the ratio of 47.5 parts of defecated secondary to 62.5 parts of raw primary. This mixture was limed and sedimented in the usual manner. The resulting defecated juice was the double-defecated product.

Another sample of the same raw secondary juice was limed to about 6.8 pH and to it was added the mud from the previous primary juice in a quantity equal to 15 per cent by volume. This was heated to boiling and defecated; the resulting juice corresponded to the defecated secondary. Other portions of raw juice were mixed in the proportion of 60 parts of primary to 50 parts of secondary (corresponding to factory dilute juice), and the mixture was limed and defecated in the usual manner. The resulting juice was the single-defecated juice.

[11] Appreciative acknowledgment is hereby expressed for the coöperation of the Insular Experiment Station of Porto Rico, which conducted the field experiments.

[12] *Ind. Eng. Chem.*, **15**, 164 (1923).

[13] Muller, *Bull. assocn. chim. sucr. dist.*, **38**, 239 (1921); Bird, *Louisiana Planter*, **69**, 61 (1922); Farnell, *Intern. Sugar J.*, **25**, 358 (1923).

[14] This investigation was suggested by C. A. Bellows, general superintendent, Fajardo Sugar Co., Fajardo, P. R., to whom appreciation is hereby expressed.

Table IV—Comparison of Single and Double Defecation

Kind of Juice	Series	Density (20° C.)	Apparent Purity	pH	Dye Value	P_2O_5 Per 100 cc.	P_2O_5 Per 100° Bx.	CaO Per 100 cc.	CaO Per 100° Bx.	Colloid Elimination
			%			Gram	Gram	Gram	Gram	%
Raw primary juice "P"	1	16.95	79.23	5.18	1156	0.0214	0.1184	0.0388	0.2141	
	2	16.60	82.64	5.34	931	0.0105	0.0592	0.0248	0.1399	
	3	16.60	77.59	4.88	1129	0.0223	0.1258	0.0270	0.1523	
	4	15.45	82.20	4.80	807	0.0238	0.1452	0.0243	0.1480	
	Av.	16.40	80.42	5.05	1006	0.0195	0.1122	0.0287	0.1636	
Raw secondary juice "S"	1	9.15	76.62	5.04	2229	0.0191	0.2020	0.0211	0.2225	
	2	9.20	78.91	5.08	2210	0.0123	0.1296	0.0167	0.1751	
	3	11.00	73.55	5.25	1829	0.0179	0.1560	0.0254	0.2212	
	4	9.00	78.44	4.82	2092	0.0182	0.1956	0.0189	0.2027	
	Av.	9.59	76.88	5.05	2090	0.0169	0.1708	0.0205	0.2054	
Raw juice mixed 60 P + 50 S, calcd.	1	13.40	78.42	...	1644	0.0204	0.1445	0.0307	0.2177	
	2	13.24	80.94	...	1512	0.0113	0.0814	0.0211	0.1514	
	3	14.05	76.15	...	1447	0.0203	0.1368	0.0262	0.1769	
	4	12.52	80.97	...	1391	0.0213	0.1620	0.0218	0.1662	
	Av.	13.30	79.12	...	1499	0.0183	0.1312	0.0250	0.1781	
Clarified juice, single defecation	1	13.20	80.84	7.52	1583	0.0052	0.0378	0.0616	0.4431	3.71
	2	13.50	81.12	7.46	1124	0.0029	0.0208	0.0583	0.4096	25.66
	3	14.00	78.95	7.12	1353	0.0039	0.0267	0.0540	0.3651	6.50
	4	12.75	80.47	7.22	1230	0.0072	0.0539	0.0632	0.4715	11.57
	Av.	13.36	80.35	7.33	1322	0.0048	0.0348	0.0593	0.4223	11.86
Clarified juice, double defecation	1	13.70	81.98	7.58	1522	0.0049	0.0340	0.0594	0.4109	7.42
	2	13.70	82.05	7.48	968	0.0030	0.0214	0.0589	0.4074	35.98
	3	14.30	79.59	7.30	1124	0.0041	0.0274	0.0486	0.3213	22.32
	4	13.25	81.89	7.46	1110	0.0048	0.0380	0.0616	0.4793	20.20
	Av.	13.74	81.38	7.46	1181	0.0042	0.0302	0.0571	0.4047	21.48
Secondary clarified juice	2	10.65	78.22	6.18	1531	0.0082	0.0739	0.0361	0.3259	30.72
	3	11.80	76.70	6.50	1406	0.0127	0.1028	0.0345	0.2796	23.13
	4	10.05	78.31	6.48	1674	0.0073	0.0699	0.0410	0.3926	19.98
	Av.	10.83	77.74	6.39	1537	0.0094	0.0822	0.0373	0.3327	24.61

Table IV shows the average results from four complete experiments, all of which are in agreement. An increased elimination of colloids as determined by the dye test was obtained with double defecation. These results were substantiated by ultra-filtration in one instance, in which the reversible and irreversible colloid contents of the double-defecated juice were found to be slightly lower than in the single-defecated juice.

There was a greater rise in apparent purity in the double-defecated juice and its general appearance was also improved. This improvement is attributable, in a measure at least, to colloid elimination by the acid defecation of the secondary juices where the quantity of mud was proportionately large.

The primary muds introduced into the slightly limed secondary raw juice gave a large volume of flocculated material which served to adsorb and carry down a considerable quantity of colloids. The phosphate content of the secondary juice was found to be equal to or greater than that of the primary juice based on 100° Brix, so that a large part of the lime added to the secondary juice passed into chemical combination and was precipitated. From these few experiments, double defecation appears to be the more effective method, but further study of this particular phase of clarification is necessary, taking into consideration possible inversion losses during acid clarification, in order to determine whether the advantages gained would be offset by any sucrose losses.

Invertase-Free Yeasts and Their Application in the Selective Fermentation of Final Cane Molasses as a Preliminary Step to Desugarization[1]

V. Birckner and H. S. Paine

Carbohydrate Division, Bureau of Chemistry and Soils, Washington, D. C.

Notwithstanding the earlier failures, selective fermentation of final cane molasses should be of industrial interest. The commercial feasibility of desugarizing final molasses after selective fermentation of its dextrose and levulose has been effected may vary with the price of the molasses in relation to that of sugar. Even if market conditions are not always favorable, the operation of the process only when advantageous might be profitable and would tend to stabilize the price of final molasses.

Attempts by earlier workers to recover the 30 to 40 per cent of sucrose contained in final molasses after subjecting it to a selective fermentation with organisms that do not attack sucrose have not found practical application. The principal reason appears to have been that the investigators worked usually with only one organism which, although free from invertase, may not have been suited for the purpose in view. The experiments described demonstrate that invertase-free organisms vary in their effectiveness for selectively fermenting final cane molasses. It is therefore necessary to employ strains which will ferment the dextrose and levulose of final molasses with the greatest possible speed and completeness. The authors' experiments in this field have been fairly successful, and it is believed that the process deserves the attention of the cane-sugar industry.

Selective fermentation, as a preliminary step to desugarization by calcium (or strontium or barium) saccharate, would not only convert the dextrose and levulose of final molasses into a valuable product, but would also obviate the formation of decomposition products of these sugars, which would have an unfavorable effect on operation of the saccharate process. When the process is operated on the plantation, it is possible that, after converting the dextrose and levulose into alcohol and recovering the sucrose by a saccharate process (preferably calcium saccharate), the remaining liquor could be returned to the fields as fertilizer, thus making possible complete utilization of the molasses. The alcohol could be utilized on the plantation as motor fuel.

Microörganisms which ferment dextrose and levulose, but which lack the power to hydrolyze sucrose and consequently are unable to ferment this disaccharide, have been described by various authors, beginning with Gayon[2] about fifty years ago. An important contribution to this subject was made more recently by Klöcker,[3] who published a detailed study of the group of yeasts commonly known as *Saccharomyces apiculatus*. As nearly all these organisms were found to be non-spore-formers, Klöcker includes them in the family of the Torulaceae and assigns to them the new generic name *Pseudosaccharomyces*. He distinguishes sixteen species, seven of which he reports as being free from invertase. He also describes a spore-forming yeast, *Hanseniaspora Valbyensis*, which likewise contains no invertase.

The idea of utilizing invertase-free microörganisms for the purpose of transforming only the dextrose and levulose of final cane molasses into ethyl alcohol, as a preliminary step to the recovery of additional sucrose, was conceived by the early workers in this field, including men who were in close contact with the cane sugar industry.[4] Until comparatively recent years, the process appears to have been experimented with occasionally, only to be abandoned on account of various difficulties.

In the writers' experiments they have used mainly the above-mentioned organisms of the genus *Pseudosaccharomyces*, cultures of which were kindly furnished by the late Prof. A. Klöcker, of Copenhagen, Denmark. The cultures were received on cotton in small vials, and no great difficulty was experienced in obtaining growth after making transfers to a suitable medium. (One of the organisms, the *Pseudosaccharomyces Lindneri*, Klöcker, had died in transit.)

[1] Received September 27, 1927.

[2] *Compt. rend.*, **86**, 52 (1878); *Ann. chim. phys.*, [5] **14**, 258 (1878).

[3] *Centr. Bakt. Parasitenk.*, II Abt., **35**, 375 (1912); also in greater detail in *Compt. rend. trav. lab. Carlsberg*, **10**, 285 (1913).

[4] Gayon, *Compt. rend.*, **87**, 407 (1878); *Ann. Agron.*, **5**, 519 (1879); Mendes, *Bull. assocn. chim. sucr. dist.*, **2**, 372 (1884); McGlashan, U. S. Patent 751,990 (February 9, 1904); Pellet and Pairault, *Bull. assocn. chim. sucr. dist.*, **23**, 639 (1905).

There was thus an opportunity to make a comparative study of a number of species of invertase-free organisms and of their behavior in cane molasses. The experiments were carried out at first with small batches of liquid (less than 1 liter), such as are commonly employed in laboratory experiments. Later the process was applied to larger volumes, 10 to 12 gallons of dilute blackstrap being subjected to the selective fermentation. It appears from this work that these invertase-free organisms are not equally well adapted to the selective fermentation of molasses. This fact has probably been overlooked in earlier attempts to utilize the process. Usually the earlier trials were conducted with only one organism, and it was not realized that for best results the organism must not only be devoid of invertase but must have a special adaptation for cane molasses; that is, it must convert the fermentable monoses of the cane molasses with the greatest possible speed and completeness.

A set of cultures of the same organisms was also purchased from the bacteriological collection of E. Przibram, in Vienna, Austria, together with cultures of two other organisms—*Schizosaccharomyces octosporus*, Beijerinck, and *Saccharomycopsis capsularis*, Schjönning. The last two organisms are reported in the literature as being unable to ferment sucrose. This was not the case, however, with the cultures received. Although apparently uncontaminated, they were either not true to name or they had as a result of faulty methods of cultivation developed invertase secondarily. In the struggle for existence an organism which contains no invertase would be more likely to succumb from starvation than its competitors. On the other hand, the formation of an enzyme by a unicellular organism would not appear to involve such profound changes in its character as to be impossible. In the course of their experiments the writers have repeatedly observed that invertase-free organisms when allowed to remain on wort-agar slants for many months or perhaps a year without being transferred, even when kept in a refrigerated room at +1° C., had acquired the property of attacking sucrose. Hence, these organisms seem to be devoid of invertase only so long as they are plentifully supplied with nutrients, especially sugar, that can be utilized without previous inversion. If the food (and moisture) supply becomes low, these organisms appear to develop invertase, thereby being able to utilize to better advantage their decreasing supply of nutrients. These views are contrary to those of Klöcker who regarded the presence or absence of invertase in a certain organism as an inherent quality of the species. In connection with the above deductions, it would be of interest to learn whether the inversion of sucrose is a necessary prerequisite for the utilization of this disaccharide as food for the organism as well as for the process of fermentation. On the basis of the researches of Will[5] this question could probably be answered in the affirmative. The work of this author forms a valuable supplement to that of Klöcker. Both men published their results as contributions to science, without being concerned with the practical aspects of the matter.

The present writers also tested a strain of *Saccharomyces apiculatus*, Reess.[6] The organisms studied are designated by number throughout this paper, the source of the culture being indicated when necessary. The following is a list of the organisms used, together with the number assigned to each species:

	No.
Pseudosaccharomyces apiculatus, Reess-Hansen	1
Pseudosaccharomyces austriacus, Klöcker	2
Pseudosaccharomyces africanus, Klöcker	3
Pseudosaccharomyces corticis, Klöcker	4
Pseudosaccharomyces Mülleri, Klöcker	5
Pseudosaccharomyces germanicus, Klöcker	6
Saccharomyces apiculatus, Reess	7
Hanseniaspora Valbyensis, Klöcker	8
Schizosaccharomyces octosporus, Beijerinck	9
Saccharomycopsis capsularis, Schjönning	10

All except a few of the last experiments were pure-culture fermentations; that is, the medium to be acted upon was sterilized by autoclaving and, after cooling, was inoculated with a pure culture of the organism used, care being taken to prevent subsequent contamination. All experiments were carried out at room temperature (about 25° C.). The organisms were kept in culture by transferring them at intervals to fresh wort-agar slants.[7] After several such transfers the various strains were allowed to grow on sterile beer wort or sterile molasses in order to prevent degeneration. After this revivification in the liquid medium, the cultures were again kept on wort agar. Although an attempt was made to keep the cultures under uniform conditions, this aim could not be fully realized. When the activities of the organisms on a given medium were studied and compared, and it was found upon repeating the comparison many months later that somewhat different results were obtained, such variations were probably due to changes in the character of the respective organisms as a result of non-uniform cultural conditions. The importance of maintaining proper moisture and food conditions for these organisms has already been stressed.

Behavior in Synthetic Media

A few experiments were made to study the behavior of the organisms on colorless media containing dextrose. An aqueous 10 per cent dextrose solution containing in 1 liter 20 cc. of yeast water was prepared, and 25-cc. portions of this solution were pipetted into 100-cc. volumetric flasks. The flasks were autoclaved and inoculated, a trace of the respective organism being introduced into each flask by means of a platinum needle. Table I*a* records the losses in weight observed with these cultures after a number of days.

Table I*a*—Fermentation of a Dextrose-Yeast Water Medium by Invertase-Free Organisms

Organism	Source	Total Loss in Weight on Various Days	
		4	7
		Gram	*Gram*
1	Copenhagen	0.079	0.156
1	Vienna	0.063	0.148
2	Copenhagen	0.080	0.156
2	Vienna	0.064	0.133
3	Copenhagen	0.090	0.170
3	Vienna	0.111	0.207
4	Copenhagen	0.060	0.130
4	Vienna	0.066	0.128
6	Copenhagen	0.064	0.125
6	Vienna	0.050	0.101
7	England	0.092	0.186

Blank determinations with flasks that had not been inoculated showed that the loss from evaporation alone was about 0.1 gram per week for each flask.

It was thought that the organisms might show greater activity if supplied with some nutrient salts. Accordingly, on the eighth day 5 cc. of each of the above cultures were transferred to other flasks by means of sterile pipets. The composition of the new medium, which showed a pH of 6.2[8] and of which 30 cc. had been placed in each flask, was as follows: one liter contained 50 grams dextrose, 5 grams $(NH_4)_2SO_4$, 4 grams KH_2PO_4, 1 gram K_2HPO_4, and 5 cc. yeast

[5] *Centr. Bakt. Parasitenk.*, II Abt., **44**, 225 (1915).

[6] Culture supplied by Edwin LeFevre, of the Food Research Division; originally obtained from England.

[7] The writers wish to express their indebtedness to Chas. Thom, then in charge of the Microbiological Laboratory of the Bureau of Chemistry, for the use of certain facilities of his laboratory.

[8] All pH values reported in this paper were determined electrometrically, using the quinhydrone electrode as described by L. E. Dawson of this laboratory [*Sugar*, **28**, 211, 262, 310, 369 (1926)].

water. The progress of the fermentations after the inoculation of this medium is shown in Table I*b*.

Table I*b*—Fermentation of a Dextrose-Salt Mixture without Nitrate Nitrogen

Organism	Source	Total Loss in Weight on Various Days			
		4	7	9	13
		Gram	*Gram*	*Gram*	*Gram*
1	Copenhagen	0.085	0.158	0.206	0.315
1	Vienna	0.091	0.226	0.277	0.398
2	Copenhagen	0.129	0.230	0.291	0.430
2	Vienna	0.120	0.219	0.269	0.377
3	Copenhagen	0.070	0.140	0.188	0.295
3	Vienna	0.076	0.146	0.202	0.318
4	Copenhagen	0.075	0.157	0.210	0.337
4	Vienna	0.067	0.138	0.193	0.313
6	Copenhagen	0.082	0.165	0.222	0.359
6	Vienna	0.060	0.131	0.177	0.290
7	England	0.109	0.205	0.260	0.397

Five cubic centimeter portions of these cultures were now transferred to another medium, the composition of which differed from the formula given above only to the extent that the 5 grams of ammonium sulfate had been replaced by 2.5 grams of ammonium nitrate. The pH of the new medium was 6.0. The loss in weight observed in this case is shown in Table I*c*.

Table I*c*—Fermentation of a Dextrose-Salt Mixture Containing Ammonium Nitrate

Organism	Source	Total Loss in Weight on Various Days				
		3	5	7	9	12
		Gram	*Gram*	*Gram*	*Gram*	*Gram*
1	Copenhagen	0.112	0.150	0.185	0.219	0.271
1	Vienna	0.083	0.160	0.237	0.303	0.390
2	Copenhagen	0.117	0.196	0.249	0.302	0.375
2	Vienna	0.158	0.272	0.391	0.475	0.587
3	Copenhagen	0.075	0.117	0.155	0.191	0.255
3	Vienna	0.085	0.126	0.172	0.217	0.282
4	Copenhagen	0.080	0.120	0.161	0.189	0.259
4	Vienna	0.075	0.112	0.148	0.185	0.241
6	Copenhagen	0.122	0.194	0.262	0.326	0.424
6	Vienna	0.089	0.139	0.181	0.224	0.290
7	England	0.134	0.224	0.274	0.318	0.390

Tables I*a* to I*c* show that the organisms differ in their behavior in these media. Nos. 3 and 7 were the most active, comparatively speaking, on the purely organic medium (Table I*a*). The addition of inorganic salts lessened the activity of organism 3. The addition of these salts was neither harmful nor beneficial to Nos. 1 and 4. The activity of Nos. 2 and 6 was distinctly increased by the salts, whereas in organism 7 no distinct improvement was observed in the medium containing only ammonia nitrogen, but the introduction of nitrate nitrogen caused a pronounced acceleration of the rate of fermentation. These findings illustrate the fact that wide variations are liable to occur in the biochemical behavior of the invertase-free organisms which were used in these experiments.

Comparison of Different Lots of Molasses

It seemed possible that the same organism might give different results with different lots of molasses. In order to investigate this point, dilutions of three lots of cane molasses were prepared, all possessing approximately the same initial pH value (5.7) and the same density (22.6° Brix). The three lots of molasses had been produced in Cuba, Porto Rico, and Louisiana. Table II shows their composition.[9]

Table II—Composition of Cane Molasses Used in Fermentation Experiments

	Cuba	Porto Rico	Louisiana
Brix reading	79.08	85.40	88.66
Total solids, per cent	75.74	79.14	81.98
Direct polarization	26.10	28.23	33.10
Sucrose (invertase method), per cent	30.66	35.00	38.58
Invert sugar, per cent	16.20	17.19	17.18

Twenty-five cubic centimeter portions of the dilute solutions were pipetted into 100-cc. volumetric flasks, which, after sterilization and cooling, were inoculated with the different organisms by means of a platinum needle. The flasks were weighed immediately after inoculation and at intervals thereafter. The results, the details of which are omitted here, showed clearly that this sample of Louisiana molasses was not well suited as a medium for the invertase-free organisms, compared with the Cuban and Porto Rican molasses. The last two were fermented about equally well. The Cuban molasses was used in most of the subsequent experiments.

Selection of Most Suitable Organism

The next problem was to determine from among the various organisms available those which would be best suited for the selective fermentation of the molasses used. In order to do this, it was necessary to compare the action of the various organisms under a variety of conditions and by means of chemical control to ascertain which strains excelled in transforming the fermentable monoses of the liquors rapidly and completely without attacking the sucrose.

Statements have appeared in the literature to the effect that the presence of chemically inert materials (adsorbents), such as carbon, kieselguhr, and kaolin, in a medium exercises a beneficial influence on yeast fermentations. Some experiments were made with the object of finding out whether these statements would apply to the organisms under investigation. The influence of the addition of one per cent of kieselguhr on the rate of fermentation was studied. A small amount

[9] These analyses were made by M. A. McCalip of this laboratory.

Table III—Influence of Kieselguhr on Selective Fermentation[a]

Organism	Source	Kieselguhr	Total Loss of Weight on Various Days after Inoculation											
			2	3	4	5	6	7	9	10	12	13	21	25
			Gram	*Gram*	*Gram*	*Gram*	*Gram*	*Gram*	*Gram*	*Gram*	*Gram*	*Gram*	*Gram*	*Gram*
2	Vienna	Without	*0.290*	*0.523*	*0.709*	*0.864*	*1.009*	*1.109*	*1.252*	*1.324*	*1.445*	*1.487*	1.651	1.723
		With	*0.280*	*0.533*	*0.732*	*0.899*	*1.040*	*1.148*	*1.302*	*1.378*	*1.510*	*1.559*	1.796	1.902
5	Copenhagen	Without	*0.134*	*0.378*	*0.581*	*0.779*	*0.975*	*1.112*	*1.318*	*1.412*	*1.561*	*1.610*	1.882	2.009
		With	*0.169*	*0.377*	*0.555*	*0.722*	*0.874*	*0.979*	*1.129*	*1.195*	*1.301*	*1.338*	1.558	1.662
6	Copenhagen	Without	*0.258*	*0.480*	*0.674*	*0.852*	*1.017*	*1.128*	*1.278*	*1.338*	*1.420*	*1.449*	1.647	1.746
		With	0.046	0.069	*0.251*	*0.535*	*0.796*	*0.972*	*1.208*	*1.302*	*1.432*	*1.475*	1.723	1.842
3	Copenhagen	Without	*0.225*	*0.574*	*0.909*	*1.191*	*1.368*	*1.450*	*1.541*	*1.582*	*1.638*	*1.659*	1.836	1.927
		With	0.048	*0.273*	*0.640*	*1.014*	*1.280*	*1.406*	*1.518*	*1.551*	*1.602*	*1.622*	1.794	1.875
3	Vienna	Without	*0.225*	*0.595*	*0.983*	*1.282*	*1.474*	*1.579*	*1.691*	*1.728*	*1.790*	*1.817*	2.022	2.122
		With	*0.120*	*0.387*	*0.692*	*1.004*	*1.267*	*1.400*	*1.528*	*1.567*	*1.627*	*1.666*	1.907	2.008
4	Copenhagen	Without	*0.325*	*0.730*	*1.052*	*1.304*	*1.449*	*1.511*	1.566	1.589	1.634	1.657	1.839	1.927
		With	*0.165*	*0.552*	*0.925*	*1.248*	*1.424*	*1.473*	1.515	1.535	1.574	1.592	1.745	1.818
4	Vienna	Without	*0.295*	*0.688*	*1.019*	*1.292*	*1.468*	*1.524*	1.583	1.607	1.658	1.680	1.871	1.963
		With	*0.182*	*0.540*	*0.905*	*1.230*	*1.422*	*1.475*	1.521	1.539	1.576	1.593	1.734	1.801
7	England	Without	0.046	0.073	*0.175*	*0.389*	*0.628*	*0.816*	*1.100*	*1.224*	*1.422*	*1.489*	1.786	1.916
		With	0.047	0.070	*0.103*	*0.195*	*0.414*	*0.609*	*0.921*	*1.062*	*1.293*	*1.379*	1.715	1.839

[a] Data obtained by H. Swett, who was temporarily connected with this laboratory. The periods of active fermentation are shown by the figures in italics.

of top yeast extract was added when preparing the molasses medium. The Brix reading of the medium, when ready for the autoclave, was 22.45°. Twenty-five cubic centimeter portions were pipetted into sixteen 100-cc. volumetric flasks, arranged in two series of eight flasks. One series was autoclaved directly, while to each flask of the other series 0.25 gram of kieselguhr was added before autoclaving. One flask of each series was inoculated by means of a platinum needle with one of the eight organisms listed in Table III. The flasks were then weighed, and the weighings were repeated daily.

The results recorded in Table III show that the kieselguhr caused a slight acceleration in organisms 2 and 6, but no acceleration (possibly even a slight retardation) in the other five strains. The active fermentation period of strain 4, as indicated by the italicized figures, was shorter than that of any other strain. By a similar experiment it was ascertained that the suspended material which is present in cane molasses, and which becomes more noticeable upon dilution, has no appreciable influence on the rate of the selective fermentation.

The change in the composition of molasses caused by these organisms was next investigated. The analytical methods used first were replaced later by others which were found more suitable. In the earlier work the method of Scales[10] was used for the reducing-sugar determinations. The absolute quantities of sugar are difficult to ascertain, however, with this iodometric method on account of the high values obtained for the blank determinations with the diluted molasses. Instead of calculating the weights of reducing sugars, the writers merely noted the number of cubic centimeters of thiosulfate solution required for the final titration which should bear a definite relation to the quantity of sugar reduced by Scales' reagent. This number is reported under the caption Reducing Sugar Index in Tables IV and V*b*. The sucrose was determined by the invertase method;[11] the figures in Tables IV to VIII*c* represent grams of sucrose found in 100 grams of the final diluted liquors, or they were derived from this source.

One hundred cubic centimeter portions of molasses diluted 1:4 (20.4° Brix) were pipetted into 200-cc. volumetric flasks, which were then plugged with cotton and autoclaved. After cooling, they were inoculated by means of a needle, and weighed at intervals. After the fermentations were completed, each flask was filled to the mark with water and the contents were analyzed. The results are shown in Table IV.

Table IV—Change in Composition of 20.4° Brix Molasses when Fermented by Invertase-Free Yeasts

Organism	Source	Loss in Weight on Various Days				Direct Polarization	Sucrose (Invertase Method)	Reducing Sugar Index
		5	7	16	30			
		Gram	*Gram*	*Grams*	*Grams*	*Grams*	%	
4	Copenhagen	0.35	0.35	1.37	2.20	4.35	4.34	3.10
4	Vienna	0.25	0.25	1.10	2.00	4.10	4.36	5.10
3	Copenhagen	0.40	0.40	1.20	2.35	4.37	4.51	4.07
3	Vienna	0.40	0.45	1.25	2.25	4.25	4.36	5.83
6	Vienna	0.40	0.30	0.60	0.95	3.80	4.49	High
2	Vienna	0.30	0.30	0.90	1.25	3.90	4.34	High
5	Copenhagen	0.40	0.55	1.43	2.25	3.90	4.05	3.94
7	England	0.30	0.35	1.20	1.85	4.21	4.26	5.22
10	Vienna	0.20	0.60	2.20	4.15	1.36	1.62	4.88
Molasses not inoculated		..	..	0.30	0.75	3.57	4.05	24.76

These data show that strain 10, obtained from Vienna, was unsuited for selective fermentation as it readily attacked sucrose. The four species of *Pseudosaccharomyces* obtained from the same source, even though free from invertase, compared unfavorably with those obtained from Copenhagen, Nos. 2 and 6 from Vienna showing very little development, and Nos. 3 and 4 from Vienna being incapable of attacking the reducing sugar of the molasses satisfactorily.

In cane molasses which has undergone complete selective fermentation the direct polarization practically coincides with the percentage of sucrose, which is not the case with unfermented molasses on account of its invert-sugar content. It is known that usually a portion of the reducing substances present in cane molasses resists the action of fermentation organisms. When fermenting Cuban blackstrap molasses with these invertase-free organisms, the quantities of nonfermentable reducing substances were never found to be less than 10 per cent of the total reducing substances (calculated as invert sugar) present before fermentation.

In the next experiment liquid starters were used. Molasses solutions of 20.4° Brix were inoculated by means of a platinum needle with organisms 4 and 5, both from Copenhagen, and these cultures served as starters for the inoculation of two series of solutions in 250-cc. volumetric flasks, each of which contained 165 cc. of molasses of the same density. One and a half cubic centimeters of actively fermenting starter were introduced into each flask by means of sterilized graduated pipets. The record of the consecutive losses of weight is given in some detail (Table V*a*), as it serves for a comparison of the two organisms and also permits one to judge to what extent variations occur.

Table V*a*—Progress of Selective Fermentation Judged by Loss in Weight

Time Fermented	Total Loss in Weight							
	Organism 4				Organism 5			
	(1)	(2)	(3)	(4)	(1)	(2)	(3)	(4)
Days	*Grams*	*Grams*	*Grams*	*Grams*	*Grams*	*Grams*	*Grams*	*Grams*
2	0.09	0.10	0.11	0.09	0.12	0.13	0.11	0.15
3	0.21	0.23	0.24	0.22	0.21	0.22	0.21	0.27
5	..	..	..	..	0.42	0.42	0.40	0.54
6	0.62	0.64	0.65	0.59	0.59	0.60	0.57	0.74
8	0.90	0.92	0.94	0.86				
9	1.07	1.09	1.10	1.02	1.05	1.07	1.03	1.31
11		1.31	1.33	1.22		1.41	1.34	1.69
12		..	..	..		1.60	1.53	1.89
14		1.61	1.63	1.51		1.81	1.72	2.10
17		1.93	1.94	1.83		2.08	2.00	2.40
20			2.22	2.10			2.30	2.73
22			2.30	2.17				
23							2.55	2.99
24			2.47	2.34				
25							2.60	3.06
27								3.24
29				2.62				
31				2.69				
32								3.52
34				2.87				3.59

At the end of the active fermentation period, and at intervals thereafter, one flask of each series was filled to the mark with water, filtered, and analyzed. To the flask which was analyzed at the beginning of the experiment the starter had been added in the same manner as with the other flasks, but the yeast was inactivated at once by the addition of 50 cc. of strong alcohol. The analytical data are shown in Table V*b*.

Table V*b*—Change in Composition of Fermenting Molasses

Time Fermented	Loss in Weight	Direct Polarization[a]	Sucrose (Invertase Method)[a]	Reducing Sugar Index
Days	*Grams*	*Per cent*		
		ORGANISM 4		
0	0	5.35	5.93	23.72
9	1.07	5.10	..	21.30
17	1.93	5.20	5.84	12.25
24	2.47	5.20	5.79	11.91
34	2.87	5.15	5.66	9.80
		ORGANISM 5		
0	0	5.35	5.93	23.72
9	1.05	5.05	..	..
17	2.08	5.27	5.71	11.76
25	2.60	5.40	5.76	9.86
34	3.59	5.65	5.29	4.11

[a] Determinations by M. A. McCalip of this laboratory.

[10] *Ind. Eng. Chem.*, 11, 748 (1919).

[11] Assocn. Official Agr. Chem., Methods, p. 185 (1925).

Judging from the results of this experiment, organism 5 would be far more suitable for the selective fermentation of Cuban molasses than organism 4. The sucrose was scarcely attacked in either case, but the reducing substances were destroyed more completely by organism 5. Although in fermentations of this type the decrease in reducing substances is continuous, the direct polarization decreases during the earlier stages. It increases again with the gradual disappearance of the fermentable monoses. This relation, which was first observed by Gayon,[12] is well demonstrated by the direct polarizations with organism 5. This variation in direct polarization is thought to be due to more rapid fermentation of dextrose than of levulose by the respective organism.

Comparison of Media

It was thought that the speed of these fermentations might be increased by employing liquid starters which had been built up on a specially suitable medium. In connection with these experiments the quantities of acid and ethyl alcohol produced in some of these cultures were determined. Hopped beer wort was obtained from a local brewery, and some unhopped wort was prepared from ground barley malt. The two worts were practically identical as to density and pH (10.25° Brix, pH 5.8 to 5.9). A dilute solution of blackstrap molasses, the sucrose of which had been inverted by adding a small amount of crude invertase solution, was compared with these two media, both with and without the addition of some dextrose. This molasses medium contained 25 grams of molasses and 10 cc. of yeast extract (invertase) in a volume of 150 cc. Its Brix reading was 12.45°, and its pH, 5.5. After several days twelve of the most actively fermenting cultures were transferred to 150-cc. portions of dilute molasses, all of the same composition, and after the fermentation of these batches had come to an end, the pH of the fermented liquors was determined. Some of the solutions were distilled, and the quantity of ethyl alcohol in the distillates was determined.

The manipulations were as follows: Thirty cubic centimeter portions of the unhopped wort were placed in five small Freudenreich flasks and sterilized. After cooling, each flask was inoculated with a trace of organisms 2, 3, 4, 5, and 6, respectively. Three days later, while actively fermenting, 5-cc. portions of each culture were transferred into five Freudenreich flasks containing 25-cc. portions of the following five media: (*a*) unhopped wort, (*b*) 5 grams of dextrose dissolved in 100 cc. of unhopped wort, (*c*) hopped wort, (*d*) 5 grams of dextrose dissolved in 100 cc. of hopped wort, (*e*) blackstrap molasses inverted by invertase. The progress of these fermentations was judged by the consecutive losses in weight of the twenty-five flasks. Thus, on the second day after inoculation the individual cultures had lost the weights shown in Table VI*a*.

Table VI*a*—Comparison of Inverted Molasses with Other Fermentation Media

Medium	Loss in Weight with Various Organisms				
	2	3	4	5	6
	Gram	*Gram*	*Gram*	*Gram*	*Gram*
Unhopped wort	0.118	0.127	0.132	0.114	0.117
Unhopped wort + dextrose	0.517	0.636	0.653	0.284	0.454
Hopped wort	0.113	0.128	0.136	0.096	0.116
Hopped wort + dextrose	0.503	0.577	0.611	0.236	0.410
Inverted molasses	0.253	0.516	0.508	0.195	0.358

It appears that the inverted molasses is a better medium for these organisms than either the hopped or the unhopped wort alone. Compared with the other organisms, No. 5 developed poorly in all these media. Possibly the wort used as starter had impaired the vitality of this strain. After making the above weighings, twelve of the cultures were transferred in bulk, with precautions against infection, to 300-cc. volumetric flasks, each of which contained a sterilized 150-cc. portion of diluted molasses (18° Brix). The ensuing fermentations appeared to be over in 3 or 4 days, with the exception of the flasks that had been inoculated with strain 5, which continued to lose appreciable weight for several more days. The fermented liquors were diluted to 300 cc. with freshly boiled distilled water. The pH values of the twelve solutions, after mixing and filtering, are given in Table VI*b*.

Table VI*b*—pH Values of Different Media after Fermentation with Invertase-Free Yeasts

Medium Used for Starter	pH Values with Various Organisms				
	2	3	4	5	6
Unhopped wort + dextrose	4.96	5.04	5.04	5.03	5.13
Hopped wort + dextrose	..	5.03	..	4.99	..
Inverted molasses	4.98	5.03	5.03	4.98	5.10

The pH values with organisms 2, 3, 4, and 5 were practically identical, being approximately 5.0. With strain 6 the final pH was slightly higher. Considering the fact that dilute molasses is a highly buffered solution, it is not surprising that the action of the organisms caused only slight changes in the hydrogen-ion concentration.

In connection with determination of alcohol it was found that other volatile substances had been formed during the selective fermentation. There was always present in the distillate a substance (possibly acetylmethylcarbinol) which reduced Fehling's solution. When the molasses solution was fermented with ordinary baker's yeast after the selective fermentation, this volatile reducing substance was no longer found. If the distillates obtained from the neutralized liquors at the end of the selective fermentation are subjected to a simple purification process with *m*-phenylenediaminehydrochloride in the manner prescribed by Neuberg,[13] and if the alcohol in 10 cc. of distillate is determined before and after this purification process, it appears that the difference between the two results should furnish an indication of the amounts of substances other than ethyl alcohol that were present in the untreated distillates. This procedure was employed in this experiment, the alcohol determinations being made by the dichromate oxidation method as described by Hoepner.[14] The results obtained with some of the molasses liquors fermented by the five organisms mentioned above are given in Table VI*c*.

Table VI*c*—Relative Purity of Ethyl Alcohol Produced by Invertase-Free Organisms

Organism	Alcohol in Original Distillate		Difference in Alcohol Content Representing Constituents Other than Alcohol
	Direct	After treatment	
	Mg. in 10 cc.		*Mg.*
2	77.71	76.74	0.97
3	80.73	79.30	1.43
4	81.74	79.94	1.80
5	75.29	72.01	3.28
6	82.31	80.33	1.98

From the same quantity of molasses organisms 3, 4, and 6 produced about equal quantities of alcohol, and more than organisms 2 and 5 produced. Organism 5, although the lowest alcohol producer, had evidently formed a considerable quantity of other products. The quantity of alcohol produced by organism 2 was somewhat low, but the quantity of other products also was low.

Use of Stimulants

Of substances that are mentioned in the literature as being capable, when present in small proportions, of increasing the

[12] *Compt. rend.*, **87**, 407 (1878).

[13] *Biochem. Z.*, **98**, 141 (1919).

[14] *Z. Nahr. Genussm.*, **34**, 453 (1917).

normal velocity of alcoholic fermentation, sodium fluoride was selected for investigation in view of the favorable results obtained with it by Effront.[15] The first experiment was carried out with organism 1. A molasses solution was prepared by diluting 50 grams of blackstrap to 1 liter. One hundred cubic centimeter aliquots were pipetted into Nessler jars containing portions of 5, 10, 15, 20, and 25 mg., respectively, of dry sodium fluoride. After the salt had dissolved the liquids were allowed to stand for several hours. Without disturbing the sediment, a 50-cc. portion of each liquor was transferred to a 100-cc. Freudenreich flask. For comparison, one flask was prepared in the same manner without addition of fluoride. To each of the six flasks 3 grams of pure dextrose were added, whereupon the flasks were sterilized in an autoclave. When cool, a 3.5-cc. portion of an actively fermenting culture of organism 1 was added to each flask. The flasks were weighed after this inoculation and at intervals later. The loss in weight indicative of the progress of the fermentations is shown in Table VII.

Table VII—Influence of Sodium Fluoride on Rate of Selective Fermentation of Diluted Molasses

Fluoride Added to Medium[a]	Loss in Weight on Various Days			
	3	4	5	6
Mg. per 100 cc.[b]	*Gram*	*Grams*	*Grams*	*Grams*
0	0.3768	0.7263	1.0503	1.3626
5	0.6378	1.0224	1.3084	1.5450
10	0.4888	0.8046	1.0620	1.2881
15	0.3548	0.6579	0.9041	1.1714
20	0.4670	0.8325	1.1252	1.3866
25	0.3882	0.6696	0.9073	1.1672

[a] The quantities of fluoride actually in solution were less than indicated, as a portion of the fluorine no doubt reacted with constituents of the molasses, such as lime, and was eliminated with the sediment in the form of insoluble compounds.
[b] Equals grams per hectoliter.

The rate of fermentation was distinctly accelerated in the culture containing the lowest concentration of fluoride (5 grams per hectoliter), but not in the other cultures. The higher concentrations of fluoride, however, appeared to have no harmful effect on the fermentation. The beneficial influence of an addition of sodium fluoride on the rate of the selective fermentation of molasses was observed in other experiments made with organisms 1 and 4. Very small quantities of fluoride stimulate particularly, but these organisms can also withstand larger additions of fluoride remarkably well. With 12° Brix molasses solutions, 15 grams of fluoride per hectoliter, and with 23° Brix molasses solutions from 60 to 90 grams could be added without decreasing the rate of fermentation. Previous cultivation of the organism in the presence of lower concentrations of fluoride did not seem necessary.

It should not be concluded, however, that the addition of fluoride will overcome all the difficulties which are likely to be found in work of this kind. In fact, the accelerating influence of this salt is manifested only when the starter used for the inoculation is in a vigorous state of activity.

Similar experiments were made for the purpose of studying the influence of phosphate on the activity of the organisms in diluted molasses. Needle inoculations were used instead of liquid starters; consequently these experiments gave no results other than the general observation that the addition of di-ammonium phosphate to a dilute solution of molasses does not influence the velocity of fermentation, whereas clarification with a neutralized solution of monocalcium phosphate causes acceleration.

Influence of Solids Concentration of Medium and Agitation during Fermentation

The important problem of concentration of the medium at which selective fermentation of molasses is best conducted was investigated by allowing the different organisms to ferment molasses solutions of varying density, and by studying the changing composition of the respective liquors. Fermentations were usually made simultaneously with three different concentrations of molasses. In one instance the following dilutions were used:

Solution I: 55.56 grams molasses diluted to 300 cc.; 13.65° Brix.
Solution II: 111.12 grams molasses diluted to 300 cc.; 25.82° Brix.
Solution III: 166.68 grams molasses diluted to 300 cc.; 36.87° Brix.

It was planned to study at the same time the influence of agitation. Two 100-cc. aliquots of the three final liquors were pipetted into 300-cc. volumetric flasks. To each flask, after sterilization, were added 8 cc. of an actively fermenting culture of organism 4 by means of a sterile pipet. The flasks were then arranged in two sets of three, one set being shaken at frequent intervals, whereas care was taken not to agitate the other three flasks more than necessary while ascertaining their respective weights. Portions of the three molasses solutions and the liquid starter were reserved for blank determinations. The progress of the fermentations as indicated by the increasing loss of weight of the flasks is shown in Table VIII*a*.

Table VIII*a*—Influence of Agitation on Rate of Selective Fermentation of Molasses

Solution	° Brix	Loss in Weight on Various Days								
		1	2	4	5	6	7	8	9	13
		Gram	*Grams*	*Grams*	*Grams*	*Grams*	*Grams*	*Grams*	*Grams*	*Grams*
					STIRRED SET					
I	13.6	0.23	1.10	1.32	1.37[a]	..	..	..	..	..
II	25.8	0.18	1.68	2.54	2.64	2.68	2.72[a]	..	..	..
III	36.9	0.08	0.94	3.33	3.83	3.98	4.05	4.11	4.13[a]	..
					UNSTIRRED SET					
I	13.6	0.19	0.82	1.26	1.35[a]	..	..	..	..	..
II	25.8	0.13	0.82	2.33	2.57	2.67	2.77[a]	..	..	..
III	36.9	0.08	0.68	1.75	2.45	3.10	3.68	3.94	4.04	4.22[a]

[a] Indicates day on which sample was removed for analysis.

The solution in each flask was diluted to 300 cc. with distilled water, and the weight of each 300-cc. lot was determined. Suspended particles and yeast cells were removed by filtration or centrifuging after addition of kieselguhr. Sucrose was determined by the invertase method;[16] invert sugar, by the Meissl and Hiller method;[17] and alcohol by Hoepner's method.[14] The data in terms of percentage by weight were recalculated to a basis of 300 cc., inasmuch as the density of a sugar solution decreases considerably when fermented, whereas only slight changes in volume occur. In the small-scale work the use of volumetric flasks, whereby all liquors were diluted to the same volume before analysis, practically eliminated changes in volume. The data are shown in Table VIII*b*.

The changes in the quantities of the various ingredients as a result of these fermentations are shown in Table VIII*c*.

It is seen from Tables VIII*a* to VIII*c* that the sucrose was left practically intact during the fermentation of solutions I and II, whereas in solution III, of higher density, it suffered a distinct loss. Agitation caused more rapid fermentation, and in solution III, a smaller loss of sucrose.

In further experiments, weights of molasses were again used in the proportion 1:2:3, and the quantities of starter were increased in the same proportion. Also, in order to compare more rigorously the activity of the organisms at the different concentrations, all three fermentations were stopped as soon as any one flask no longer showed an appre-

[15] See, for example, his review in *Chimie & industrie*, 9, 1076 (1923).

[16] Assocn. Official Agr. Chem., Methods, p. 185 (1925)

[17] *Ibid.*, p. 194.

ciable loss of weight. When this point had been reached, the fermentations were stopped by adding 2 grams of dry sodium fluoride per 100 cc. of fermented liquor.

Table VIII*b*—Composition of Molasses Liquors after Selective Fermentations with and without Agitation

Solution	°Brix	Agitation	At Start[b]	5th Day	7th Day	9th Day	13th Day	Final pH Value
			Grams in 300 cc.					
			SUCROSE VALUES					
I	13.6	With	6.72	5.72				5.2
		Without	6.72	5.60				5.4
II	25.8	With	11.30		11.38			5.2
		Without	11.30		11.07			5.4
III	36.9	With	16.65			15.18		5.2
		Without	16.65				12.92	4.7
			INVERT SUGAR VALUES[a]					
I	13.6	With	3.92	0.91				
		Without	3.92	0.90				
II	25.8	With	7.34		1.64			
		Without	7.34		1.63			
III	36.9	With	10.77			2.46		
		Without	10.77				2.50	
			ALCOHOL VALUES					
I	13.6	With	0.02	1.44				
		Without	0.02	1.55				
II	25.8	With	0.02		2.72			
		Without	0.02		2.72			
III	36.9	With	0.02			4.10		
		Without	0.02				5.97	

[a] Total reducing substances were calculated as invert sugar.
[b] These figures include the quantities introduced into each flask with the 8 cc. of starter—i. e., 0.51 gram of invert sugar, 0.84 gram of sucrose, and 0.02 gram of alcohol.

Table VIII*c*—Relative Efficiency of Selective Fermentation with and without Agitation

Determination	Solution I (13.65° Brix)		Solution II (25.82° Brix)		Solution III (36.87° Brix)	
	Stirred	Not stirred	Stirred	Not stirred	Stirred	Not stirred
Reducing substances not fermented, calcd. as invert sugar, per cent of total	23.2	22.9	22.3	22.2	22.9	23.2
Alcohol produced, per cent of theory	96.0	100.0	97.0	93.0	84.2	98.4
Loss of sucrose, per cent of total	0.0	1.8	0.0	2.0	8.8	22.4

In the first experiment conducted according to this plan the starter was prepared from a culture of organism 3. The fermentations were stopped on the fifth day after inoculation. An excessively large proportion of the fermentable monoses was still present in the solutions, and one-fifth to one-fourth of the sucrose had disappeared. This unsatisfactory result was probably due to two causes. The starter was built up from an agar-slant culture which had been kept at +1° C. for about 9 months without being transferred. Moreover, it had already been repeatedly observed that organism 3, even when in prime condition, was not an active fermenter.

In another experiment of this series a culture of organism 2 was used, and the liquors to be fermented were prepared from Porto Rican molasses. The general arrangement was the same as that outlined before, but the results, after 6 days of fermentation, were again unsatisfactory.

Cuban blackstrap was again employed in the next experiment; organism 1 was used for inoculation. The experiment differed from the previous experiments in that the three fermentation flasks were fastened upon an inclined wooden table, which was rotated continuously in the inclined position by means of an electric motor, thereby causing the three solutions to be agitated mildly during fermentation. The quantities of original molasses in the final 100-cc. portions, their densities before autoclaving, and the volumes of starter added in each case were as follows:

Solution I: 16.665 grams molasses in 100 cc.; 12.2° Brix; 15 cc. starter

Solution II: 33.335 grams molasses in 100 cc.; 23.2° Brix; 30 cc. starter

Solution III: 50.000 grams molasses in 100 cc.; 33.2° Brix; 45 cc. starter

The fermentations were stopped on the fourth day, the respective loss in weight having been as follows:

Solution	3-Day Loss	4-Day Loss
	Grams	*Grams*
I	1.64	1.65
II	3.42	3.47
III	2.40	4.20

The analytical results are shown in Table IX. Beginning with this experiment the sugar values were obtained by reduction of Fehling's solution, both the sucrose and invert sugar being calculated from the reduction figures before and after inversion with invertase, by using the table of Munson and Walker.[18]

Table IX—Changes in Composition of Different Concentrations of Diluted Molasses Due to Selective Fermentation

Time of Test	Sucrose[a]	Invert Sugar[a]	Alcohol[a]	Sucrose Lost	Alcohol Formed	Reducing Substances Not Fermented, Calcd. as Invert Sugar
	Grams	*Grams*	*Grams*	*Per cent*[b]	*Per cent*[c]	*Per cent*[b]
	SOLUTION I (12.20° BRIX) 15 CC. STARTER					
At start	4.644	4.238	0.414	..	...	...
After 3 days' fermentation	4.558	0.790	1.806	1.86	80.08	18.64
	SOLUTION II (23.18° BRIX) 30 CC. STARTER					
At start	9.138	8.648	0.832	..	...	...
After 3 days' fermentation	9.136	1.608	3.957	0.03	90.43	18.60
	SOLUTION III (33.15° BRIX) 45 CC. STARTER					
At start	13.087	13.170	1.239	..	...	...
After 3 days' fermentation	13.378	4.158	5.223	..	90.09	31.60

[a] Total in 300-cc. flask.
[b] Per cent of total.
[c] Per cent of theory.

The favorable influence of the agitation of the liquors is apparent from the rapid completion of the fermentations and from the analytical data recorded in Table IX. The values pertaining to solution II represent a fairly satisfactory result. In the values shown for solution III an analytical error is doubtless responsible for the low sucrose figure at the start. However, the loss of sucrose, which in previous experiments had been large in liquors of this density, was greatly reduced. The fermentation of the dextrose and levulose, however, had not been completed at the end of 3 days. A similar experiment was made with a culture of the same organism (No. 1), which was introduced into molasses of two different densities. The fermentations were allowed to proceed to the end in this case. In a duplicate experiment sodium fluoride was added to the medium. The stimulating effect of this salt, however, did not manifest itself, probably because the starter was not in the best condition. In general, the results were not so satisfactory as in the previous experiment.

The work thus far described shows that these invertase-free organisms can be utilized for the selective fermentation of the dextrose and levulose of dilute cane molasses, provided the initial density of the molasses does not greatly exceed 25° Brix, provided arrangements are made for agitation of the liquors, and provided the culture used as a starter is in a vigorous state of activity. The choice of the proper organism is also an important factor, as not all invertase-free organisms were well suited for the selective fermentation of final cane molasses. Variations in the results obtained with different organisms, or with the same organism at different times, were often due to lack of uniformity in the respective

[18] Assocn. Official Agr. Chem., Methods, p. 434.

starters—a condition difficult to overcome in small-scale experimentation.

Larger Scale Experiments

Fermentation was next conducted on a somewhat larger scale. The fermenter consisted of a substantial cylindrical copper tank of about 20 gallons capacity, tin-lined and provided with a cover that could be bolted tightly to permit the contents to be sterilized by steam under pressure. The tank stood upright, being mounted on four metal legs. The steam inlet, consisting of a 0.5-inch valve, was near the bottom. Close to this valve was a small cock through which a current of sterilized compressed air could be blown through the liquor to provide agitation. Near its top the tank bore a pressure gage, a 0.5-inch gate valve, through which the inoculations were made, and a small cock, to which an air filter was attached. This cock was opened during the cooling of the sterilized charge. During fermentation it served for the escape of the carbon dioxide. This gas was passed through a dilute sulfuric acid solution, and the number of bubbles emitted from the unagitated charge during a given time indicated the progress of the fermentation. There was a small sampling cock about half way between the bottom and the top of the tank.

The molasses solution, before being inoculated, was autoclaved by closing all the openings of the tank, admitting live steam into the liquor, and allowing the pressure to rise to approximately 20 pounds per square inch. This pressure was maintained for about 40 minutes, whereupon the steam was shut off, and the charge, appreciably diluted by condensation of steam, was allowed to cool. Since the usual volume to be fermented in this tank was 10 to 12 gallons or more, a correspondingly large starter had to be used. The starter was always built up in culture vessels made from regular Pyrex laboratory glassware. Particular care was given to the building up of the starters, as it was realized that success or failure of a selective fermentation experiment depended more on this than on any other single factor. Diluted molasses solutions without filtration or addition of nutrient substances were used in these larger scale experiments. In most of them organism 4 was employed because it appeared to be especially well adapted to the molasses medium.

Note—From the data in Tables XII to XIV it is seen that as a result of this rigorous and prolonged heat treatment a considerable portion of the sucrose originally present in the molasses had been inverted. This loss of sucrose, which, when applying the selective fermentation process in practice, should, of course, not be permitted to take place, may be avoided by adding lime to the dilute molasses liquor before the heat treatment. A more rapid cooling of the sterilized liquor would also be of assistance in maintaining the original sucrose content. In these experiments the primary object was to avoid as far as possible a loss of sucrose due to the action of the organisms. Losses of sucrose resulting from the treatment of the molasses liquor before its inoculation were of no immediate concern, and therefore no precautions were taken to avoid this loss.

Table X—5-Day Selective Fermentation of 10 Gallons of Diluted Molasses, Using Organism 4

Determination	At Start	5th Day
	Grams in 100 cc.	
Sucrose	3.87	3.94
Reducing substances, as invert sugar	5.38	0.72
Reducing substances not fermented, per cent of total, as invert sugar	...	13.39
Sucrose lost	...	None

The record of one of the earlier experiments is as follows: A sterilized charge in the fermentation tank was inoculated with slightly more than 1 liter of starter. Sterile air was blown through the solution at indefinite intervals, especially during the early stages of fermentation. After 4 days gas production had decreased greatly. On the fifth day it had become slow and a sample was withdrawn for analysis. The composition of the tank liquor at the start and after 5 days' fermentation is shown in Table X.

The yield of alcohol was high, over 90 per cent of the theoretical quantity. The exact figure is not available, but the fact was established that a large part of the theoretical quantity of alcohol, calculated on sugar consumed, was formed in dilute cane molasses as a result of the action of organism 4 in vigorous condition. The principal data required for judging the degree of success of an experiment with this organism were, therefore, the quantity of sucrose lost and the proportion of reducing substances present at the end of a fermentation. As shown in Table X, the results were favorable; the duration of the fermentation (5 days), however, was somewhat long.

In another experiment the fermented liquor was analyzed on the fourth day. (Table XI) The outcome of this experiment was considered rather satisfactory.

Table XI—4-Day Selective Fermentation of 10 Gallons of Dilute Molasses, Using Organism 4

Determination	At Start	4th Day
	Grams in 100 cc.	
Sucrose	5.788	5.814
Reducing substances, as invert sugar	8.130	1.270
Alcohol	0.230	3.074
Brix reading	21.50	14.85
Alcohol formed, per cent of theory		84.54
Reducing substances not fermented, per cent of total, as invert sugar	...	15.6
Sucrose lost	...	None

An experiment using the low-alcohol producing organism 5 required a fermentation period of 6 days. (Table XII)

Table XII—6-Day Selective Fermentation of 10 Gallons of Diluted Molasses, Using Organism 5

Determination	At Start	6th Day
	Grams in 100 cc.	
Sucrose	3.774	3.192
Reducing substances, as invert sugar	4.792	0.480
Alcohol	0.092	1.439
Brix reading	14.09	8.10
Alcohol formed, per cent of theory		54.65
Reducing substances not fermented, per cent of total, as invert sugar	...	10.02
Sucrose lost	...	15.42

A second trial with this organism failed, owing to complete destruction of the sucrose, presumably through contamination. The fermentation caused by this organism is evidently of a type different from that effected by other invertase-free organisms. The quantity of alcohol produced was only slightly more than one-half the theoretical. At the same time the reducing substances had been destroyed to a greater extent than by any of the other strains. Moreover, this organism seems inclined to destroy the sucrose.

Industrial Application

In applying the results to large-scale operation, the following principal phases would have to be considered: (1) the selective fermentation process, (2) the recovery of sucrose, and (3) the recovery of the products of fermentation. The second and third phases should offer no serious obstacles to the technologist when the difficulties inherent in the fermentation problem have been overcome. This paper is largely concerned with the first phase, and on the basis of their experience the writers feel justified in stating that its operation in practice should be possible. Success would appear to depend largely upon the proper organism, upon the apparatus for propagating this organism in pure culture, and upon the intelligent management of all operations connected with the building up of the starters and the conduct of the fermentations proper.

Fermentation processes of the strictly pure culture type, although successfully employed in some industries, naturally involve greater expenditure for equipment and operation than similar ones in which the pure culture principle is not applied to the final batches. It was desirable, therefore, to consider whether or not it is necessary to work under rigorously controlled pure-culture conditions. By introducing a vigorous starter—itself a pure culture—into a tank in which diluted molasses had been sterilized merely by heating, it seemed possible that fermentation of the levulose and dextrose might be effected before competing organisms would have time to destroy any material quantity of sucrose. If this could be accomplished it would be possible to operate the selective fermentation process at a lower cost, since closed fermenters, with their intricate and more expensive mode of operation, could be eliminated.

Some experiments along this line were made with 10-gallon batches of diluted blackstrap molasses which had been briefly boiled in the copper tank on the afternoon before the date of inoculation. The inoculation was made with varying quantities of vigorously fermenting cultures of organism 4. After inoculation the tank was loosely covered and the liquor was stirred by an air current until the fermentation was well under way. Several experiments using 1 and 2 liters of starter were unsuccessful. With 3 liters of starter the results were more favorable, as shown in Tables XIII and XIV.

Table XIII—Selective Fermentation in Open Tank, Using Organism 4

Determination	At Start	3rd Day
	Grams in 100 cc.	
Sucrose	9.47	9.16
Reducing substances, as invert sugar	5.66	1.12
Brix reading	22.90	18.66
Reducing substances not fermented, per cent of total, as invert sugar		19.8
Sucrose lost, per cent of total		3.3

Table XIV—Selective Fermentation in Open Tank, Using Organism 4

Determination	At Start	2nd Day	3rd Day
	Grams in 100 cc.		
Sucrose	7.766	7.621	7.590
Reducing substances, as invert sugar	4.565	1.216	1.160
Brix reading	19.1	15.6	15.6
Reducing substances not fermented, per cent of total, as invert sugar		26.64	25.41
Sucrose lost, per cent of total		1.87	2.27

These results compare favorably with those obtained under strictly pure culture conditions. By using a still larger volume of starter—for instance, 1 gallon or 10 per cent of the volume of liquor to be fermented—even more favorable results could no doubt be obtained. At any rate, it appears possible to conduct the selective fermentation of molasses satisfactorily in loosely covered tanks provided a sufficiently large volume of starter is used.

For the purpose of recovering the sucrose after completion of the selective fermentation, the saccharate process appears to be the most feasible method. Mendes[19] stated in 1884 that cane molasses after selective fermentation would have a composition similar to that of beet molasses, and that its desugarization should therefore be possible by the same methods that are applicable to beet molasses. The same view is held today, and recent patents describe the application of the calcium saccharate process, which is used in many beet-sugar factories, to selectively fermented diluted cane molasses.[20] It does not appear that a large part of the sucrose could be recovered in the case of molasses by direct crystallization after selective fermentation, as proposed by McGlashan.[21]

Certain details regarding the practical operation of the selective fermentation process remain to be worked out—for example, the precise temperature at which the liquors should be held in order to obtain the best results. When working on a large scale, means for regulating the temperature of the liquors should be provided. Addition of lime to the diluted molasses may be necessary when the acidity is high, or when heating under pressure in order to sterilize the liquor before inoculation. Regarding the choice of the proper organism for a fermentation process of this kind, it has been the experience of the writers that some invertase-free organisms are very sensitive to slight changes in environment, whereas others appear to be less easily influenced. In the second group, comprising strains of more stable character, may be included organisms 1 and 4, both of which seem well suited for the selective fermentation of cane molasses.

. . . . . .

Addendum—While this article was in press a paper appeared by W. L. Owen [*Planter Sugar Mfr.*, **79**, 527 (1927)], in which the possible feasibility of producing alcohol directly from the juice of prolific sugar-cane varieties is discussed. It is obvious that by conducting the fermentation of cane juices with invertase-free yeasts the sucrose of the juice could subsequently be recovered. In this case, owing to the absence of large amounts of salts, desugarization could probably be accomplished by direct crystallization.

[19] *Bull. assocn. chim. sucr. dist.*, **2**, 372 (1884).

[20] Olivarius, U. S. Patent 1,401,433 (1921); Paine, Walton, and Birckner, U. S. Patent 1,572,359 (1926).

[21] U. S. Patent 751,990 (1904).

Determination of Small Amounts of Carbon Monoxide in Air[1]

G. M. Edell

Syracuse University, Syracuse, N. Y.

It seemed desirable to test air for smaller concentrations of carbon monoxide than had previously been reported.[2] Oxidation by means of iodine pentoxide was selected as the most accurate method in use. Several test analyses were made from each of four different concentrations of carbon monoxide in air, using an apparatus modeled after Graham's portable type[3] with the bromine tube omitted. One-liter samples of the two more concentrated mixtures and 3-liter samples of the dilute mixtures were used.

It was found that only the purest iodine pentoxide should be used. Even then there was a constant, though small, liberation of iodine when pure air was drawn through the tube; the rate of decomposition, however, was nearly uniform. It had to be determined and corrections made in computing the results of the analyses. One tube filled with an inferior grade of iodine pentoxide gave untrustworthy results due to a high and uneven rate of decomposition. Water displacement of the gas sample from the reservoir and sampling bulb gave results fully as accurate as vacuum displacement.

Analytical Results

No. of Determinations	Carbon Monoxide Computed	Carbon Monoxide Determined	Deviation of Determined Percentages from Computed: Average	Maximum	Minimum
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*
6	0.0575	0.0599	+0.0024	+0.0031	+0.0010
4	0.0094	0.0109	+0.0015	+0.0023	+0.0007
5	0.0018	0.0027	+0.0009	+0.0020	+0.0001
7	0.0008	0.0011	+0.0003	+0.0008	+0.0001

The excellent checks obtained on the work of other investigators and the accuracy of determinations on still more dilute concentrations mark the method as one having greater refinement than is generally known, and one whose limit of usefulness has not yet been determined.

[1] Received February 17, 1928. Abstract from thesis under the direction of C. R. McCrosky, Syracuse University.

[2] Kinnicut and Sanford, *J. Am. Chem. Soc.*, **22**, 14 (1900), reported concentrations as low as 0.0023 per cent.

[3] *J. Soc. Chem. Ind.*, **38**, 10T (1919).

Factors Influencing Char Filtration—II[1]

E. W. Rice and G. W. Murray, Jr.

National Sugar Refinery, Yonkers, N. Y.

SINCE the presentation of the previous paper under this title[2] explanations of some of the results have been asked; therefore, data covering these points will first be presented.

The figures on the adsorption of invert sugar showed an apparent selective adsorption of levulose by the bone char, and it was thought that this might be due to a chemical combination of the levulose with free ammonia and a subsequent greater adsorption. Ammonia is known to be present in appreciable quantity in reactivated bone char. Therefore, the following experiment was tried:

A portion of bone char was washed for 3 days with distilled water and, after drying, a solution of invert sugar was percolated upward through this char and simultaneously through a sample of unwashed char. The filtered material was collected in 50-ml. portions and polarized and the invert sugar determined by copper precipitation. The results show no appreciable difference in the solution from the two chars, although again the large differences in polarization are not borne out by the amounts of invert determined by copper precipitation. This experiment was purposely made on a more concentrated solution to determine if the same tendency to change in polarization would persist. The results are presented in Table I.

Table I—Invert Sugar in Successive Portions of Solutions Treated with Bone Char

(50-ml. portions analyzed)

	Original Solution	1	2	3	4
	POLARIZATION				
Off washed char	−3.1	−1.5	−2.0	−2.2	−2.3
Off unwashed char	−3.1	−1.5	−2.1	−2.3	−2.5
	GRAVIMETRIC				
Off washed char	2.98	2.55	2.87	2.93	2.95
Off unwashed char	2.98	2.60	2.99	2.95	2.93

Since many calcium salts are more soluble in cold than in hot solvents, it was thought likely that the large adsorption of $CaH_4(PO_4)_2$ which was originally indicated might have been due to a precipitation during the passage through the hot filter. In making up solutions of $CaH_4(PO_4)_2$ it was observed that when the solutions were heated a slight precipitate was formed.[3] The precipitate was slight with the first bottle of salt purchased, but a succeeding bottle gave a much heavier precipitate. Solutions of $CaH_4(PO_4)_2$ were found to be strongly acid to phenolphthalein and upon addition of calcium carbonate to a pH of 7.0 a very heavy precipitate was formed. Since there is from 2 to 5 per cent of calcium carbonate in bone char, it was decided that the adsorption of $CaH_4(PO_4)_2$ could not be reliably determined under the conditions of the experiments and further work with this salt was discontinued.

Effect of Varying Strength of Solution

As a continuation of the previous paper it was determined to try varying strengths of solutions to learn some of the limits which might be anticipated when using char as an adsorber. Two series of filtrations were made using 1 and 4 per cent solutions of four of the salts which had been used previously. The results are set forth in Table II. The amounts of salts present were determined by measuring their conductivity as described in the previous paper.[2] The results of filtrations using 2 per cent of salts are those reported in the previous paper, but are again included for comparison.

Table II—Salts in Successive Portions of Solutions Treated with Bone Char

(Figures indicate grams per 100 ml.; 50-ml. portions analyzed)

Original Solution *Per cent*	1	2	3	4	5
	SODIUM SULFATE				
1.00	0.05	0.40	0.60	0.80	0.95
2.00	0.16	0.68	1.60	1.80	1.80
4.00	0.53	3.50	3.70	3.85	3.90
	SODIUM CITRATE				
1.00	0.34	0.73	0.84	0.94	0.97
2.00	0.60	1.80	1.98	2.04	2.40
4.00	2.10	3.75	3.80	3.85	3.90
	SODIUM CHLORIDE				
1.00	0.85	1.00	1.00	1.00	1.00
2.00	1.98	2.06	2.06	2.06	2.06
4.00	3.85	5.15	5.15	5.15	5.15
	CALCIUM ACETATE				
1.00	0.05	0.35	0.80	0.90	0.95
2.00	0.27	1.40	1.98	2.04	2.40
4.00	0.75	3.90	3.90	3.90	3.90

It will be noted that the minus adsorption with sodium chloride is very large in the 4 per cent run and apparently gives results which might be anticipated from the results from the other concentrations. The 2 per cent solutions of sodium citrate and calcium acetate are not followed by minus adsorptions in the 4 per cent run. This is perhaps due to the fact that the 2 per cent runs were made in filters of brass and copper and some metal may have been dissolved, while the 1 and 4 per cent runs were made after the filters had been coated on the inside with Bakelite lacquer. The first three portions in all cases appear to conform to an adsorption isotherm, although the figures are too few to indicate definitely.

Table III—Salts in Successive Portions of Bone Char Treated Solution with Varying Sugar Concentrations

(Figures indicate grams salts per 100 ml.; 50-ml. portions analyzed)

Solution	0° Bx.	5° Bx.	20° Bx.	31° Bx.	51° Bx.	60° Bx.
	SODIUM SULFATE					
Original	2.00	2.00	2.00	2.00	2.00	2.00
1	0.16	0.06	0.11	0.08	0.04	0.08
2	0.68	0.68	0.62	0.50	0.50	0.50
3	1.60	1.60	1.38	1.16	0.98	0.96
4	1.80	1.76	1.72	1.66	1.40	1.24
5	1.80	1.84	2.00	1.86	1.60	1.50
	CALCIUM ACETATE					
	0° Bx.	15° Bx.	20° Bx.	29° Bx.	40° Bx.	58° Bx.
Original	2.00	2.00	2.00	2.00	2.00	2.00
1	0.27	0.10	0.11	0.32	0.18	0.22
2	1.40	1.06	1.04	1.06	0.96	0.86
3	1.98	1.70	1.67	1.64	1.60	1.30
4	2.04	1.78	1.76	1.80	1.84	1.54
5	2.40	1.86	1.86	1.92	1.90	1.62

Combinations of Salts with Sugar Solution

It was next decided to use combinations of salts with sugar solution and in Table III will be found results of ten filtrations using 2 grams of Na_2SO_4 and $Ca(C_2H_3O_2)_2$ per 100 ml. in sugar solutions of varying densities as indicated. The 0° Brix column is copied from the original paper.[2] The figures show an increase in the adsorption of the salt as the per-

[1] Presented before the Division of Sugar Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

[2] *Ind. Eng. Chem.*, **19**, 214 (1927).

[3] Watts, Dictionary of Chemistry, Vol. IV, p. 109; "up to 1 part in 200 a clear solution is found." Solubility given in the Handbook published by Chemical Rubber Publishing Co.: 1.8 parts = 1.0 parts P_2O_5 in 100 of H_2O at 30° C.; and Van Nostrand Chemical Annual, 1922, gives 4.0 parts in 100 at 15° C. = 2.2 parts P_2O_5.

centage of sugar increased. This is probably due to a decrease of solubility of the salt as the amount of sugar increases in the solution. This indicates the reason for the known fact, in practice, that the ratio of sugar to salts decreases very rapidly, as the density drops, during the process of sweetening off char filters.

Conclusion

It appears from these experiments that in refining sugars the solutions should be kept as dense as possible where the maximum of ash is to be removed from the solutions by the use of bone char.

The Free Energies of Some Hydrocarbons[1]

Alfred W. Francis

Arthur D. Little, Inc., Cambridge, Mass.

Equations have been derived for the free energies of formation of methane, ethane, octane, ethylene, acetylene, benzene, toluene, naphthalene, and cyclohexane as functions of temperature. These equations have been plotted with the ordinates reduced to free energy of formation per carbon atom to show the true stability relations between various hydrocarbons.

The equations have been simplified to linear equations for cracking temperatures, 427–727° C. By suitable interpolations similar equations for the other paraffin, olefin, acetylene, and naphthene hydrocarbons have been estimated. The equations have been tested and found consistent with several known reactions. Some predictions as to the possibility of other desirable reactions have been made.

The direct production of higher paraffin hydrocarbons from lower ones is shown to be impossible except with simultaneous production of still lower ones in at least equivalent amounts. The catalytic formation of acetylene in more than traces is likewise impossible. The direct removal of hydrogen from a paraffin to form an olefin with the same number of carbon atoms is possible only at high temperatures and to a very limited extent. The synthesis of gasoline from water gas can take place only below about 450° C. The isomerization of olefins to naphthenes requires temperatures below about 430° C., while the production of aromatics requires 550–900° C.

THE recent interest in synthetic gasoline makes it desirable to have reliable free-energy values for the pure hydrocarbons involved.[2] Such data would throw light also upon the chemistry of cracking and other reactions involving hydrocarbons. From the free-energy change of a proposed reaction predictions may be made as to its possibility and the conditions of temperature and pressure required.

Some of the data assumed in the present calculations are only approximate, but in many cases this fact does not introduce the error which it seems to do. An error in the specific-heat equation of a substance, for example, makes a tremendous difference in the chemical constant, I, but because of compensating errors, the resulting free energy is almost unchanged. The values of free energy calculated will be tested by several known reactions. Consistency with them will increase the reliability of the results. The figures are offered only as estimates, which can be revised when more data become available, but they are believed to be sufficiently accurate for any prediction that is made from them. The symbols used throughout conform to the system of Lewis and Randall.[3]

Methane

Methane is the only hydrocarbon with sufficient stability for accurate data on equilibrium with its elements, and even with this compound the numerous calculations which have been made are not very consistent because some of them are based upon equilibria with "amorphous carbon," which is not a definite chemical individual, and which is converted gradually to graphite during the experiments. For this reason graphite is taken as the standard form of carbon in this paper.

The heat of formation of methane from graphite and hydrogen is given by Lewis and Randall[4] as $\Delta H_{291} = -18{,}300$.

The specific-heat data employed by them were admittedly by a rough estimate, and should be replaced by those of Dixon, Campbell, and Parker[5] as calculated by Partington and Shilling.[6]

$$C_p = 2.57 + 0.0231T - 0.0_5 42T^2 \quad (1)$$

Similarly for hydrogen[6]

$$C_p = 6.65 + 0.0007T \quad (2)$$

and for graphite[7]

$$C_p = 1.1 + 0.0048T - 0.0_5 12T^2 \quad (3)$$

(except in the case of methane, (3) will be simplified to

$$C_p = 1.1 + 0.004T) \quad (4)$$

Combining (1), (2), and (3)

$$\Delta C_p = -11.83 + 0.0169T - 0.0_5 3T^2 \quad (5)$$

Then

$$\Delta H_{291} = H_0 - 11.83T + 0.00845T^2 - 0.0_5 1T^3 = -18{,}300 \quad (6)$$

from which

$$\Delta H_0 = -15{,}500 \quad (7)$$

Employing the same equilibrium data as given by Lewis and Randall,[8] the value of I is found to be -52.07 ± 0.17, with slightly better agreement than that found by them.

Then, for $C + 2H_2 \longrightarrow CH_4$

$$\Delta F = -15{,}500 + 11.83T\ln T - 0.00845T^2 + 0.0_6 5T^3 - 52.07T \quad (8)$$

$$\Delta F_{298} = -11{,}670 \quad (9)$$

This is intermediate between the value of Lewis and Randall,

[1] Presented before the Division of Petroleum Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

[2] Since this paper was written, calculations for a few of these hydrocarbons have been published by Smith, *Ind. Eng. Chem.*, **19**, 801 (1927); but the present paper is much more comprehensive, and different methods have been used in the calculations.

[3] "Thermodynamics," McGraw-Hill Book Co., New York, 1923, (hereinafter abbreviated "L. and R.").

[4] L. and R., pp. 80, 571.

[5] *Proc. Roy. Soc.* (*London*), **A100**, 1 (1921).

[6] "Specific Heats of Gases," p. 206, Ernest Benn, Ltd., London, 1924.

[7] L. and R., p. 569.

[8] L. and R., p. 572.

−12,800, and that found by Parks and Kelley,[9] −9800, by an entirely different method.

Since equations of the type of (8) are awkward to employ, and since they give practically straight lines when plotted (Figure 1), they can be simplified to linear equations. The temperature range 700–1000° K. (427–727° C.) is selected as covering the cracking temperatures, but the equations are only slightly less accurate at other temperatures.

$$\Delta F = -20{,}000 + 26.2T \qquad (10)$$

Octane

To estimate the free energy of a substance for which equilibrium values are not available, it is preferable to employ the third law of thermodynamics. The paraffin hydrocarbon for which heat of combustion data are most accurate is octane, which is fortunately in the middle of the gasoline range. It was considered best to calculate the free energy of this compound and to estimate those of the other paraffin hydrocarbons by interpolation and extrapolation.

The specific heat of liquid octane at 25° C. is 0.5052.[10] The molar heat capacity, C_p, is therefore 57.66. Bushong and Knight[11] have shown that the specific heats of paraffin hydrocarbons are proportional to absolute temperature, both as liquid and solid. On this basis, for octane

$$C_p = 0.193T \qquad (11)$$

The latent heat of fusion is not known for any pure paraffin hydrocarbon. The heat of solution of paraffin wax in petroleum distillate is given by French, McGill, and Sullivan[12a] as 40.3 calories per gram. This must be almost identical with the heat of fusion,[12b] and is probably nearly independent of the molecular weight, since this is true of the specific heats of the members of the paraffin series. Assuming that the above figure is the heat of fusion of octane, by combination with the molecular weight and absolute melting temperature, the entropy of fusion is

$$\frac{40.3 \times 114.14}{216.5} = 21.2$$

The total entropy of liquid octane at 25° C. is

$$S^\circ_{298} = 0.193 \times 298 + 21.2 = 78.7 \qquad (12)$$

For $8C + 9H_2$,

$$S^\circ_{298} = 10.4 + 265^{13} = 275.4 \qquad (13)$$

$$\Delta S^\circ_{298} = -196.7 \qquad (14)$$

The heat of combustion of octane is 1,300,700 calories.[14] Combining with the heat of combustion of its elements,[4] the heat of formation of octane is

$$\Delta H_{298} = -68{,}000 \qquad (15)$$

From which

$$\Delta F_{298} = \Delta H - T\Delta S = -9300 \qquad (16)$$

The vapor pressure of octane at 25° C. is 15.4 mm.[15] For the evaporation,

$$\Delta F = -RT\ln\frac{P}{760} = +2300$$

and for $8C + 9H_2 \longrightarrow C_8H_{18}$ (gas)

$$\Delta F_{298} = -7000 \qquad (17)$$

However, we are interested primarily in the free energies at higher temperatures, at which most of the reactions of petroleum chemistry take place. For ordinary temperatures the heat capacity of liquid octane is represented by

$$C_p = 10 + 0.161T \qquad (18)$$

better than by (11). From (2), (4), and (18) for liquid octane

$$\Delta C_p = -58.6 + 0.122T \qquad (19)$$

$$\Delta H_{298} = \Delta H_0 - 58.6T + 0.061T^2 = -68{,}000 \qquad (20)$$

(see equation 15)

from which

$$\Delta H_0 = -56{,}000 \qquad (21)$$

$$\Delta H_{398} = -69{,}650 \qquad (22)$$

From (16), (19), and (21), for $8C + 9H_2 \longrightarrow C_8H_{18}$ (liquid)

$$\Delta F = -56{,}000 + 58.6T\ln T - 0.061T^2 - 159.2T \qquad (23)$$

$$\Delta F_{398} = +19{,}200 \qquad (24)$$

$$(25)$$

for either liquid or vapor.

The specific heat of octane vapor is not known. It is estimated as follows: The latent heat of vaporization, ΔH_v, is 8060 calories[16] at its boiling point, 125° C.; those of hexane are 6820 at 70° C. and 7680 at 0° C. Assuming that the relative rate of increase of ΔH_v for octane with decreasing temperature is the same as that of hexane (since this is true for a short temperature interval, 2 per cent for 10° C.), the value $\Delta H_v = 9500$ at 25° C. is estimated. The total heat capacity of octane vapor between 25° and 125° C. is that of liquid octane between the same temperatures, plus ΔH_v at 125° C., minus ΔH_v at 25° C., plus a correction due to the Joule-Thomson effect at 25° C., which is assumed equal to that of benzene, below—namely, 70 calories.[17]

$$6242 + 8060 - 9500 + 70 = 4832 \text{ calories} \qquad (26)$$

$$\text{Mean } C_p = 4832/100 = 48.32 \qquad (27)$$

Let us assume

$$C_p = 35 + 0.0383T^{18} \qquad (28)$$

From (2), (4), and (28) for octane vapor

$$\Delta C_p = -33.6 \qquad (29)$$

$$\Delta H = \Delta H_0 - 33.6T \qquad (30)$$

From (22)

$$\Delta H_{398} = \Delta H_v - 69{,}650 = -61{,}600 \qquad (31)$$

Combining (30) and (31)

$$\Delta H_0 = -48{,}200 \qquad (32)$$

From (25), (29), and (32), for $8C + 9H_2 \longrightarrow C_8H_{18}$ (gas)

$$\Delta F = -48{,}200 + 33.6T\ln T - 53.4T \qquad (33)$$

$$\Delta F_{298} = -7000 \qquad (34)$$

The agreement with (17) is a check upon some of the assumptions made.

Simplifying (33)

$$\Delta F = -76{,}100 + 206.6T \qquad (35)$$

Ethane

An interpolation between (10) and (35) might be made to estimate the free-energy equations of ethane and other paraffin hydrocarbons. Thus for ethane

$$\Delta F = -28{,}000 + 52T \qquad (36)$$

However, since methane lacks a carbon-carbon bond, it may be slightly inconsistent with the other paraffins, and since specific heat values are available for ethane, we will evaluate its equation independently. At room temperature we will accept Smith's value[2]

$$\Delta F_{298} = -10{,}700 \qquad (37)$$

The heat capacity of ethane is estimated[19] as

$$C_p = 6.26 + 0.0181T \qquad (38)$$

from which

$$\Delta C_p = -15.88 + 0.008T \qquad (39)$$

$$\Delta H = \Delta H_0 - 15.88T + 0.004T^2 \qquad (40)$$

---

[9] *J. Am. Chem. Soc.*, **47**, 2096 (1925).

[10] Mabery and Goldstein, *Proc. Am. Acad. Arts Sci.*, **37**, 539 (1902).

[11] *Ind. Eng. Chem.*, **12**, 1197 (1920).

[12] (*a*) *Ind. Eng. Chem.*, **19**, 1041 (1927); (*b*) Gehlhoff, *Z. physik. Chem.*, **98**, 252–9(1921); *C. A.*, **15**, 3419 (1921).

[13] L. and R., p. 464.

[14] *J. Am. Chem. Soc.*, **49**, 2478 (1927).

[15] Landolt-Börnstein-Roth-Scheele, "Tabellen," p. 1356 (1923); (hereinafter abbreviated "L-B").

[16] L-B, p. 1481.

[17] It is about 50 calories for H_2O and about 200 calories for CH_3OH.

[18] The slope of equation (28) is taken as about double those for methane and ethane, but so that $\Delta\Gamma_2 = 0$ for convenience. However, any other equation which satisfied (27) would give practically the same values for free energy as those obtained.

[19] Shilling, *op. cit.*, p. 194, 195, 201.

From the heat of formation at 18° C. from diamonds,[20] we estimate

$$\Delta H_{298} = -23{,}075 \quad (41)$$
$$\Delta H_0 = -18{,}595 \quad (42)$$

From (37), (39), and (42) for $2C + 3H_2 \longrightarrow C_2H_6$

$$\Delta F = -18{,}595 + 15.88T\ln T - 0.004T^2 - 62.8T \quad (43)$$

Simplified for the cracking range

$$\Delta F = -29{,}000 + 53.3T \quad (44)$$

which compares favorably with (36).

Interpolating now between (35) and (44), for any normal paraffin vapor, C_nH_{2n+2}, approximately

$$F = -13{,}300 - 7850n + 2.2T + 25.55nT \quad (45)$$

Branched-chain paraffin hydrocarbons probably have slightly greater stability (more negative values for ΔF). This is based upon the work of Richards and Jesse[21] on the heats of combustion of the isomeric octanes, which are lower than that of normal octane in three cases out of four. The differences in heats, and probably also in free energies, are of the order of 1000 to 2000 calories.

Ethylene

From the heat of formation of ethylene from diamonds 14,600 calories[20]

$$\Delta H_{298} = 14{,}865 \quad (46)$$

The heat capacity is estimated[19] as

$$C_p = 4.4 + 0.0204T \quad (47)$$

from which

$$\Delta C_p = -11.1 + 0.011T \quad (48)$$
$$\Delta H = \Delta H_0 - 11.1T + 0.0055T^2 \quad (49)$$

Combining (46) and (49)

$$\Delta H_0 = 17{,}680 \quad (50)$$

Employing the results of Pring and Fairlie[22]

T	$K = \frac{(C_2H_4)}{(H_2)^2}$	$-RT\ln K$	I
1548	$0.0_{6}32$	46,150	−54.72
1673	$0.0_{4}5$	33,000	−64.09
2048	$0.0_{4}1$	46,600	−59.41
2223	$0.0_{3}2$	36,600	−64.85
2323	$0.0_{3}56$	34,700	−66.00

The agreement in the value of I is poor. It seems probable that this is due to partial hydrogenation during cooling, $C_2H_4 + 2H_2 \longrightarrow 2CH_4$, as suggested by the authors. If this is true, the ethylene found would be too low, and the free energy, $-RT\ln K$, too large. It seems preferable to reject the first and third values and take the mean of the other three, which agree more closely. We will take $I = -65$. Hence for $2C + 2H_2 \longrightarrow C_2H_4$

$$\Delta F = 17{,}680 + 11.1T\ln T - 0.0055T^2 - 65T \quad (51)$$

Or, approximately

$$\Delta F = 12{,}260 + 11.6T \quad (52)$$

Acetylene

The heat of formation of acetylene is given[20]

$$\Delta H_{298} = 53{,}880 \quad (53)$$

The heat capacity is estimated[23] as

$$C_p = 6.1 + 0.015T \quad (54)$$

from which

$$\Delta C_p = -2.75 + 0.0066T \quad (55)$$
$$\Delta H = \Delta H_0 - 2.75T + 0.0033T^2 \quad (56)$$
$$\Delta H_0 = 54{,}400 \quad (57)$$

Employing the data of Pring and Fairlie,[22] Pring,[24] and von Wartenberg[25]

T	$K = \frac{C_2H_2}{H_2}$	$-RT\ln K$	I
2097	0.0013	27,800	−26.35
2223	0.0031	25,600	−26.34
2273	0.0088	21,500	−27.80
2323	0.008	22,400	−26.92
2373	0.0027	27,850	−24.34
2773	0.38	18,050	−25.23
2973	0.029	21,000	−22.77

The falling off in the value of I at high temperatures may be due partly to the formation of atomic hydrogen,[26] since that would decrease the concentration of molecular hydrogen (H_2); but probably it is due mainly to decomposition of acetylene during cooling, as suggested by the authors.[22] We will take $I = -26.4$. Hence for $2C + H_2 \longrightarrow C_2H_2$

$$\Delta F = 54{,}400 + 2.75T\ln T - 0.0033T^2 - 26.4T \quad (58)$$

or approximately,

$$\Delta F = 54{,}400 - 10.8T \quad (59)$$

Higher Unsaturated Hydrocarbons

The specific heat data on higher olefins and acetylenes are too meager for calculations of their free energies. A rough approximation might be obtained by applying the increments of (45) to (52) and (59) giving for olefins

$$\Delta F = 27{,}960 - 7850n - 39.5T + 25.55nT \quad (60)$$

and for acetylenes

$$\Delta F = 70{,}100 - 7850n - 61.9T + 25.55nT \quad (61)$$

but this would imply that the free energy of hydrogenation of the double or triple bond is independent of the molecular weight. Since the heats of hydrogenation are not identical, it seems preferable to assume the corresponding variations in the free energies. From the heats of combustion of the several hydrocarbons, the following heats of hydrogenation were calculated:

Olefin	C_2H_4	C_3H_6	C_4H_8	C_5H_{10}	C_6H_{12}	C_8H_{16}
Heat	−38,260	−35,580	−31,780	−33,280	−30,080	−19,080
Olefin			$C_{10}H_{20}$			
Heat			−34,780			
Acetylene			C_2H_2	C_7H_{12}		
Heat			−76,900	−80,800		

The values for olefins are somewhat erratic because they are small differences between large values, which are not extremely accurate. Smoothing out the values, the heats of hydrogenation are

$$\text{For olefins} \quad \Delta H = -41{,}400 + 1550n \quad (62)$$
$$\text{For acetylenes} \quad \Delta H = -75{,}300 - 800n \quad (63)$$

Correcting (60) and (61) for the formation of olefins, $nC + nH_2 \longrightarrow C_nH_{2n}$ (gas)

$$\Delta F = 31{,}060 - 9400n - 39.5T + 25.55nT \quad (64)$$

and for acetylenes $nC + (n-1)H_2 \longrightarrow C_nH_{2n-2}$ (gas)

$$\Delta F = 68{,}400 - 7000n - 61.9T + 25.55nT \quad (65)$$

Benzene

For liquid benzene, Lewis and Randall[27] give

$$\Delta H_{298} = 11{,}700 \quad (66)$$
$$\Delta F_{298} = 27{,}100 \quad (67)$$

The heat capacity is estimated[28]

$$C_p = 7.1 + 0.084T \quad (68)$$
$$\Delta C_p = -19.45 + 0.058T \quad (69)$$

from which

$$\Delta H_0 = 14{,}920 \quad (70)$$
$$\Delta H_{353} = 11{,}670 \quad (71)$$

for $6C + 3H_2 \longrightarrow C_6H_6$ (liquid)

[20] L-B, p. 1492.

[21] *J. Am. Chem. Soc.*, **32**, 292 (1910).

[22] *Ind. Eng. Chem.*, **4**, 812 (1912). Although amorphous carbon was used in some of this work, the text makes it evident that in the second experiment above (at 1673° K.) the carbon had been graphitized completely. The same can be assumed for those at higher temperatures.

[23] L-B, p. 1275.

[24] *J. Chem. Soc. (London)*, **89**, 1591 (1907); *C. A.*, **1**, 550 (1907).

[25] *Z. anorg. Chem.*, **52**, 299 (1907); *C. A.*, **1**, 1122 (1907).

[26] Langmuir, *Ind. Eng. Chem.*, **19**, 668 (1927).

[27] L. and R., p. 573.

[28] Williams and Daniels, *J. Am. Chem. Soc.*, **46**, 912 (1924).

$$\Delta F = 14{,}920 + 19.45T\ln T - 0.029T^2 - 61.3T \quad (72)$$

From the heat of vaporization,[29] $\Delta H_{v298} = 8040$, and the vapor pressure,[30] 94.5 mm., both at 25° C., combined with (66) and (67), for benzene vapor

$$\Delta H_{298} = 19{,}740 \quad (73)$$
$$\Delta F_{298} = 28{,}340 \quad (74)$$

We estimate[24]

$$C_p = 6.55 + 0.052 \quad (75)$$
$$\Delta C_p = -20 + 0.026T \quad (76)$$

from which

$$\Delta H_0 = 24{,}545 \quad (77)$$
$$\Delta H_{353} = 19{,}100 \quad (78)$$

for $6C + 3H_2 \longrightarrow C_6H_6$ (gas)

$$\Delta F = 24{,}545 + 20T\ln T - 0.013T^2 - 97.4T \quad (79)$$

Adding ΔH_{v353}, which is 7360,[29] to (71), for benzene vapor

$$\Delta H_{353} = 19{,}030 \quad (80)$$

which checks (78) satisfactorily, the slight difference being due probably to the Joule-Thomson effect. From (72) for liquid benzene

$$\Delta F_{353} = 29{,}965 \quad (81)$$

and from (79) for benzene vapor

$$\Delta F_{353} = 29{,}970 \quad (82)$$

The agreement at the boiling point increases the reliability of the results. Simplifying (79), approximately

$$\Delta F = 17{,}000 + 35.3T \quad (83)$$

Toluene

From the heat of combustion of toluene, 935,230 calories[31]

$$\Delta H_{298} = 2250 \quad (84)$$

Let us assume that the mean atomic entropy is the same as that of benzene—namely, 3.[32] This assumption is supported by the fact that the entropy of ethane, 47, exceeds that of methane, 38, by 9, and that that of the latter exceeds that of hydrogen, 29.44,[13] by nearly the same figure. The entropy of fusion of toluene, 6.5, is calculated from its heat of fusion, 1150 calories.[33] The total entropy of toluene is therefore $15 \times 3 + 6.5 = 51.5$. The entropy of $7C + 4H_2$ is 126.9.[13] Combining, $\Delta S°_{298} = -75.4$. Then

$$\Delta F_{298} = \Delta H - T\Delta S = 24{,}700 \quad (85)$$

The vapor pressure at 25° C. is 28 mm.,[30] from which, as in (17), for toluene vapor

$$\Delta F_{298} = 26{,}650 \quad (86)$$

The heat capacity of liquid toluene is estimated[34] as $13 + 0.078T$, from which

$$\Delta C_p = -21.3 + 0.0472T \quad (87)$$

From (84) and (87)

$$\Delta H_0 = 7950 \quad (88)$$

and from (85), (87), and (88) for $7C + 4H_2 \longrightarrow C_7H_8$ (liquid)

$$\Delta F = 7950 + 21.3T\ln T - 0.0236T^2 - 58.17T \quad (89)$$
$$\Delta F_{383} = 30{,}750 \quad (90)$$

Since equation (90) holds also for toluene vapor, we have, with (86) the value of ΔF at two different temperatures, so that a very rough approximation of the heat capacity will suffice to extrapolate the free energy to higher temperatures. Let us assume

$$C_p = 10.3 + 0.052T \quad (91)$$
$$\Delta C_p = -24 + 0.02T \quad (92)$$

Then adjusting ΔH_0 and I to satisfy (86) and (90), for $7C + 4H_2 \longrightarrow C_7H_8$ (gas)

$$\Delta F = 19{,}270 + 24T\ln T - 0.01T^2 - 109T \quad (93)$$

or, approximately,

$$\Delta F = 6860 + 59.2T \quad (94)$$

It is interesting to note that if (83) is subtracted from (94), the last coefficient, 23.9, is nearly the same as those in (45), (64), and (65), which are thus considered typical of homologs.

Naphthalene

Proceeding as with toluene, for solid naphthalene the heat of combustion is 1,231,600[31]

$$\Delta H_{298} = 15{,}840 \quad (95)$$
$$S°_{298} = 54,\ \Delta S°_{298} = -76.8$$
$$\Delta F_{298} = 38{,}730 \quad (96)$$
$$C_p = 0.137T^{35} \quad (97)$$
$$\Delta C_p = -37.6 + 0.094 \quad (98)$$
$$\Delta H_0 = 22{,}880 \quad (99)$$

for $10C + 4H_2 \longrightarrow C_{10}H_8$ (solid)

$$\Delta F = 22{,}880 + 37.6T\ln T - 0.047T^2 - 147.1T \quad (100)$$
$$\Delta F_{353} = 42{,}960 \quad (101)$$

for either solid or liquid naphthalene. Adding the latent heat of fusion, 4560,[36] to (99), and combining with (101), for $10C + 4H_2 \longrightarrow C_{10}H_8$ (liquid)

$$\Delta F = 27{,}440 + 37.6T\ln T - 0.047T^2 - 160T \quad (102)$$
$$\Delta F_{491} = 51{,}940 \quad (103)$$

The vapor pressures[37] are: at 25° C., 0.092 mm.; at 80° C., 7.4 mm.; and at 218° C., 760 mm. From these and (96), (101), and (103) we find for naphthalene vapor, $\Delta F = 44{,}100$, 46,200, and 51,940, respectively. Combining these and a rough estimate of the heat capacity of the vapor, for $10C + 4H_2 \longrightarrow C_{10}H_8$ (gas)

$$\Delta F = 38{,}540 + 21T\ln T - 0.01T^2 - 98T \quad (104)$$

or for the cracking range,

$$\Delta F = 28{,}100 + 47.5T \quad (105)$$

Cyclohexane

The equilibria between benzene, hydrogen, and cyclohexane have been studied by Burrows and Lucarini.[38] They find at 266.5° C., $Kp = 5.47$ and at 280° C., $Kp = 1.62$. From these

$$\Delta F_{539.6} = -1820 \quad (106)$$
$$\Delta F_{553} = -531 \quad (107)$$

We estimate for C_6H_{12} vapor[23]

$$C_p = 6.8 + 0.075T \quad (108)$$

whence, for the reaction $C_6H_6 + 3H_2 \longrightarrow C_6H_{12}$

$$\Delta C_p = -19.75 + 0.023T \quad (109)$$

For the reaction as liquids[38]

$$\Delta H_{293} = -51{,}600 \quad (110)$$

Assuming the latent heats of vaporization to be the same (110) holds for vapors and

$$\Delta H = \Delta H_0 - 19.75 + 0.0115T^2 \quad (111)$$

from which

$$\Delta H_0 = -46{,}800 \quad (112)$$

Combining (109) and (112) with (106) or (107), $I = -34.5$ and for $C_6H_6 + 3H_2 \longrightarrow C_6H_{12}$ (gas)

$$\Delta F = -46{,}800 + 19.75T\ln T - 0.0115T^2 - 34.5T \quad (113)$$

or, simplifying

$$\Delta F = -55{,}200 + 98.8T \quad (114)$$

Combining with (83), the free energy of formation of cyclohexane $6C + 6H_2 \longrightarrow C_6H_{12}$ (gas), is

[29] L-B, p. 1483.
[30] L-B, p. 1370.
[31] Richards and Davis, *J. Am. Chem. Soc.*, **42**, 1614 (1920).
[32] Lewis and Gibson, *Ibid.*, **39**, 2575 (1917).
[33] Nakatsuchi, *C. A.*, **20**, 1020 (1926).
[34] L-B, p. 1272.
[35] L-B, p. 1271.
[36] L-B, p. 1474. This is permissible if the heat capacity equation (97) holds for both solid and liquid naphthalene, since this would make the heat of fusion independent of temperature.
[37] L-B, p. 1371.
[38] *J. Am. Chem. Soc.*, **49**, 1160 (1927).

$$\Delta F = -38{,}100 + 134T \quad (115)$$

This is nearly the mean between those of hexane and hexene by (45) and (64). Accordingly, for naphthenes in general we will use nearly the mean increments of these of paraffins and olefins. For $nC + nH_2 \longrightarrow C_nH_{2n}$ (gas)

$$\Delta F = 12{,}900 - 8500n - 19.3T + 25.55nT \quad (116)$$

Oxygenated Compounds

For convenience the free-energy equations for formation of steam, carbon monoxide, and carbon dioxide are included.

Steam,[39] $H_2 + {}^1/_2O_2 \longrightarrow H_2O$ (gas),

$$\Delta F = -57{,}410 + 0.94T\ln T + 0.00165T^2 - 0.0_637T^3 + 3.92T \quad (117)$$

Carbon monoxide,[40] $C + {}^1/_2O_2 \longrightarrow CO$,

$$\Delta F = -26{,}600 - 2.15T\ln T + 0.00215T^2 - 0.0_62T^3 - 7.48T \quad (118)$$

Carbon dioxide,[40] $C + O_2 \longrightarrow CO_2$,

$$\Delta F = -94{,}110 + 0.60T\ln T - 0.00065T^2 + 0.0_611T^3 - 2.30T \quad (119)$$

These can be simplified without much error

$$\text{For } H_2O\ \Delta F = -58{,}910 + 13.2T \quad (120)$$
$$CO\ \Delta F = -26{,}080 - 20.9T \quad (121)$$
$$CO_2\ \Delta F = -94{,}300 + 1.5T \quad (122)$$

Recapitulation

For comparison the following equations are repeated.

Compound	Free Energy of Formation (Gas)	
CH_4	$-20{,}000 + 26.2T$	(10)
C_2H_6	$-29{,}000 + 53.3T$	(44)
C_8H_{18}	$-76{,}100 + 206.6T$	(35)
C_2H_4	$12{,}260 + 11.6T$	(52)
C_2H_2	$54{,}400 - 10.8T$	(59)
C_6H_6	$17{,}000 + 35.3T$	(83)
C_7H_8	$6{,}860 + 59.2T$	(94)
$C_{10}H_8$	$28{,}100 + 47.5T$	(105)
C_6H_{12}	$-38{,}100 + 134T$	(115)
C_nH_{2n+2} (paraffins)	$-13{,}300 - 7850n + 2.2T + 25.55nT$	(45)
C_nH_{2n} (olefins)	$31{,}060 - 9400n - 39.5T + 25.55nT$	(64)
C_nH_{2n} (naphthenes)	$12{,}900 - 8500n - 19.3T + 25.55nT$	(116)
C_nH_{2n-2} (acetylenes)	$68{,}400 - 7000n - 61.9T + 25.55nT$	(65)

The original equations for the individual hydrocarbons have been plotted in the figure. At any given temperature the tendency of a reaction is from a higher to a lower line in the figure. The close approach to straight lines justifies the use of the above linear equations. The line of zero free energy is marked "$C + H_2$," since it corresponds to the elements.

The ordinates have been reduced to free energy of formation per carbon atom. A comparison of free-energy equations of hydrocarbons on any other basis leads to erroneous conclusions. This is evident, since if it were proposed to make benzene from methane, for example, it would require six molecules of the latter,

$$6CH_4 \longrightarrow C_6H_6 + 9H_2$$

The figure shows that for a substantial yield by this reaction a temperature of 850° C. must be exceeded. Moreover, because of the increase in volume the application of pressure would oppose rather than favor the reaction. Smith[2] concludes incorrectly (p. 803) that the tendency to form higher paraffin and aromatic hydrocarbons (at 300° C.) is greater than that to form lower paraffin hydrocarbons. Although benzene is theoretically capable of formation from water gas at moderate temperatures, the chance of its production in preference to that of the more stable hydrocarbons and alcohols is so small that with our present limited knowledge of catalysts, investigations with that aim are unpromising.

[39] L. and R., p. 485.

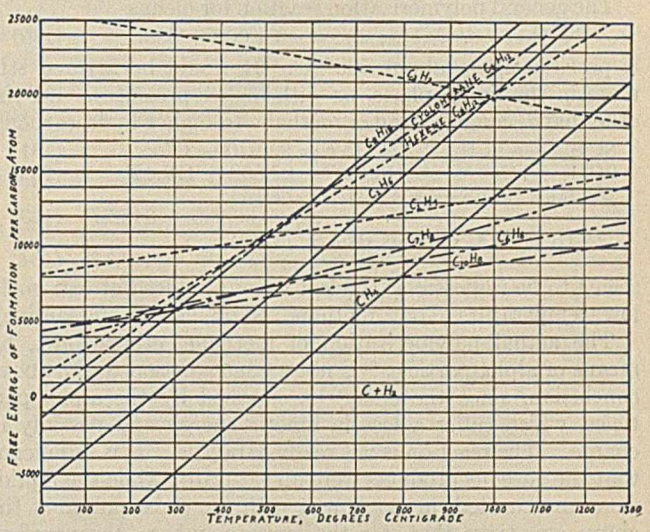
[40] L. and R., p. 576, as modified by Eastman and Evans, *J. Am. Chem. Soc.*, **46**, 902 (1924).

Discussion

The paraffin hydrocarbons—methane, ethane, octane—have nearly parallel lines. The aromatics—benzene, toluene, naphthalene—have lines which slope much less (the most aromatic with the least slope), indicating less decomposing effect of temperature. Ethylene has a line nearly parallel with those of the aromatics, but the higher olefins—for example, hexene—partake more of the nature of paraffins. Naphthenes, such as cyclohexane, are intermediate between paraffins and olefins. Acetylene is the only hydrocarbon whose stability is increased by temperature, but it never becomes stable with respect to its elements. Even at 5000° C., where it would be stable according to equation (59), this is not the case, because far below that temperature hydrogen is dissociated to atomic hydrogen, and the acetylene equilibrium would be $C_2H_2 \leftrightarrows 2C + 2H$, which is displaced to the right by increasing temperatures.

Although for convenience the equations for the formation of gas (or vapor) will be used in all cases, this is not intended to imply that all cracking operations are in the vapor phase. The difference in result for liquid-phase reactions will be considered qualitatively in each case where applicable. For any individual case, calculations for liquids can be made readily from the vapor pressures, but no general equation can be set up.

It is understood also that certain reactions which normally would be accompanied by a slight increase in free energy can be forced to proceed under pressure, if there is a decrease



in volume; but practical pressures will not usually overcome an unfavorable free-energy change of more than 5000 calories. Moreover, a reaction found thermodynamically impossible cannot be induced to proceed by means of a catalyst.

It will be observed that according to the above equations and the figure, only the paraffins and the higher olefins have any thermodynamic stability whatever, and above 260° C. methane is the only stable hydrocarbon. This seems inconsistent with the ordinary cracking reactions, in which large quantities of olefins and some aromatics are produced from paraffin hydrocarbons.

Let us assume the following as typical cracking reactions:

$$C_nH_{2n+2} \longrightarrow C_{n-1}H_{2n-2} + CH_4;$$
$$\Delta F = 33{,}760 - 1550n - 41.05T \quad (123)$$
$$C_{2n}H_{4n+2} \longrightarrow C_nH_{2n+2} + C_nH_{2n};$$
$$\Delta F = 31{,}060 - 1550n - 39.5T \quad (124)$$

which become negative at cracking temperatures even in the case of the lowest members. Thermodynamics does not show which mechanism is preferred. Liquid-phase reactions

would be very slightly less favored, but could be calculated readily from (123) and (124) if the pressures employed and the vapor pressures of the reactants were known. The simultaneous production of coke and hydrogen is even more consistent with the equations. Similarly in the case of benzene and naphthalene from ethane,[41] as shown also by the figure,

$$3C_2H_6 \longrightarrow C_6H_6 + 6H_2;\ \Delta F = 104{,}000 - 124.6T \quad (125)$$
$$5C_2H_6 \longrightarrow C_{10}H_8 + 11H_2;\ \Delta F = 173{,}100 - 219T \quad (126)$$

which are evidently possible at the temperatures employed (above 550° C.). Similar conclusions would apply to the production of aromatics in high-temperature cracking.

$$C_6H_{14} \longrightarrow C_6H_6 + 4H_2;\ \Delta F = 77{,}400 - 120.2T \quad (127)$$

The explanation is, of course, that in all cracking operations true chemical equilibrium is never attained, but only a condition nearer to equilibrium—that is, lower free energy. It is significant that members of the acetylene series are not found in the products of cracking operations, since these would require a much higher temperature (above 850° C. in the most favorable case, acetylene).

$$C_{2n}H_{4n+2} \longrightarrow C_nH_{2n+2} + C_nH_{2n-2} + H_2$$
$$\Delta F = 68{,}400 + 800n - 61.9T \quad (128)$$

In the Fischer synthesis of gasoline

$$8CO + 17H_2 \longrightarrow C_8H_{18} + 8H_2O;$$
$$\Delta F = -338{,}740 + 479.4T \quad (129)$$

which is negative up to 700° K. or 427° C. His operating temperature for gasoline is 275–300° C. Higher temperatures give lower hydrocarbons, especially methane, as should be expected.

The general polymerization reaction for olefins

$$2C_nH_{2n} \longrightarrow C_{2n}H_{4n};\ \Delta F = -31{,}060 + 39.5T \quad (130)$$

is possible up to about 500° C. It would be favored still more in the liquid phase, or with higher pressures. On the other hand, condensation of methane to higher hydrocarbons,

$$8CH_4 \longrightarrow C_8H_{18} + 7H_2;\ \Delta F = 83{,}910 - 3T \quad (131)$$
$$9CH_4 + 7C \longrightarrow 2C_8H_{18};\ \Delta F = 27{,}800 + 177.4T \quad (132)$$
$$25CH_4 + 7CO_2 \longrightarrow 4C_8H_{18} + 14H_2O;$$
$$\Delta F = 30{,}960 + 345.7T \quad (133)$$
$$17CH_4 + 7CO \longrightarrow 3C_8H_{18} + 7H_2O;$$
$$\Delta F = -118{,}110 + 413.1T \quad (134)$$

seems to be impossible (the last should proceed at extremely low temperatures, but methane is much too unreactive).

The actual polymerization of methane, ethane, etc., by means of alpha particles[42] is not a contradiction to the above conclusion, since the energy is supplied by the alpha particles, which suffer a loss in kinetic energy and possibly in charge. The reaction is not really catalytic. It is significant that the gaseous products were all saturated while the liquids were unsaturated, in agreement with the consequence of the above equations that, for the lower members, the paraffins are more stable than the olefins with the same number of carbon atoms, while for the higher ones the olefins are more stable [*cf.* equation (138)].

Similarly, as shown also by the figure, the formation of acetylene from methane

$$2CH_4 \longrightarrow C_2H_2 + 3H_2;\ \Delta F = 94{,}400 - 63.2T \quad (135)$$
or
$$CH_4 + 3C \longrightarrow 2C_2H_2;\ \Delta F = 128{,}800 - 47.8T \quad (136)$$

could take place only at very high temperatures, at which all but a trace of the acetylene would be decomposed.

By analogy with (131) no paraffin hydrocarbon should be capable of direct condensation to a higher hydrocarbon; but if lower ones are formed simultaneously with higher ones, there is no change in free energy according to (45) for gaseous reactions. In the case of liquid hexane with aluminum chloride at room temperature,[43] the change in free energy can be calculated from the vapor pressures of hexane and dodecane.

$$3C_6H_{14} \longrightarrow 2C_3H_8 + C_{12}H_{26};\ \Delta F_{298} = -2100 \quad (137)$$

The reverse of this type of reaction is said to be accomplished in a recent patent,[44] which employs high pressures.

The conversion of a paraffin into an olefin of the same number of carbon atoms would be desirable in some cases.

$$C_nH_{2n+2} \longrightarrow C_nH_{2n} + H_2;$$
$$\Delta F = 44{,}360 - 1550n - 41.7T \quad (138)$$

In order to make ΔF negative, the temperature or the number of carbon atoms, or both, must be fairly high—conditions which favor the more profound disruption of the molecule.

The partial removal of hydrogen by means of atmospheric or other form of oxygen with the purpose of obtaining olefins or higher paraffins is possible thermodynamically because of the high free energy of formation of steam; but actually the chance of success would be very small because the products would be much more reactive with the oxidizing agent than was the starting material.

The synthesis of benzene from acetylene

$$3C_2H_2 \longrightarrow C_6H_6;\ \Delta F = -146{,}200 + 68.1T \quad (139)$$

is possible except at extremely high temperatures, as shown also by the figure.

The isomerization of olefins to naphthenes in presence of aluminum chloride should take place up to about 430° C.

$$\text{Olefin} \longrightarrow \text{naphthene};$$
$$\Delta F = -18{,}160 + 900n + 18T \quad (140)$$

[41] Williams-Gardner, *Fuel Science Practice*, **4**, 430 (1925).

[42] Lind and Bardwell, *J. Am. Chem. Soc.*, **48**, 2355 (1926).

[43] Schneider and Norris, paper read before the Division of Petroleum Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.

[44] McAfee, U. S. Patent 1,608,328 (1926).

European Cartels

Thirteen important international cartels enumerated below, most of them formed in the last two years by industrial interests chiefly in Europe, have been listed by the Department of Commerce, and half a dozen more are in process of formation.

These industrial combinations are only a few of those organized since the World War as a result of keener competition for world trade caused by the larger entry of the United States into the export markets. No complete list is available, since a great many of those established have never been acknowledged by the interests involved.

Europe had international cartels before the World War, but they were chiefly of an economic character, whereas the new ones are credited with having a distinctly political flavor which, some think, will lead eventually to closer political connection between the countries interested.

Commodity	Countries Involved	Organized
Raw steel	France, Germany, Belgium, Czechoslovakia, Luxembourg, Austria, Hungary	September, 1926
Rails	Great Britain, France, Germany, Belgium, Luxembourg	June, 1926
Tubes	Germany, France, Belgium, Luxembourg, Great Britain, Austria, Czechoslovakia, Poland	June, 1926
Aluminum	France, Germany, Great Britain, Switzerland, Norway (in part), Austria (in part)	August, 1926
Enamelware	Germany, Poland, Czechoslovakia, Austria, Hungary	1926
Glue	Most European countries	July, 1926
Artificial silk	Great Britain, Germany, Italy (including a number of plants controlled by Great Britain and Germany in United States)	January, 1927
Copper	United States, Spain, Belgium, Jugoslavia, Great Britain	October, 1926
Electric bulbs	Germany, United States, Canada, Netherlands, France, Italy, Scandinavian countries, Great Britain, Austria, Hungary	1924
Plate glass	France, Belgium	1904
Glass bottles	Germany, France, Austria, the Scandinavian countries, Czechoslovakia, Hungary, Holland	1907
Borax	Great Britain, United States, Germany, France, Austria	1899[a]
Wire	Germany, Belgium, Czechoslovakia, Netherlands	February, 1927

[a] Not certain as to present existence.

The Free Energies of Some Alcohols[1,2]

Alfred W. Francis

Arthur D. Little, Inc., Cambridge, Mass.

Equations have been derived for the free energies of formation of nine alcohols. These have been simplified to linear equations for the range 227–427° C. A general equation for normal alcohols has been derived, and this has been compared with that for olefins to find conditions for dehydration or hydration of the olefins; and with that for carbon monoxide to find conditions for synthesis.

IN ANOTHER paper[3] the free energies of formation of several hydrocarbons have been calculated or estimated. In order to throw more light upon the chemistry of petroleum products, it seemed desirable to calculate the free energies of some of the aliphatic alcohols in a similar manner. The results are important in connection with the synthesis of higher alcohols as well as methanol from water gas.[4]

The free energies of several alcohols have been calculated by Parks and his collaborators[5] at room temperature by means of the third law of thermodynamics, employing specific heats at low temperatures. However, most of the reactions for which such data would be of value take place at much higher temperatures, 250° to 400° C., and in the vapor state.

The free energy of methanol vapor as a function of temperature has been calculated by Kelley.[6] His calculations could be improved in two particulars: (*a*) His equation for the heat capacity of methanol vapor, $C_p = 6.16 + 0.0183T$, was only a guess, whereas data are available[7] for a better estimate,

$$C_p = 0.6 + 0.0335T \quad (1)$$

(*b*) In finding ΔH for the vapor he employed the latent heat of vaporization of methanol at 25° C.—namely, 9000 calories—without correcting for the Joule-Thomson effect in the vapor, which in this case would make an error of 160 calories if equation (1) were employed, or 190 calories using his equation. It would have been preferable to evaluate ΔH and ΔF of the vapor at the boiling temperature from the same functions for the liquid at that temperature. This procedure will be followed in the present paper. A further reason for doing this is that the heat capacities of the liquids can be estimated more accurately than those of the vapors, so that by carrying the free-energy figures to the boiling temperature by means of the liquid phase the less accurate extrapolation for the vapor phase need not be carried through so great a temperature range in order to reach the reaction temperatures.

The calculations will be given in detail for methanol, but since the method is the same the calculations for the other alcohols will be given in tabular form.

Calculations for Methanol

The free energy and heat of formation of liquid methanol are given by Parks and Kelley[5] as follows:

$$\Delta F_{298} = -44{,}500 \quad (2)$$
$$\Delta H_{298} = -59{,}890 \quad (3)$$

The heat capacity of liquid methanol and the latent heat of vaporization at the boiling temperature, 64.5° C., are estimated[8]

$$C_p = 5.45 + 0.047T \quad (4)$$
$$\Delta H_{v337.6} = 8480 \quad (5)$$

From the heat capacities of the elements, for carbon[3]

$$C_p = 1.1 + 0.0048T - 0.0_5 12T^2 \quad (6)$$

or approximately

$$C_p = 1.1 + 0.004T \quad (7)$$

for hydrogen[3]

$$C_p = 6.65 + 0.0007T \quad (8)$$

for oxygen[9]

$$C_p = 6.98 + 0.0002T \quad (9)$$

that of $C + 2H_2 + {}^1/_2\,O_2$ is

$$C_p = 17.89 + 0.0055T \quad (10)$$

From (4) and (10)

$$\Delta C_p = -12.44 + 0.0415T \quad (11)$$

Combining with (3)

$$\Delta H = -58{,}030 - 12.44T + 0.02075T^2 \quad (12)$$
$$\Delta H_{337.6} = -59{,}860 \quad (13)$$

Adding (5), for methanol vapor

$$\Delta H_{337.6} = -51{,}380 \quad (14)$$

From (1) and (10)

$$\Delta C_p = -17.29 + 0.028T \quad (15)$$

Combining with (14)

$$\Delta H = -47{,}130 - 17.29T + 0.014T^2 \quad (16)$$

From (12) and (2) for liquid methanol

$$\Delta F = -58{,}030 + 12.44\,T\ln T - 0.02075T^2 - 19.36T \quad (17)$$
$$\Delta F_{337.6} = -42{,}450 \quad (18)$$

for either liquid or vapor.

From (16) and (18) for methanol vapor

$$\Delta F = -47{,}130 + 17.29\,T\ln T - 0.014T^2 - 82T \quad (19)$$
$$\Delta F_{298} = -43{,}450 \quad (20)$$

From the vapor pressure of methanol at 25° C. 125 mm.,[6] for the evaporation,

$$\Delta F = -RT\ln\left(\frac{125}{760}\right) = 1070 \quad (21)$$

which agrees well with the difference between (2) and (20).

For the temperature range 500° to 700° K. with which we are concerned, equation (19) can be simplified without appreciable inaccuracy

$$\Delta F = -52{,}450 + 29T \quad (22)$$

Discussion

From the linear equations for the four normal alcohols—ethanol, *n*-propanol, *n*-butanol, and *n*-heptanol—the general equation

$$\Delta F = -43{,}540 - 7010n + 24.2nT \quad (23)$$

[1] Presented before the Division of Petroleum Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

[2] Since this paper was written calculations for three of these alcohols have been published by Smith, *Ind. Eng. Chem.*, **19**, 801 (1927), but the present paper is more comprehensive. The symbols used throughout conform to the system of Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923.

[3] *Ind. Eng. Chem.*, **20**, 277 (1928).

[4] Patart, International Conference on Bituminous Coal, Carnegie Institute of Technology, p. 154 (1926).

[5] *J. Am. Chem. Soc.*, **47**, 338, 2094 (1925); **48**, 1506, 2788 (1926).

[6] *Ind. Eng. Chem.*, **18**, 78 (1926).

[7] C_p = 14.7 at 162° C., 21.43 at 340° C. Landolt-Bornstein-Roth-Scheele, "Tabellen," p. 1275 (1923) (hereinafter abbreviated "L-B"); C_p = 12.56 at 77° C., Dixon and Greenwood, *Proc. Roy. Soc.* (*London*), **A105**, 199 (1924); *C. A.*, **18**, 2986 (1924).

[8] L-B, pp. 1270, 1482.

[9] Partington and Shilling, "The Specific Heats of Gases," p. 145, D. Van Nostrand Co., New York, 1924.

Data for Free Energies of Higher Alcohols

	Ethanol C_2H_5OH	*n*-Propanol C_3H_7OH	Isopropanol $(CH_3)_2CHOH$	*n*-Butanol C_4H_9OH
(*a*) Boiling point	351.5° K.	370.9° K.	355.4° K.	390.8° K.
(*b*) Vapor pres. at 25° C.	59 mm.	20.8 mm.	44.0 mm.	6.5 mm.
(*c*) ΔH_v at boiling point	9500	9890	9580	10,410
(*d*) ΔH_{298}	−65,660	−72,260	−77,500	−78,770
(*d*) ΔF_{298}	−44,000	−44,100	−47,700	−44,100
(*e*) C_p of elements	$25.64 + 0.0118T - 0.0_5 24T^2$	$33.38 + 0.0149T$	$33.38 + 0.0173T - 0.0_5 36T^2$	$41.13 + 0.0228T - 0.0_5 48T^2$
(*f*) C_p liquid	$5.92 - 0.004T + 0.000248T^2$	$-12.1 + 0.16T$	$-17.6 + 0.163T + 0.0_5 96T^2$	$-6.28 + 0.122T + 0.0_5 1333T^2$
(*g*) C_p vapor	$5.31 + 0.0364T$	$10 + 0.0393$	$7.66 + 0.0379T$	$14.72 + 0.0422T$
ΔC_p liquid	$-19.72 - 0.0158T + 0.0002504T^2$	$-45.48 + 0.1451T$	$-50.98 + 0.1457T + 0.0_4 132T^2$	$-47.41 + 0.0992T + 0.0_5 1381T^2$
ΔC_p vapor	$-20.33 + 0.0262T$	$-23.38 + 0.0244T$	$-25.72 + 0.023T$	$-26.41 + 0.0226T$
ΔH liquid	$-61,310 - 19.72T - 0.0079T^2 + 0.0_4 835T^3$	$-65,110 - 45.48T + 0.07255T^2$	$-68,890 - 50.98T + 0.07285T^2 + 0.0_5 44T^3$	$-70,270 - 47.41T + 0.0496T^2 + 0.0_4 46T^3$
ΔH_b liquid	−65,550	−72,000	−77,140	−78,470
ΔH_b vapor	−56,050	−62,110	−67,560	−68,060
ΔH vapor	$-50,520 - 20.33T + 0.0131T^2$	$-55,110 - 23.38T + 0.0122T^2$	$-59,820 - 25.72T + 0.0115T^2$	$-59,470 - 26.41T + 0.0113T^2$
ΔF liquid	$-61,310 + 19.72T\ln T + 0.0079T^2 - 0.0_4 42T^3 - 53T$	$-65,110 + 45.48T\ln T - 0.07255T^2 - 166.8T$	$-68,890 + 50.98T\ln T - 0.07285T^2 - 0.0_5 22T^3 - 197.3T$	$-70,270 + 47.41T\ln T - 0.0496T^2 - 0.0_4 23T^3 - 165.6T$
ΔF_b	−40,100	−37,140	−41,900	−33,326
ΔF vapor	$-50,520 + 20.33T\ln T - 0.0131T^2 - 85T$	$-55,110 + 23.38T\ln T - 0.0122T^2 - 85.4T$	$-59,820 + 25.72T\ln T - 0.0115T^2 - 96.5T$	$-59,470 + 26.41T\ln T - 0.0113T^2 - 86.8T$
ΔF_{298} vapor	−42,470	−41,970	−45,920	−41,320
ΔF_{298} evaporation	1511	2135	1691	2820
ΔF_{500} vapor	−33,130	−28,285	−31,045	−23,635
ΔF_{700} vapor	−23,220	−13,770	−15,120	−4660
ΔF vapor	$-57,880 + 49.5T$	$-64,590 + 72.6T$	$-70,840 + 79.6T$	$-71,090 + 94.9T$

	Isobutanol $(CH_3)_2CHCH_2OH$	*Tert*-Butanol $(CH_3)_3COH$	Active Amyl Alcohol $C_2H_5(CH_3)CHCH_2OH$	*n*-Heptanol $C_7H_{15}OH$
(*a*) Boiling point	380.4° K.	355.9° K.	401.1° K.	448.9° K.
(*b*) Vapor pres. at 25° C.	12.2 mm.	42.0 mm.	3.4 mm.	...
(*c*) ΔH_v at boiling point	10,100	9700	10,600	12,200
(*d*) ΔH_{298}	−80,000	−88,400	−87,880	−100,580
(*d*) ΔF_{298}	−45,900	−49,900	−45,900	−44,100
(*e*) C_p of elements	$41.13 + 0.0228T - 0.0_5 48T^2$	$41.13 + 0.0196T$	$48.88 + 0.0243T$	$64.38 + 0.0337T$
(*f*) C_p liquid	$-14.34 + 0.1332T + 0.0002T^2$	$-18 + 0.1796T$	$-18.2 + 0.2303T$	$-30.7 + 0.3237T$
(*g*) C_p vapor	$12.36 + 0.0408T$	$10 + 0.0396T$	$16.83 + 0.0443T$	$28.85 + 0.0509T$
ΔC_p liquid	$-55.47 + 0.1104T + 0.0002048T^2$	$-59.13 + 0.16T$	$-67.08 + 0.206T$	$-95.08 + 0.29T$
ΔC_p vapor	$-28.77 + 0.0212T$	$-31.13 + 0.02T$	$-32.05 + 0.02T$	$-35.53 + 0.0172T$
ΔH liquid	$-70,170 - 55.47T + 0.0552T^2 + 0.0_4 683T^3$	$-77,890 - 59.13T + 0.08T^2$	$-77,040 - 67.08T + 0.103T^2$	$-85,140 - 95.08T + 0.145T^2$
ΔH_b liquid	−79,530	−88,790	−87,374	−98,640
ΔH_b vapor	−69,430	−79,090	−76,774	−86,440
ΔH vapor	$-60,020 - 28.77T + 0.0106T^2$	$-69,290 - 31.13T + 0.01T^2$	$-65,527 - 32.05T + 0.01T^2$	$-72,230 - 35.53T + 0.0086T^2$
ΔF liquid	$-70,170 + 55.47T\ln T - 0.0552T^2 - 0.0_4 341T^3 - 215.22T - 36,540$	$-77,890 + 59.13T\ln T - 0.08T^2 - 219.22T - 42,390$	$-77,040 + 67.08T\ln T - 0.103T^2 - 247.16T - 31,435$	$-85,140 + 95.08T\ln T - 0.145T^2 - 360.96T - 15,750$
ΔF_b	$-60,020 + 28.77T\ln T - 0.0106T^2 - 106.16T$	$-69,290 + 31.13T\ln T - 0.01T^2 - 103.87T$	$-65,527 + 32.05T\ln T - 0.01T^2 - 103.06T$	$-72,230 + 35.53T\ln T - 0.0086T^2 - 87.29T$
ΔF_{298} vapor	−43,440	−48,260	−42,695	−38,637
ΔF_{298} evaporation	2450	1718	3206	...
ΔF_{500} vapor	−26,360	−27,000	−19,977	−7628
ΔF_{700} vapor	−7620	−4170	+4382	+26,366
ΔF vapor	$73,210 + 93.7T$	$-84,075 + 114.15T$	$-80,880 + 121.8T$	$-92,630 + 170T$

(*a*) International Critical Tables, Vol. I, p. 180, McGraw-Hill Book Co., 1926.
(*b*) L-B, p. 1362, Parks and Barton, *J. Am. Chem. Soc.*, **50**, 25 (1928).
(*c*) L-B, p. 1480. The value used for *tert*-butanol was estimated from Trouton's rule.
(*d*) Reference 5. The heats of formation of iso-butanol, active amyl alcohol, and *n*-heptanol were estimated from their heats of combustion, L-B, p. 1592. The free energy of *n*-heptanol at 25° C. was assumed to be the same as those of the other normal alcohols. Those of iso-butanol and active amyl alcohol were assumed to be the mean between those of normal and those of secondary alcohols (iso-propanol).
(*e*) References 3 and 9.
(*f*) Williams and Daniels, *J. Am. Chem. Soc.*, **46**, 912 (1924); L-B, p. 1266. The heat capacities of active amyl alcohol and *n*-heptanol are extrapolations from those of the lower primary alcohols. That of *tert*-butanol was found by adding to that of *n*-butanol twice the difference between those of iso-propanol and *n*-propanol.
(*g*) The heat capacities of methanol and ethanol vapors were obtained from reference 7. Those of the other alcohols are suitable extrapolations of these two. Moderate errors in the heat capacities make very little differences in the free energies calculated, because of the compensating effect of the chemical constant, *I*.

can be derived, where n is the number of carbon atoms. Methanol was omitted from this calculation because it lacks a carbon-carbon bond. The branched-chain primary alcohols—isobutanol and active amyl alcohol—are slightly more stable, just as the branched-chain hydrocarbons are more stable than the straight-chain hydrocarbons. Secondary and tertiary alcohols have still more negative free energies, as might be predicted from the fact that hydration of olefins gives practically no primary alcohol (except in the case of ethylene). The differences decrease at higher temperatures, however.

The most important reaction of alcohols with relation to the petroleum industry is the dehydration to olefins. The conditions for this can be calculated. From the other paper[3] the free energies of formation of water and olefins in the range 500–700° K. are as follows (modified slightly because the equations there given were for the range 700–1000° K.):

For H_2O $\Delta F = -58,360 + 12.4T$ (24)
For olefins $\Delta F = 29,930 - 8420n - 38T + 24.2nT$ (25)

Adding these and subtracting (23) we have for the reaction

$$C_nH_{2n+1}OH \longrightarrow C_nH_{2n} + H_2O \quad (26)$$
$$\Delta F = 15,110 - 1410n - 25.6T \quad (27)$$

According to this, for the dehydration of ethanol the free energy would become zero at about 207° C. This is consistent with the actual catalytic operations which are carried on at higher temperatures, 250–400° C.[10] It would be of great theoretical and practical value if a true equilibrium could be established and studied for equation (26). The reverse reaction[11] would be of industrial importance, especially for higher olefins. If (27) is accurate, however, it would be necessary to carry it out at temperatures not much above boiling, or else with high pressure.

The coefficients of the nT terms, 24.2, in equations (23) and (25) are alike. This number may be characteristic of homologous series.

[10] *C. A.*, **18**, 50, 813 (1924); **19**, 2026 (1925).
[11] *C. A.*, **18**, 1976 (1924); **20**, 1996 (1926).

The free energy of carbon monoxide can be expressed by the equation

$$\Delta F = -26{,}080 - 20.9T \quad (28)$$

Combining this with (22) and (23), we have for the synthesis of methanol and other alcohols, respectively, from carbon monoxide and hydrogen

$$\Delta F = -26{,}370 + 49.9T \quad (29)$$
$$\Delta F = -17{,}460 - 7010n + 20.9T + 24.2nT \quad (30)$$

Applying (29), we have for the methanol synthesis

° C.	ΔF	$K = \frac{(CH_3OH)}{(CO)(H_2)^2}$
227	−1420	4.17
327	+3570	0.05
427	+8560	0.0021

Synthesis of Methanol from Carbon Monoxide and Hydrogen[1]

W. K. Lewis and Per K. Frolich

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Mass.

A study has been made of some of the factors governing the synthesis of methanol from carbon monoxide and hydrogen under high pressure and in the presence of a catalyst. The literature on methanol catalysts is discussed in the light of experimental data, and the methanol equilibrium as calculated from thermal data is compared with results obtained with a catalyst composed of the oxides of copper, zinc, and aluminum.

The methanol formed by the reaction has a purity of between 99 and 100 per cent provided that the variables temperature, pressure, and rate of flow are chosen within the limits most desirable from the point of view of maximum yield. Under these same conditions only a small amount of carbon monoxide is lost in wasteful side reactions, leading to the formation of carbon dioxide, methane, and water. Studies made with several chambers in series have demonstrated that the catalyst contained in the first chamber protects the catalyst in successive chambers against poisoning.

In the spring of 1925, when the experimental work on the high-pressure synthesis of methanol from carbon monoxide and hydrogen was initiated in this laboratory, considerable publicity had already been given to the new methanol synthesis, although actual data on operation of the process were meager. A German patent of 1913[2] covered the process of synthesizing oxygenated organic compounds from carbon monoxide and hydrogen in a broad and general way, while more specific information was available in a patent and a paper by Patart.[3] An article by Audibert also appeared at that time.[4] From these sources it was apparent that methanol could be produced by passing a mixture of carbon monoxide and hydrogen over a heated metallic oxide catalyst at high pressure.

Thermodynamic Considerations

The simplest possible reactions involving carbon monoxide and hydrogen are as follows:

$$\underset{1\text{ vol.}}{CO} + \underset{1\text{ vol.}}{H_2} = \underset{1\text{ vol.}}{HCHO} + 2000\text{ cal.} \quad (1)$$
$$\underset{1\text{ vol.}}{CO} + \underset{2\text{ vols.}}{2H_2} = \underset{1\text{ vol.}}{CH_3OH} + 24{,}685\text{ cal.} \quad (2)$$
$$\underset{1\text{ vol.}}{CO} + \underset{3\text{ vols.}}{3H_2} = \underset{1\text{ vol.}}{CH_4} + \underset{1\text{ vol.}}{H_2O} + 50{,}000\text{ cal.} \quad (3)$$
$$\underset{2\text{ vols.}}{2CO} + \underset{2\text{ vols.}}{2H_2} = \underset{1\text{ vol.}}{CH_4} + \underset{1\text{ vol.}}{CO_2} + 60{,}282\text{ cal.} \quad (4)$$

(The heats of reaction are for reactants and products in the gaseous state.)

The third and fourth of these, the methane reactions, have been studied in detail by Sabatier and his associates,[5] and data on the equilibria are available through the researches of Mayer and co-workers.[6] Apparently methane was the only organic product derived from the reduction of carbon monoxide with hydrogen at atmospheric pressure, as evidenced by Sabatier's extensive investigations,[5] although a number of patents claim the possibility of securing small yields of formaldehyde and even methanol.[7]

From a consideration of the volumes entering in the reactions it is apparent that the formation of methanol goes with the largest volume decrease—viz., from three to one and hence would be most favored by increased pressure. The parallelism between the methanol reaction and the reaction for synthesis of ammonia is striking in this respect.

Calculations of the methanol equilibrium are bound to be more or less inaccurate owing to the lack of adequate data on the specific heat and the equation of state of the alcohol. The fact that the synthesis is carried out at temperatures of 300° C. and up—that is, in the neighborhood of and above the critical temperature of methanol (240° C.)—further reduces the quantitative significance of equilibrium calculations. In a qualitative way, however, free-energy considerations show how the tendency for the reaction to go varies with temperature. Calculations of the free energy of the reaction are now available in the literature and check within the limits of error with those made in this laboratory at the start of the present investigation:

For the reaction, $CO_{(gas)} + 2H_{2(gas)} = CH_3OH_{(gas)}$

$$\Delta F = -20{,}480 + 43.1\,T \log T - 0.01545\,T^2 - 69.8\,T$$

$\Delta F_{300°\,A.}$	$\Delta F_{700°\,A.}$	
−10,810	+8930	Authors
−10,800	+9050	Kelley[8]
−10,790	+9242	Smith[9]

[1] Received January 18, 1928.

[2] German Patent 293,787 (March 8, 1913), with additions 295,202 (May 31, 1914) and 295,203 (June 23, 1914); French Patent 468,427 (February 13, 1914); British Patent 20,488 (1915); U. S. Patent 1,201,850 (October 17, 1916).

[3] French Patent 540,343 (August 19, 1921); *Chimie & industrie*, **13**, 179 (1925); *Compt. rend.*, **179**, 1330 (1924); see also Lormand, *Ind. Eng. Chem.*, **17**, 430 (1925).

[4] *Chimie & industrie*, **13**, 186 (1925),

[5] *Compt. rend.*, **124**, 1358 (1897); *Ann.*, **3447**, 34, 360, 418, 435, 477 (1905); *Ann. chim. phys.*, [8] **4**, 418 (1905).

[6] *J. Gasbel.*, **52**, 166, 194, 242, 326 (1909). A complete review of the literature on the subject up to 1923 is contained in a paper by Haslam and Forrest, *Gas Age-Record*, **52**, 615 (1923).

[7] Jahn, *Ber.*, **32**, 989 (1899); Orlow, *Chem. Zentr.*, **801**, 735 (1909); Dreyfus, British Patents 108,855 (July 23, 1917); 157,047 (August 25, 1917); Calvert (editorial), *Chem. Age (London)*, **5**, 153 (1921); Bone and Wheeler, *J. Chem. Soc. (London)*, **81**, 541 (1902); **83**, 1074 (1903). Likewise, the following references have direct bearing on the subject: Berthelot, *Ann. chim. phys.*, [5] **10**, 72 (1877); Losanitch and Jovitschich, *Ber.*, **30**, 135 (1897); Hemptine, *Chem. Zentr.*, **76**, 171 (1905); Berthelot and Gaudechon, *Compt. rend.*, **150**, 1690 (1910).

[8] *Ind. Eng. Chem.*, **18**, 78 (1926).

[9] *Ibid.*, **19**, 801 (1927).

It is interesting to note that the equilibrium constant of the reaction changes with temperature in such a manner that at atmospheric pressure and room temperature methanol would be perfectly stable, while at 300° C. equilibrium would be attained with less than 2 per cent methanol, starting with a mixture of carbon monoxide and hydrogen in the theoretical ratio of 1:2. Even with the best catalysts it has apparently been impossible to suppress the reaction temperature much below 300° C., corresponding practically to no methanol at atmospheric pressure. This clearly shows why past attempts to synthesize methanol from the gases in question at atmospheric pressure were bound to meet with failure. On the other hand, the calculations indicate that at a pressure of 1000 pounds per square inch, or 68

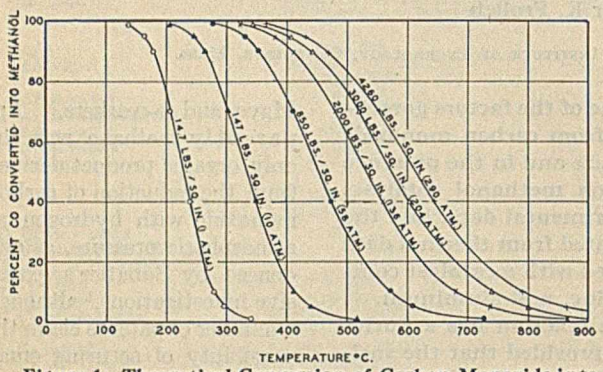


Figure 1—Theoretical Conversion of Carbon Monoxide into Methanol as a Function of Temperature at Various Pressures, Calculated from Thermal Data for a Gas Mixture Consisting of 26% CO, 70% H_2, and 4% Inert

Reaction: $CO + 2H_2 \rightleftarrows CH_3OH + 24{,}685$ cal.

atmospheres, the equilibrium would still be favorable to practically 100 per cent methanol at 300° C. Even with selective catalysts it becomes desirable, however, to employ considerably higher pressure in order to favor methanol formation at the expense of the two methane reactions. Furthermore, it is to be expected that the rate of reaction increases with pressure owing to the higher concentrations.

Figures 1 and 2 give the calculated percentages of carbon monoxide converted to methanol at equilibrium for any combination of temperature and pressure. The calculations are for a gas mixture containing 26 per cent carbon monoxide and 70 per cent hydrogen in order to permit direct comparison with the experimental results reported later in this paper.

Types of Catalysts Used in Synthesis of Methanol

In addition to the papers and patents cited above, there has appeared during the last two years a great deal of information relative to the types of catalysts suitable for methanol formation.[10] The most important group of catalysts consists of combinations of non-reducible metallic oxides in which it is generally essential to have the most basic component present in preponderating quantities.[11] While a number of the first patents claimed the necessity of complete exclusion of iron from the reaction zone, it is now generally agreed that iron may be present, presumably in a non-active form.[12]

[10] U. S. Patents 1,558,559 (October 27, 1925); 1,569,775 (September 4, 1924); German Patent 415,686 (July 24, 1923); French Patents 571,285 (May 14, 1924); 571,354 (May 16, 1924); 571,355 (May 16, 1926); 571,356 (May 16, 1924); 575,913 (August 8, 1924); 581,816 (December 6, 1924); 581,169 (February 23, 1925); British Patents 227,147 (1925); 228,959 (1925); 229,714 (1925); 229,715 (1925); 231,285 (1925); 237,030 (1925); 238,319 (1925); 240,955 (1925); 254,760 (1926); French Patent 540,543 (July 12, 1922); *Tech. Eng. News*, December, 1926.

[11] U. S. Patent 1,558,559 (October 27, 1925); French Patent 571,354 (May 16, 1924); British Patent 227,147 (1925).

[12] British Patent 254,760 (1926); U. S. Patents 1,608,643 (November 30, 1926); 1,609,593 (December 7, 1926); 1,625,924; 1,625,925; 1,625,926; 1,625,927; 1,625,928; 1,625,929 (April 26, 1927).

The term "non-reducible," when referring to the oxides used as catalysts, becomes rather indefinite. A compound like zinc oxide, for example, which normally is not reduced by carbon monoxide or hydrogen at the temperatures in question (300° to 400° C.) shows all indications of being at least partially reduced, when intimately mixed with copper oxide.[13] It has even been stated[14] that metallic oxides which, when alone, are reduced to the corresponding metals do not completely part with their oxygen when mixed with more basic oxides.

Patart[3] claims to have based his catalyst search in connection with the methanol synthesis, on the observations by Sabatier and Maihle[15] and Jahn[16] on the reverse reaction—i. e., the catalytic decomposition of methanol at elevated temperatures. After having tried a number of the individual catalysts studied by these investigators, Patart, however, ultimately came to the conclusion that mixed catalysts were required for best results, although the data disclosed in his first paper would indicate that zinc oxide alone is a good catalyst. Similar observations on zinc oxide are reported by Fischer,[17] but the present writers have not had much success with catalysts consisting of a single oxide. In general, it has been found advantageous to use mixtures of two or more metallic oxides of which one, at least, is non-reducible with reference to carbon monoxide and hydrogen under atmospheric pressure at the temperature in question.

Owing to the exothermic character of the methanol reaction, 26,150 calories per mol of gaseous methanol formed at 327° C., it was found beneficial to support the catalyst on a good heat conductor in order to prevent local overheating of the contact material. Granulated metallic copper proved satisfactory for this purpose.

While a large number of catalysts have been studied, the data reported below were all obtained with a mixture originally consisting of 36 per cent zinc oxide, 44 per cent copper oxide, and 20 per cent aluminum oxide supported on metallic copper, the ratio of active catalyst to copper support being 1:3. This catalyst is of medium activity.

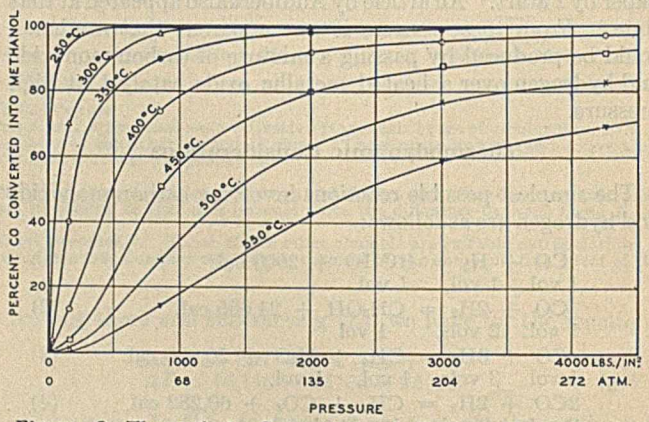


Figure 2—Theoretical Conversion of Carbon Monoxide into Methanol as a Function of Pressure at Various Temperatures, Calculated from Thermal Data for a Gas Mixture Consisting of 26% CO, 70% H_2, and 4% Inert

Reaction: $CO + 2H_2 \rightleftarrows CH_3OH + 24{,}685$ cal.

Method of Preparing Catalyst

A study of different ways of preparing catalysts for methanol synthesis led to the adoption of a method similar to

[13] This observation is supported by a statement in British Patent 237,030 (1925) and by a paper by Rogers, *J. Am. Chem. Soc.*, **49**, 1432 (1927).

[14] British Patent 254,760 (1926).

[15] *Compt. rend.*, **146**, 1376 (1908); **148**, 1734 (1909); "Catalysis in Organic Chemistry," p. 678 (1923).

[16] *Ber.*, **12**, 983 (1880).

[17] "Conversion of Coal into Oils," 1925; *Ind. Eng. Chem.*, **17**, 574 (1925).

the one described by Evans and Newton.[18] The hydroxides of the metals in question are precipitated by ammonium hydroxide from an aqueous solution of the nitrates at 85° C., the purest grade of chemicals being used throughout. Upon careful washing, the hydroxides are obtained as a gel into which the supporting copper is mixed prior to drying at 110° C. A granular, rugged catalyst may thus be obtained.

After having been placed in the reactor, the catalyst is brought up to a temperature of 180° to 200° C. and subjected to the action of the carbon monoxide-hydrogen mixture under reduced pressure, say 100 to 400 pounds per square inch (6.8 to 26.1 atmospheres), for 2 to 4 hours. During this process the copper oxide is presumably reduced to metallic copper, while the hydrated aluminum oxide is dehydrated partly, but probably not completely. Reduction to lower stages of oxidation of the zinc and aluminum may also take place, since this has been shown to be the case for zinc oxide mixed with copper oxide, as mentioned above.

Apparatus

A diagrammatic layout of the apparatus used for the synthesis of methanol is shown in Figure 3. The essential features are (1) mixing of the carbon monoxide and hydrogen in desired proportions, (2) compression of the gas mixture, (3) oil filtration, (4) further purification of gases if desired, (5) storage of compressed gas to provide for intermittent compression, (6) regulation of pressure of outflowing gas by means of proper reducing valves, (7) reaction of carbon monoxide and hydrogen in electrically heated chrome vanadium steel reactors, (8) condensation under pressure of the liquid product in water-cooled condensers, (9) separation of liquid from gas, followed by (10) discharge of liquid and gas through separate valves and (11) determination of liquid yield and of exit gas flow. Valves are installed for withdrawal of gas samples for analysis and special holders are connected with the exit gas lines to permit collection of composite samples. The diagram also shows alternative connections for operation of two or three chambers in series. High-pressure flowmeters may be inserted at the entrance to the reactors, although the entering gas flow can readily be followed from the exit rate when correction is made for the products formed per unit time.

The reaction chambers are constructed of chrome-vanadium steel with bolted-on heads. They are copper-lined and provided with thermocouple wells permitting measurement of the temperature of the gas in the reaction zone or at any other point throughout the reactor. The catalyst occupies only about one-third of the free space in the chamber, the lower and upper parts being filled with copper shot to secure good temperature control.

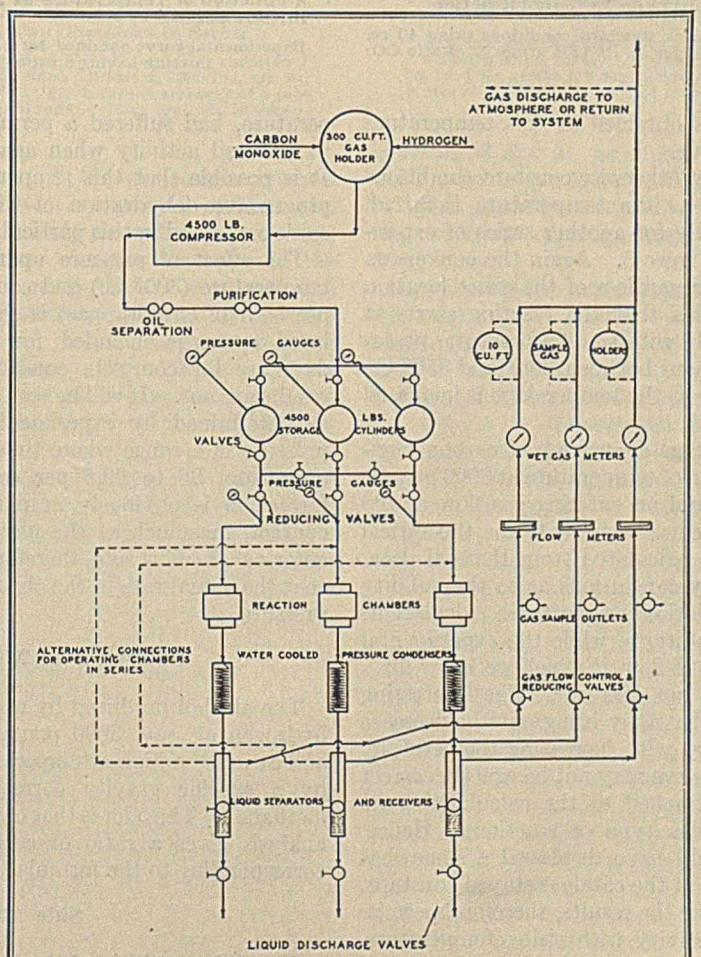


Figure 3—Diagram of Apparatus for Synthesis of Methanol

Effect of Different Variables on Operation of Methanol Process

With a mixture of carbon monoxide and hydrogen flowing through the reactor at pressures from about 1000 pounds per square inch (68 atmospheres) and up, methanol begins to form as soon as the temperature of the catalyst has reached about 300° C. The minimum reaction temperature varies with the catalyst and decreases somewhat with increasing pressure, but rarely goes below 280° C.

While the thermodynamic calculations presented graphically in Figures 1 and 2 predict the temperature and pressure ranges within which the process may be operated most successfully, they fail to take into account two essential variables: (1) rate of reaction, or space-time yield, and the effect of temperature on it; and (2) change in activity of the catalyst with time and temperature, as well as its susceptibility to poisoning. Hence it becomes necessary to study the effect of these different factors by actual experiments.

Figure 4 gives the rate of methanol formation as a function of the rate of entering gas flow under a constant pressure of 3000 pounds per square inch (204 atmospheres). It appears that the yield of methanol is a linear function of the rate of gas flow. No attempt will be made to explain this result at present, since the effect of rate of diffusion and other factors involved are not known.

From Figure 4 it will also be noticed that the methanol yield decreases with increasing temperature. No data are given on this plot for 300° C., because it was impossible to get a representative curve from the observations made at that temperature in this series of experiments. The irregular results at 300° C. are not surprising when it is considered that this is, practically speaking, the temperature at which the reaction starts, and it is well known that results are hard to reproduce at the point where a catalyst commences to become active, especially when the reaction in question is exothermic.

While the quantity of methanol formed per unit time increases with the rate of gas flow, the percentage conversion of carbon monoxide decreases owing to the shorter time of contact between the reacting gas and the catalyst. Percentage conversion *vs.* rate of flow is plotted in Figure 5 for various temperatures at 3000 pounds pressure (204 atmospheres). The curve for 300° C. is somewhat uncertain on account of the wide variations in the ob-

[18] *Ind. Eng. Chem.*, **18**, 513 (1926).

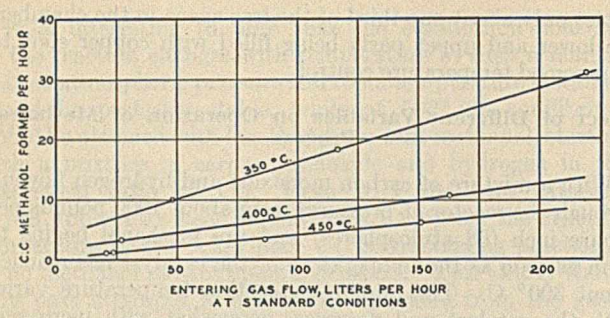


Figure 4—Yield of Methanol as a Function of Rate of Gas Flow

Using 40 cc. of catalyst at various temperatures at a pressure of 3000 lbs. per sq. in. (204 atmos.). Ratio CO:H_2 in entering gas about 0.37

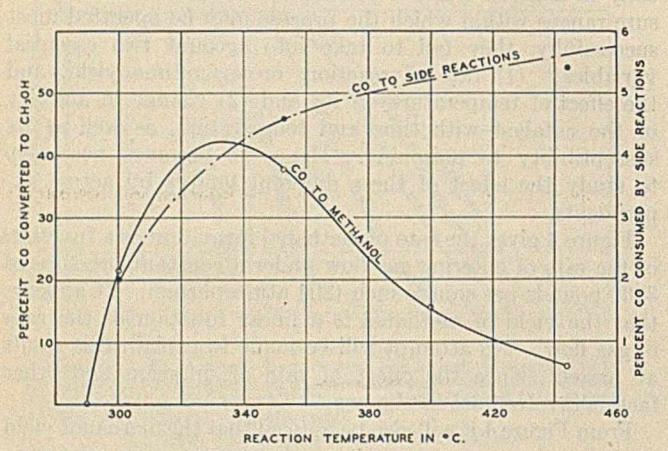


Figure 6—Effect of Temperature on Methanol Reaction

Entering gas rate 80 liters per hour at standard conditions using 40 cc. of catalyst at a pressure of 3000 lbs. per sq. in. (204 atmos.). Ratio CO:H_2 in entering gas about 0.37

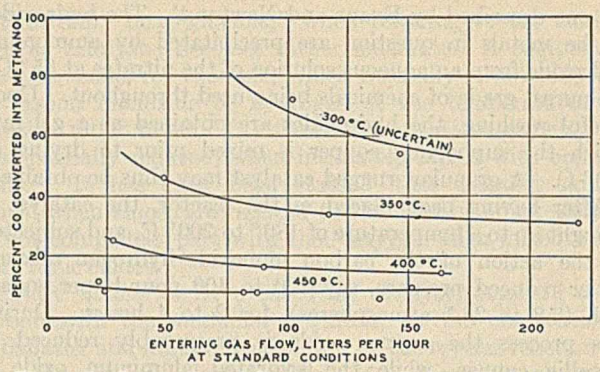


Figure 5—Conversion of Carbon Monoxide into Methanol as a Function of Rate of Gas Flow

Using 40 cc. of catalyst at various temperatures at a pressure of 3000 lbs. per sq. in. (204 atmos.). Ratio CO:H_2 in entering gas about 0.37

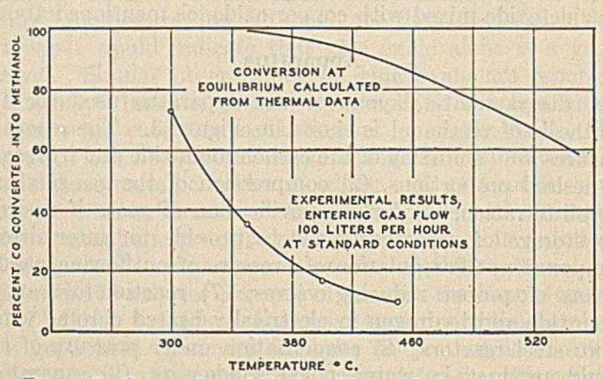


Figure 7—Conversion of Carbon Monoxide into Methanol as a Function of Temperature at a Pressure of 3000 lbs. per sq. in. (204 atmos.)

Experimental curve obtained by using 40 cc. of catalyst with a gas mixture having a ratio of CO:H_2 of about 0.37

servations, the highest yields obtained at this temperature being used in plotting the curve.

The yield of methanol under otherwise constant conditions passes through a maximum as the temperature is raised. Figure 6 shows this graphically for another series of experiments than that plotted in Figure 5. Again the conversion at 300° C. is uncertain, but regardless of the exact location of this point, the fact remains that the reaction starts at 290° C., increases very rapidly with the temperature, passes through a maximum somewhere between 300° and 350° C., and then falls off considerably as the temperature is increased to 450° C.

Figure 7 shows the percentage conversion of carbon monoxide to methanol as a function of temperature at 3000 pounds pressure (204 atmospheres) and an entering gas flow of 100 liters per hour. The upper curve represents the theoretical conversion at equilibrium as calculated from thermal data. The plot does not permit any conclusions as to the validity of the thermodynamic calculations, since these calculations are based on equilibrium conditions, while the experimental results are obtained at a rate of flow at which we know for a certainty that equilibrium is not attained. The interesting point about these curves is that they bring out the decrease in the activity of the catalyst with increasing temperature. Even though the calculated curve may not be exactly correct owing to the uncertainty attached to the calculations, its course is characteristic of this type of reactions. Hence, the experimental curve should have displayed a somewhat similar slope had the activity of the catalyst stayed constant. This particular way of plotting the results, therefore, permits a study of the change in activity with rising temperature. That the activity actually had decreased was demonstrated by the fact that a catalyst, once operated at a higher temperature, had suffered a permanent change as evidenced by its reduced activity when again run at lower temperature. It is possible that this temperature effect may be due to a progressive dehydration of the partly hydrated aluminum oxide contained in this particular catalyst.

The effect of pressure upon the conversion at constant temperature (300° C.) and constant rate of flow (150 liters per hour of entering gas) is shown in Figure 8. The calculated curve is included for comparison. The calculated data are for complete equilibrium while the experimental results are not. It will be seen that the percentage conversion as determined by experiment increases considerably with pressure in a range where the calculated conversion changes only from 98 to 99.5 per cent. The increased methanol formation is obviously in part due to the longer time of contact, inasmuch as the plot is based on constant rate of entering gas flow and therefore does not take into account that the actual rate in the chamber is lowered with increasing pressure.

Character of Methanol Formed

The alcohol produced by reaction of carbon monoxide and hydrogen at, say, 3000 pounds pressure (204 atmospheres) and at not too high a temperature is very pure, as evidenced by a specific gravity corresponding to 99–100 per cent methanol. The odor is that of pure methanol, and combustion analysis gives a ratio of carbon to hydrogen and oxygen corresponding to the formula CH_3OH.

Side Reactions

From the analysis of the liquid product it is evident that side reactions do not occur to any appreciable extent under

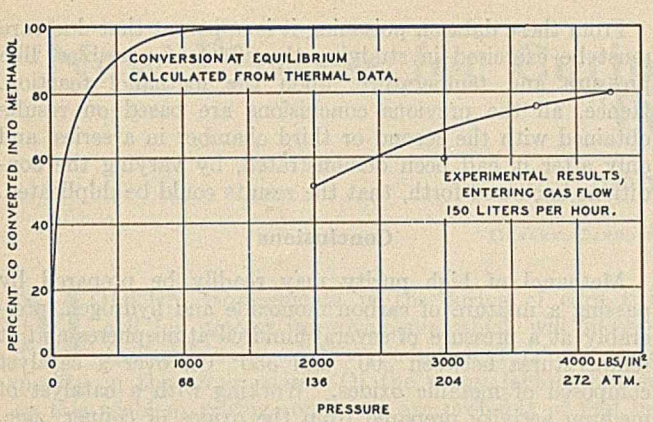


Figure 8—Conversion of Carbon Monoxide into Methanol as a Function of Pressure at 300° C.

Experimental curve obtained by using 40 cc. of catalyst with a gas mixture having a ratio of CO : H_2 of about 0.37

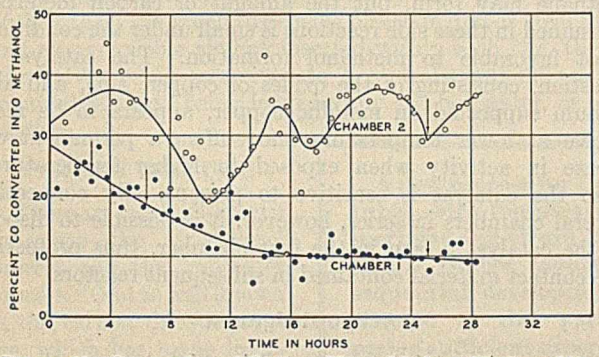


Figure 10—Conversion of Carbon Monoxide into Methanol in a Discontinuous Run with Two Chambers in Series

Gas entering chamber 1 has a ratio of CO : H_2 = 0.322; chamber 1 contains 20 cc. catalyst, chamber 2, 40 cc.; pressure 3000 lbs. per sq. in. (204 atmos.), temperature 300° C.; gas leaves chamber 2 at a rate of 80 liters per hour at standard conditions; arrows indicate interruption of experiment

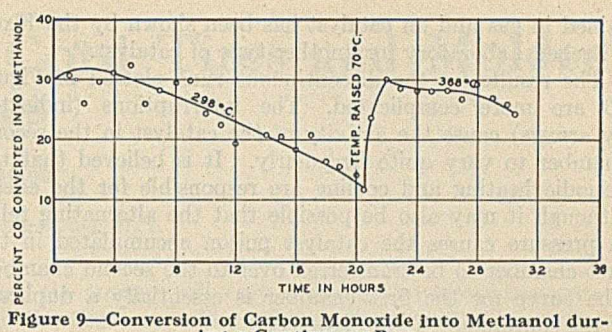


Figure 9—Conversion of Carbon Monoxide into Methanol during a Continuous Run

Ratio of CO : H_2 in entering gas = 0.458. Pressure 3000 lbs. per sq. in. (204 atmos.); temperature 298° and 368° C.; exit gas rate 80 liters per hour at standard conditions

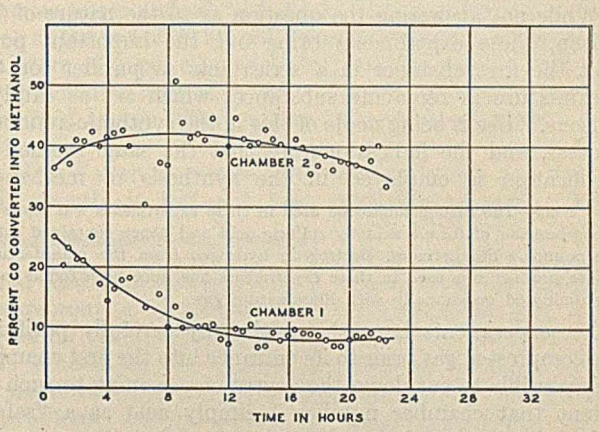


Figure 11—Conversion of Carbon Monoxide into Methanol in a Continuous Run with Two Chambers in Series

Gas entering chamber 1 has a ratio of CO : H_2 = 0.473; chamber 1 contains 20 cc. catalyst, chamber 2, 40 cc.; pressure 3000 lbs. per sq. in. (204 atmos.), temperature 300° C.; gas leaves chamber 2 at a rate of 80 liters per hour at standard conditions

the most favorable conditions. If the pressure is lowered for constant temperature, however, carbon dioxide and methane begin to form, presumably according to reactions (3) and (4). Since the volume changes for both of the methane reactions are 2 to 1 while that of the methanol reaction is 3 to 1, it is apparent that a decrease in pressure will favor the methane reactions, which evolve about twice the heat of the methanol reaction. The ratio of methane to carbon dioxide in the exit gas, as well as the low water content of the methanol produced, proves that of the two reactions number (4) predominates.

Increasing the temperature at constant pressure has a similar effect as far as the side reactions are concerned, although the result is more complicated in that higher alcohols tend to form, as will be discussed in the next paper of this series. Figure 6 shows how the percentage of carbon monoxide entering into side reactions increases with increasing temperature for constant pressure. In this particular case the percentage carbon monoxide going to side reactions between 300° and 350° C., from 2 to 4 per cent, is higher than usual.

Catalyst Life and Catalyst Poisoning

In order to study the length of catalyst life, a series of experiments was run in which no attempt was made to purify the gas mixture, consisting of electrolytic hydrogen and of carbon monoxide from the decomposition of formic acid with sulfuric acid. The catalyst was the one already mentioned, prepared from the oxides of copper, zinc, and aluminum and supported on granulated copper. The percentage carbon monoxide in the entering gas varied between 23 and 31, as shown by the ratios of carbon monoxide to hydrogen given in Figures 9 to 11. The rate of flow is in this case expressed in liters per hour of exit gas at standard conditions of temperature and pressure (0° C. and 760 mm.).

In Figure 9 the percentage conversion of carbon monoxide into methanol is plotted versus time for a run which was made with a single chamber and lasted for nearly 31 hours. During the first 20 hours at an average temperature of 298° C., the yield drops from 32 to 12 per cent, showing that the activity of the catalyst decreases with the time when only a single chamber is used. Raising the temperature from 298° to 368° C. brings the yield back to 30 per cent followed by a gradual decrease as before.

The data plotted in Figures 10 and 11 were obtained with two chambers connected in series, the unconverted gas from chamber 1 being fed into chamber 2. Figure 10 represents a 24-hour discontinuous run, and Figure 11 a 23-hour continuous run. The results demonstrate that the decrease in activity is due to poisoning. Figure 11 brings this out most clearly. The conversion in the first chamber decreases from 25 per cent and reaches a constant value of about 8 per cent, while the second chamber, which is protected against poisoning by the first chamber, gives a constant yield of from 40 to 42 per cent for about 18 hours. At the end of the run the catalyst in chamber 2 commences to show a decrease in activity, which may be explained as follows: The constant state arrived at in the first chamber indicates that the catalyst contained therein has become saturated with the substances responsible for the poisoning, and these substances can therefore pass over into the second chamber. That an equilibrium actually is set up between poison con-

tained in gas and on catalyst has been shown by the Fixed Nitrogen Laboratory for another type of catalyst.[18]

The results for the discontinuous runs plotted in Figure 10 are more complicated. The interruptions (indicated by arrows) cause the activity of the catalyst in the second chamber to vary quite irregularly. It is believed that the periodic heating and cooling are responsible for the effect, although it may also be possible that the alternating relief in pressure causes the catalyst poison accumulated in the first chamber to be transferred over to the second chamber. The curve for the first chamber is essentially a duplicate of the continuous run in Figure 11.

The curves for the second chamber in a series show that the maximum activity of the catalyst is not reached until a couple of hours after the experiment is started.

While not answering the question as to the nature of the poison, these experiments bring out the important point that the first chamber in a series acts as purifier for the gas mixture in removing substances which act as catalyst poisons. Use is being made of this in the synthetic-ammonia process, and the indications are that the same method of purification is employed in the synthesis of methanol.[2]

Note—The carbon monoxide used in these experiments was made by decomposition of formic acid by sulfuric acid and hence contained sulfur compounds. Furthermore, electrolytic hydrogen from the manufacturer whose product was used in these experiments has since been found to be contaminated occasionally with illuminating gas.

Other experiments have shown that by carefully purifying the compressed gas prior to its entrance into the first chamber it is possible to cut down the degree of poisoning to such an extent that chamber number 1 simply acts as a "safety valve" for the remainder of the system. Once the poisoning effect has been eliminated, the life of the catalyst should be considerable, although there are indications that the particular contact substance dealt with here may suffer a gradual decrease in activity due to progressive dehydration of the partly hydrated aluminum oxide.

From these data on poisoning it is apparent that due care must be exercised in studying the effect of variables, like pressure and temperature, upon the methanol reaction. Hence, all the previous conclusions are based on results obtained with the second or third chamber in a series, and only after it had been demonstrated, by varying the conditions back and forth, that the results could be duplicated.

Conclusions

Methanol of high purity may readily be prepared by passing a mixture of carbon monoxide and hydrogen, preferably at a pressure of several hundred atmospheres and at temperatures between 300° and 350° C., over a catalyst composed of metallic oxides. Working with a catalyst of medium activity prepared from the oxides of copper, zinc, and aluminum, it is possible to reach nearly theoretical conversion depending upon the pressure, temperature, and rate of gas flow employed. Carbon dioxide, water, and methane may form, but the amount of carbon monoxide consumed in these side reactions is small under the conditions most favorable to methanol formation. The catalyst in question, consisting of the oxides of copper, zinc, and aluminum supported on metallic copper, appears to be most active at lower temperature and suffers a permanent decrease in activity when exposed to higher temperatures. Also the catalyst is sensitive to poisons. By connecting several chambers in series, however, it is possible to dispose of the catalyst poison in the first chamber, thus protecting the contact material contained in subsequent reactors.

Acknowledgment

The experimental data reported in this paper are the outcome of investigations conducted by the Research Laboratory of Applied Chemistry, and the writers wish to acknowledge the active participation of a number of members of the laboratory staff.

A Modified Thermoregulator[1]

Alexander Lehrman

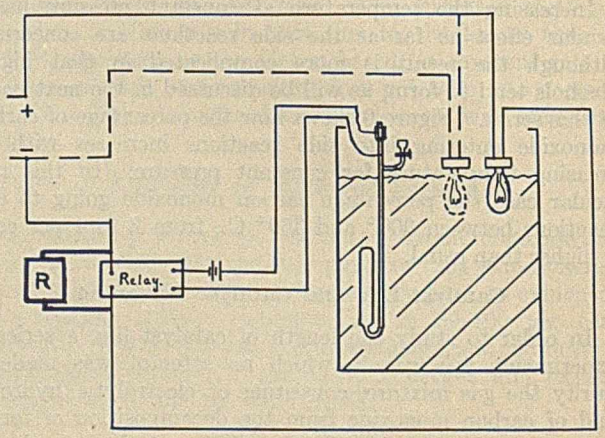
THE COLLEGE OF THE CITY OF NEW YORK, NEW YORK, N. Y.

THE heating element of a thermostat is usually in two parts: (1) a constant heater which delivers heat almost but not quite sufficient to keep the bath at the desired temperature; and (2) an intermittent heater of low heat capacity, to bring the temperature up to the desired value and then to be cut off as a heat supply. This is usually accomplished by the use of two separate heaters. In small thermostats a large fraction of the total space is taken by the stirrer, regulator, and heaters. By combining the two heaters considerable space can be saved.

The accompanying figure shows the wiring diagram of the usual thermostat bath. The heavy lines show the addition necessary to make it work on a single heater. The dotted lines show the part that can be discarded. When contact is made in the mercury-toluene regulator and the relay circuit broken, the current, instead of being cut off, passes through the resistance, *R*, and the heater. When contact is broken in the mercury-toluene regulator, the current passes through the relay to the heater. The resistance, *R*, should be capable of being varied, and kept at such a value that the heat supplied by the heater when in series with the resistance is just insufficient to maintain the bath at the desired temperature.

[1] Received December 20, 1927.

The writer built a small water thermostat of this type, using as a heater a 100-watt lamp on a 230-volt d. c. circuit. The resistance is four lamps in series, thus allowing a variation



in the resistance by use of lamps of different power consumption. He found no trouble in maintaining 25°, 27.5°, and 30° ± 0.02° C.

New Process for Curing Cord Tires and Molded Tubes[1]

Henry R. Minor

General Carbonic Co., New York, N. Y.

A new process for the curing of cord tires and molded tubes, with temperature-pressure control by means of inert gas and steam, is presented for the consideration of the rubber industry. This process is the logical sequential development of a number of years' labor devoted to this particular problem, during which period sufficient experimental and commercial application has been made to warrant the optimistic outlook held for it.

It has the advantages of each of the older processes and the disadvantages of neither; it is distinctly different and, beyond the observation of certain simple precautions, apparently offers few difficulties in its application.

MODERN requirements in the curing of cord tires call for process improvements which will increase the uniformity of the product and permit equal quality in the larger sizes. Of the many factors bearing on this problem, curing conditions are probably of first importance. The manner in which a tire is cured not only affects the uniformity of the product but is a substantial item of the tire cost. Most tires are cured today in pot heaters holding from twenty to thirty tires piled one on top of the other, the green tires being placed in iron or steel molds and an expansible air bag inserted within each tire, the air-bag valves being connected to a central manifold and the required pressure being furnished by air, hot water, or other medium.

Processes Now Used

There are two well-known processes—the air-glycerol process and the hot-water process. Not so well known is the carbon dioxide process, which has made interesting progress in recent years because of sound theory and improvements in the process itself.

Air-Glycerol Process—In the air-glycerol process it is customary to add small amounts of glycerol or other preservative to the air bag from time to time as a preventive of oxidation, and in curing to supply the pressure with air. This process has the advantages that it is relatively simple, the workmen are used to it, the reports of air-bag life appear to equal or exceed the best reports with other processes, and the time of cure appears to be just as short as in any other.

The air-glycerol process has its disadvantages, however. Leakage of air into the heater from the manifold and air-bag connections during the cure is an objectionable feature; from two to four times as much air passes into the heater to mix with steam as is actually required for pressure purposes. Air settling to the bottom of the heater causes undercuring of tires; wherever air pockets a badly cured tire results and air mixed with steam interferes seriously with the heat transfer from steam to the mold. This condition has long been recognized by the rubber industry. Some companies endeavor to improve conditions by agitation of the steam-air mixture; others blow off large quantities of steam from the bottom of the heater to remove air at a cost of from $25 to $100 per day; still others both agitate and blow. It is doubtful, however, if conditions are ever equal to those where no air is present.

The dope used to protect the inner surface of the air bag from the effects of oxidation softens the inner surface and in a measure this must be compensated for by added thickness. In adding dope to an air bag there is a gradual accumulation and the amount will vary from bag to bag causing variation in the tire cure. The spitting of dope when removing hot bags from tires causes further variation, loss, painful burns, and slippery floors.

The air used to supply and maintain pressure frequently carries water and oil with it, so that examination of an air bag at the end of its life will frequently reveal a heterogeneous mixture of dope, oil, and water, and the wonder is that the bag lasted as long as it did. The last tires cured obviously received a very different cure than those when the air bag was new.

Hot-Water Process—This process is not new but until recently it had not been generally adopted. Manufacturers were hesitant about installing a process which from the standpoint of air-bag life and air-bag cost offered no apparent advantages over the air-glycerol process, while on the other hand there was an expensive installation to consider—expensive to install and expensive to maintain—the argument that by curing from two sides a quicker cure was obtained being offset by the fact that in actual time of cure users of the air-glycerol process were competing favorably with the best in hot water.

With the advent of thicker tires made necessary by the phenomenal growth of busses, much greater interest has been evidenced in the hot-water process. With eight-, ten-, and twelve-ply tires in daily production it is obvious that where heat is applied from the outside of the tire only the inner plies are going to be undercured. Further, if this is the best process for the larger sizes, why isn't it the best process for all sizes?

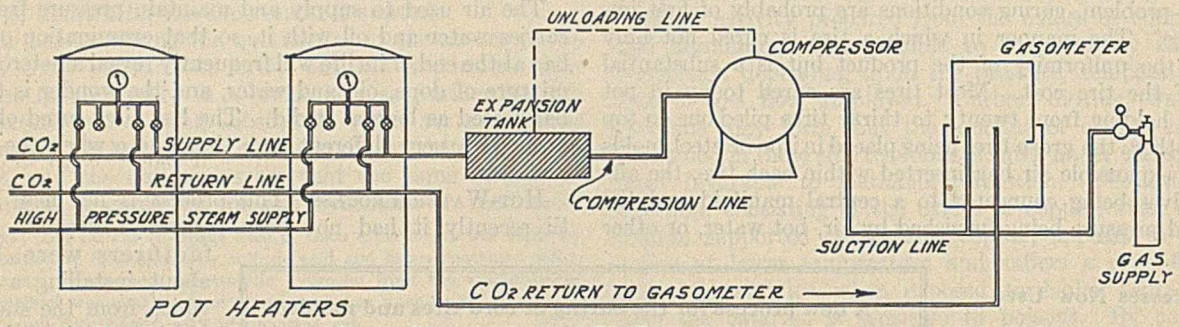
In this process it is customary to supply all the pressure with hot water, air being removed from the bag by an initial application of steam, which also serves to raise the initial temperature of the bag. The addition of heat units to the inside of a bag so that curing progresses from two sides towards a center is manifestly an advantage, particularly in view of the bus-tire development. When hot water is used as the pressure medium there will be no leakage of air from the manifold and bag connections to mix with the steam in the heater; consequently the conditions of heat transfer from the steam to the mold are superior to what are obtained in the air-glycerol process.

The disadvantages of this process, aside from its high cost of installation and maintenance, are the relatively short life of the air bags due to the weakening effect of water and the harsh treatment of the bags themselves, wet floors and tables, the necessity of evacuating the bags with a costly vacuum system, the cost of raising water to a high temperature

[1] Received January 6, 1928.

and pumping it at a high pressure, the hazard attendant on its use, the effect of only a slight leakage when the medium pumped is of an incompressible nature, and that while the water cure transfers heat rapidly at the start it slowly cools off and it is not possible to maintain uniform temperature conditions within the air bag.

Curing by steam has been attempted many times, but the fact that for any particular temperature there is a corresponding pressure has hitherto limited its use to relatively low pressures. For example, in the curing of tubes on mandrils this operation is now conducted in open steam at approximately 45 pounds steam pressure, the temperature limitations preventing the use of higher pressures which would give admittedly superior products.



Plan Showing Method of Curing Tires by Means of CO_2 Gas and Steam with Recovery of Gas for Re-use

Carbon Dioxide Process—This process has interested many because the bags are dry at all times, a more uniform cure is obtained than with air-glycerol, and the air-bag life seems to be enhanced. On the other hand, the objectionable features of gas leakage into the steam of the vulcanizer still remain, and this process offers no means for adding heat to the inside of the tires. The slight saving over the air-glycerol process is too small to warrant any extensive installation in an industry where a process may see a complete change in the short space of one year.

Principle of New Process

An effort has been made to provide a new process having the advantages of both the air-glycerol and the hot-water processes and the disadvantages of neither, as applied to the curing of cord tires and molded tubes. The process consists in first bringing a part of the pressure up to a predetermined point with an inert gas, such as carbon dioxide, then shutting off the gas and turning on steam at the curing pressure and leaving it on throughout the period of the cure. The first effect of the steam is to heat the inert gas, causing it to expand and thus cutting down the partial pressure of the steam that can enter the bag, thereby insuring any desired inner temperature which may be easily computed for any particular case. The inert gas acts as a dry preservative for the inner surface of the air bag, preventing oxidation; and it also acts as an automatic valve controlling the amount of heat units that may be added to the bag. Phrased differently, a means is proposed which permits obtaining any temperature at any desired pressure always under inert gas conditions; a means which is applicable not only to curing of tires, molded tubes, and other processes in the rubber industry, but also to many processes in other industries.

As a typical example, assume that tires are being cured at 260° F. or 20 pounds gage, and that the pressure maintained on the air bag and thence to the tire in the mold is 200 pounds; required, the proper gage pressure of the carbon dioxide which when backed by 200 pounds of steam will maintain the same curing temperature within the air bag as exists without the mold.

200 pounds gage = 215 pounds absolute

260° F. = 20 pounds gage or 35 pounds absolute

Then 215 − 35 = 180 pounds, which is the partial pressure of the carbon dioxide under the desired conditions.

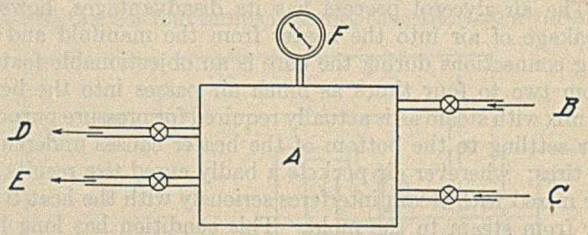
Assume original temperature of carbon dioxide as 100° F. = 560° absolute, and final temperature of carbon dioxide as 260° F. = 720° absolute.

Then $180 \times \frac{560}{720} = 139.86$ or absolute pressure of carbon dioxide at 100° F., which = 125 pounds gage. That is, to obtain 260° F. within air bag, carbon dioxide should be supplied at 125 pounds gage and backed by the 200 pounds gage of steam.

Pressure and Temperature Equilibria

As the temperature and pressure within the closed volume decrease because of heat transfer, additional steam supply enters, thus maintaining pressure equilibrium. Temperature equilibrium is dependent on partial pressure of steam and is best determined experimentally for each general case.

The extremes of this process may be considered as ranging from inert gas at atmospheric pressure and steam at any desired pressure, in which case the temperature within the container would be practically the temperature of the maintaining steam, to the condition where the inert gas is supplied at the same pressure as the steam, when of course there would be no transfer of heat units. In between there is any desired degree of variation. In this method the gas is used in such fashion as to make of itself an automatic valve controlling, not only its own temperature, but also the number of heat units which may be added to it and thence to a neighboring medium such as an article to be cured or a chemical reaction to be effected. In other words, by proper variation heat units may be added with but a small amount of condensation from the steam or there may be a sufficient flow of steam over an extended period of time such that a considerable condensation of moisture may take place.



A—Closed vessel
B—Source of inert gas supply as CO_2
C—High pressure steam supply
D—Release to atmosphere
E—To recovery apparatus
F—Gage

Temperature Pressure Control by Means of Inert Gas and Steam

It is impracticable to use air in place of inert gas in this process, as the oxidation of the inside of the air bag would be greatly promoted by the increased temperature obtained.

Temperature equilibrium is obtained immediately and continues substantially constant throughout the cure. The reason for this is obvious. At the start of operations there is direct contact between the inert gas and steam at an initial temperature higher than that represented by the final partial

pressure which results from the expansion of the inert gas, and this intimate mixing takes place within an insulated space, thereby insuring a rapid rise of temperature. The partial pressure of the steam must, however, be high enough to compensate for such heat transfer as may be taking place, and it should be borne in mind that such small condensation as takes place serves to decrease the total volume, increasing slightly the partial pressure of the inert gas and decreasing the partial pressure of the maintaining steam.

Thermocouple readings taken within an air bag indicate that the temperature of the pressure gas is very sensitive to changes in steam pressure.

In the curing of molded tubes it is desirable to have the initial pressure of the gas sufficiently high to form the tube because of the rapidity of temperature rise within the tube.

Carbon Dioxide as Inert Gas

Carbon dioxide as used in this process should increase air-bag life. This gas has been used in the past on any and all kinds of air bags on the theory that with an inert gas, compounding played no part. On the contrary, it has been proved in practice that an air bag heavily loaded with gas black does not react favorably with carbon dioxide, the bag becoming porous and the gas black at curing temperatures acting to break down the carbon dioxide. Iron oxide acts in a somewhat similar manner. Moisture is essential to the securing of the best results from carbon dioxide. Practically all tests in the past have been made with gas liquefied at high pressure in cylinders and the users have not stopped to consider that this product was an excellent dehydrating agent. So long as the air bag is not used beyond seventy-five heats it is not so important, but beyond this point the cumulative effect of a dehydrating agent becomes increasingly evident both in the superficial appearance of the interior of the bag and in its physical characteristics.

Carbon dioxide used only in the initial cure of an air bag has been found by laboratory test to increase the modulus of elasticity about 20 per cent as compared with the usual air cure and the superficial appearance after being used with air-glycerol subsequent thereto would indicate a continuation of this marked improvement.

Condensation is of importance, particularly in molded tubes. Only so much condensation can take place as is necessary to bring the weight of rubber up to the curing temperature. In the case of a 6-inch molded tube, assuming an equal amount of heat from both inside and outside, the condensation would amount to approximately 5 ounces of water, all of which would quickly evaporate on release of pressure. Table I gives the results of some preliminary tests on molded tubes.

The amount of inert gas used in this process is relatively small and the cost negligible. In general, only one-third of the pressure is supplied with gas and if desired two-thirds of this may be easily recovered for re-use.

The inert gas used in this process is ample in amount for complete protection of the inside of the air bag. There is no accumulation in the air bag; consequently the cure does not vary from bag to bag as in the air-glycerol process. Carbon dioxide has long been known by the rubber industry as not only an economical inert gas easily applied, but as having a definite preservative effect on the rubber itself. Apparatus has recently been developed which greatly facilitates its use.

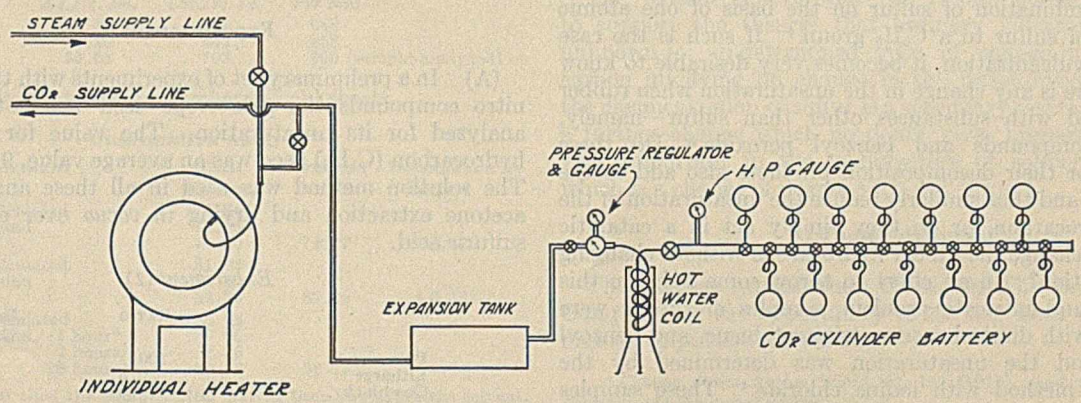
Substitution of Steam for Air Pressure

By substituting steam for the air ordinarily used in maintaining pressure, certain economies are effected; air costs from $^2/_3$ to 1 cent per tire, whereas a similar amount of steam costs but 0.002 cent. Moreover, the leakage of air into heaters is eliminated; the importance of this factor has already been emphasized. Leakage of steam from the manifold connections would benefit rather than harm curing conditions. The amount is very small compared with the volume of steam used within the heater. By eliminating air in the heater the tires at the bottom of the heater receive exactly the same cure as those at the top. Hitherto this has been one of the main points in favor of the hot-water process.

Table I—Tests on Molded Tubes Cured on Carbon Dioxide

[10-minute cure at 45 pounds (3.1 kg. per sq. cm.) pressure]

Pressure	Load at 200% Elongation		Load at 400% Elongation		Tensile at Break		Elongation at Break
	Lbs.	*Kg.*	*Lbs.*	*Kg.*	*Lbs./in.²*	*Kg./cm.²*	%
75 lbs. (5.3 kg.) air	400	181	1525	692	3025	213.7	730
75 lbs. CO_2	450	204	1600	726	3100	218.3	730
37.5 lbs. (2.7 kg.) CO_2 + 80 lbs. (5.5 kg.) steam	500	227	1700	732	3375	237.7	730
Aged 6 days in geer oven							
75 lbs. air	575	261	2050	931	3400	239.4	700
75 lbs. CO_2	575	261	1975	897	3575	251.7	730
37.5 lbs. CO_2 + 80 lbs. steam	600	272	2125	965	3900	274.7	730



Plan Showing Method of Curing Molded Tubes with CO_2 Gas and Steam

The pressure means, being gaseous, are completely evacuated by the blow-down at the end of cure. It is not necessary to collapse the air bags by a costly vacuum system as in the hot-water process with its loss of valuable time and its weakening effect on the bags.

Number of Heat Units and Rate of Heat Transfer

This new process permits the addition of as many or more heat units than may be added by the hot-water process. Assume an air bag of $^1/_2$ cubic foot volume. If hot water is added at a temperature of 350° F. and during the cure drops to 250° F., the total number of B. t. u.'s available is

$\frac{62.5}{2} \times 100 = 3125$. If in this new process only 4 pounds of steam are condensed, 4000 B. t. u.'s are released for heating and there is a vast difference between removing 30 odd pounds of water and a matter of 4 pints, most, if not all, of which may itself evaporate on release of pressure. As a matter of fact, fewer heat units need be added to the bag because of reduced thickness required as compared with general hot-water practice.

It was recently stated[2] that if heat were transmitted equally to two sides of a rubber slab $^1/_2$ inch thick it would take 15 minutes for the center of the slab to reach the impressed temperature (in this case 280° F.), but if the slab were 1 inch thick an hour would be required. This emphasizes the advantage of the relatively thin bag that may be used in the new process and its bearing on the rate of heat transfer. A further important fact is that the conductivity of a mixture of one-third gas and two-thirds steam is much greater than that of static water.

The uniformity of heat transfer compares favorably with the hot-water process. Pressure being supplied by steam, considerable leakage may exist without affecting the cure, whereas with a liquid medium a small leak will cause pronounced change in pressure conditions. In the hot-water process owing to change in water density during progress of cure, there is a marked difference in the temperature of the water at different points in the bag, while at the top there is a variable pocket of air and steam.

In the new process temperature conditions are practically constant, owing to rapid diffusion of gases mixed under conditions of curing temperature and pressure, and if the particular conditions applied call for a large addition of heat units it is simple to secure a continuous movement of the steam-gas mixture circumferentially.

Advantage in Manufacture of Molded Tubes

Molded tubes are now being cured by this process with a 25 per cent reduction in curing time and without any moisture remaining in the tube. The quality of molded tubes cured with carbon dioxide and steam is outstanding as compared with tubes cured by any other process. Under the severe treatment accorded molded tubes by the busses, this superior quality is a factor of first importance.

[2] Blaker and Shade, *India Rubber World*, **76**, 313 (1927).

Chemical Unsaturation of Rubbers Vulcanized with Polynitro Compounds and Benzoyl Peroxide, and Its Possible Bearing on Vulcanization[1]

Harry L. Fisher[2] and A. E. Gray[3]

THE B. F. GOODRICH COMPANY, AKRON, OHIO

STUDIES on the chemical unsaturation of ordinary vulcanized rubber show that vulcanization has caused no change in the unsaturation of the rubber hydrocarbon beyond that which can satisfactorily be accounted for by the chemical combination of sulfur on the basis of one atomic equivalent of sulfur to a C_5H_8 group.[4] If such is the case with sulfur vulcanization, it becomes very desirable to know whether there is any change in the unsaturation when rubber is vulcanized with substances other than sulfur—namely, polynitro compounds and benzoyl peroxide.[5] Do these substances or their decomposition products also add to the olefin bonds and thus similarly reduce the unsaturation of the rubber hydrocarbon, or do they simply act in a catalytic fashion and change the rubber hydrocarbon without changing its unsaturation? In an effort to throw some light on this interesting and intricate problem, samples of rubber were vulcanized with dinitrobenzene, trinitrotoluene, and benzoyl peroxide, and the unsaturation was determined by the Kemp-Wijs method with iodine chloride.[4] These samples dissolved with considerable difficulty, but a modified procedure, in which each sample cut into very thin pieces was allowed to swell in the solvent for many hours, worked very well. The results so far obtained are not so complete as the writers would like to have them, because each one changed his business connection before the full plans could be realized. However, the results appeared so satisfactory that it has seemed worth while to publish the work as far as it has gone.

Experimental

(A) In a preliminary set of experiments with the two polynitro compounds the pale crepe used was not previously analyzed for its unsaturation. The value for the rubber hydrocarbon (C_5H_8) used was an average value, 91.7 per cent. The solution method was used in all these analyses, after acetone extraction and drying *in vacuo* over concentrated sulfuric acid.

Experiment (1)

	Ratio	Batch
		Grams
Pale crepe	100	400
Litharge	9.5	38
Gas black	10.5	42
m-Dinitrobenzene	3.0	12
		492

Vulcanized 60 minutes at 141° C., 15 by 20 by 0.2 cm. (6 by 8 by $^3/_{32}$ inch) sheet; tensile, 200.50 kg. per sq. cm. (2852 lbs. per sq. in.); elongation, 613 per cent.

Experiment (2)

	Grams
Pale crepe	100
Litharge	8
Trinitrotoluene	4[6]
	112

Mixed on a small laboratory mill; vulcanized as gravity disks, 20 minutes at 135° C.

[1] Presented before the Rubber Division at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927. Received October 25, 1927.

[2] Present address, U. S. Rubber Co., 561 West 58th St., New York, N. Y.

[3] Present address, Lehigh University, Bethlehem, Pa.

[4] Spence and Scott, *Kolloid-Z.*, **8**, 308 (1911); also private communication from Kemp, author of the Kemp-Wijs method for the determination of the rubber hydrocarbon, *Ind. Eng. Chem.*, **19**, 531 (1927); and unpublished work of the writers.

[5] Ostromislenski, *J. Russ. Phys. Chem. Soc.*, **47**, 1462, 1885 (1915); *C. A.*, **10**, 1943, 3177 (1916).

[6] Stevens, *J. Soc. Chem. Ind.*, **36**, 107 (1917).

Unsaturation Tests

		C_5H_8	Difference
		Per cent	*Per cent*
(1)	Calculated	74.55	
	Found	75.24	+0.69
(2)	Calculated	81.86	
	Found	82.73	+0.87

(B) A new set of experiments was therefore run using an analyzed lot of pale crepe which, after acetone extraction, showed in two separate determinations, 91.77 and 91.79 per cent C_5H_8.

The samples were all vulcanized as 15 by 20 by 0.2 cm. (6 by 8 by $^3/_{32}$ inch) sheets between tin in a press for the times specified. The highest and best cures were then acetone-extracted for 48 hours, dried *in vacuo* over concentrated sulfuric acid for 72 hours, and analyzed by allowing very thin strips to swell in carbon bisulfide for 24 hours and then letting the reagent act upon them in this condition for 24 hours more at 0° C. in the dark. The calculated values all refer to the original weights before the acetone extraction.

Experiment (3)

Same recipe as (1).

Cure (135° C.)	Tensile		Elongation
Minutes	*Kg./sq. cm.*	*Lbs./sq. in.*	*Per cent*
45	197.40	2808	670 (sample analyzed)
60	190.37	2708	635
75	165.63	2356	610

Experiment (4)

Same recipe as (2), but using 400 grams of the pale crepe.

Cure (135° C.)	Tensile		Elongation
Minutes	*Kg./sq. cm.*	*Lbs./sq. in.*	*Per cent*
5	4.64	66	785
10	13.64	194	830
20	27.00	384	905 (sample analyzed)

Experiment (5)

	Grams
Pale crepe	400
Benzoyl peroxide[6]	27
	427

Cure (135° C.)	Tensile		Elongation
Minutes	*Kg./sq. cm.*	*Lbs./sq. in.*	*Per cent*
10	52.80	751	948
15	38.10	542	858
20	55.68	792	935 (sample analyzed)

All were clear, transparent, amber-colored sheets.

Unsaturation Analyses

Experiment		C_5H_8	Average	Difference
		Per cent	*Per cent*	*Per cent*
(3)	Calculated	74.84		
	Found	74.56		
		74.00	74.27	−0.57
(4)	Calculated	81.92		
	Found	81.80		
		82.36	82.08	+0.16
(5)	Calculated	85.98		
	Found, 1 hour[a]	39.06		
	2 hours	52.75		
	20 hours	86.12	86.12	+0.14

[a] Refers to time the sample, after having been swelled in the solvent, was in contact with the iodine chloride reagent.

Discussion of Results

The preliminary set of experiments indicated that the change in unsaturation of the rubber hydrocarbon was not greater than 1 per cent. Since the unsaturation of different lots of pale crepe often varies 1 per cent, it seemed as if there were really no change in the vulcanized samples.

The results of the analyzed lot of pale crepe calculated in terms of the percentage of C_5H_8 groups, varied from −0.57 to +0.16 per cent from the calculated amounts. Since a different reagent was used in each of the three cases—namely, dinitrobenzene, trinitrotoluene, and benzoyl peroxide—and under different degrees of compounding, it does not seem that such close agreement with the calculated value could be fortuitous. It must be concluded, therefore, that either there is no change in the unsaturation of the rubber hydrocarbon with these reagents, or, if there is, it is very small in amount.

Ostromislenski, who discovered these methods of vulcanization without sulfur, believed that the reaction was due to oxidation. Molecular oxygen, so far as is known, does not vulcanize rubber as sulfur does. The products formed when rubber is treated with oxygen or allowed to stand in air are very different physically, and probably chemically. Of course, sulfur does not vulcanize rubber at room temperatures except in the presence of a catalyst. Then, as, for example, with an ultra-accelerator, the air-cured, vulcanized rubber may contain as little as 0.5 per cent of combined sulfur.[7] With a catalyst such as platinum black, oxygen is absorbed by the purified rubber hydrocarbon in solution until finally an amount is absorbed equivalent to the formation of a completely saturated compound $(C_5H_8O)_x$, and if perbenzoic acid is used, the same or similar compound—it has the same empirical formula—is obtained.[8] These reactions correspond in a general way to those with sulfur. Now oxygen is very closely related to sulfur chemically, and by analogy it ought to vulcanize rubber if the proper conditions could be found. If it does and the amounts correspond to those with sulfur, then using the 0.5 per cent of combined sulfur mentioned above, as a possible minimum, the equivalent of oxygen would be just one-half ($^{16}/_{32}$) and the per cent of oxygen would be 0.25. Perhaps the polynitro compounds and the benzoyl peroxide do oxidize the rubber hydrocarbon and thus cause vulcanization. If they do, and oxygen thus adds chemically as the sulfur does, then from the data given above, the amount added must be very low—less than 0.14 per cent, since this would be the amount equivalent to the greatest deviation, 0.57, which is approximately the same as the recognized error with the Kemp-Wijs method, 0.5 per cent of C_5H_8. The ratio of oxygen to C_5H_8 is 16:68 or 0.24. No reliable method for directly determining such a small amount of oxygen in chemical combination is known.

The writers believe that the results herein given help to support the theory[9] that ordinary vulcanization is an unknown or undetermined type of change in the hydrocarbon involving no change in the unsaturation, and that the chemical union of sulfur is a secondary reaction producing a further change which no doubt gives properties that are very important in the manufacture of rubber goods, but which is a change of degree only, not of kind.

Acknowledgment

The authors express their thanks to The B. F. Goodrich Company for the opportunity to do this work and for permission to publish the results.

[7] Cranor, *India Rubber World*, **61**, 137 (1919), and unpublished observations of the senior writer.

[8] Pummerer and Burkard, *Ber.*, **55**, 3458 (1922).

[9] Compare Harries, "Untersuchungen über die Natürlichen und Künstlichen Kautschukarten," p. 105 (1919).

Significance of the Word "Alum"

A little brochure of ninety-three pages on "The Current Significance of the Word 'Alum'" has recently appeared, of which W. D. Richardson is the author. A great deal of space is devoted to a discussion of the significance of the word "alum," its derivation and early history, as well as the modern definitions of the word. The book concludes with a bibliography divided into the broad headings of general literature, industrial literature, chemical literature, and medical literature. It is published by the Commonwealth Press of Chicago, from whom it may be purchased for one dollar.

Aging of Stretched Rubber[1]

Arthur Kelly, Bert S. Taylor, and Webster N. Jones

THE B. F. GOODRICH COMPANY, AKRON, OHIO

THE function of an accelerated aging test is to approximate quickly the ability of stocks to withstand deterioration during storage and service. The Geer oven and the Bierer-Davis bomb methods of accelerated aging are carried out on tensile strips which are not subjected to stresses. A large number of rubber articles are, by virtue of their use, and sometimes under conditions of storage, subjected to stress. For some time investigations have been in progress on the effect of aging of stretched rubber in order to distinguish between the relative merits of various compounds which are subjected to stress during service. Since an article is made of rubber in order that it will have flexibility and permit deformation, some measure should be made of the relative deterioration of compounds under stress. Data have been collected in an endeavor to correlate aging in sunlight with other accelerated aging tests on both unstretched and stretched samples. No direct relationship has been found between the aging in sunlight and the other methods, but a number of interesting facts have been discovered.

Sunlight Aging Tests

The first step in sunlight aging of stretched rubber was to expose for several weeks during the summer months four compounds initially stretched to different degrees, periodically measuring the tensile strength of test strips. Obviously, the stress on the exposed samples became less as the stock took a permanent set under stretch. For this study a tread stock, a tube stock, a shoe upper, and a golf-ball thread rubber were used. The data on tread stock and shoe-upper stock are included in this report (Tables I and II, and Figures 1 and 2). In general, it was found that during the first few weeks deterioration was more rapid at low elongation than at high elongation. There was a reversal of this condition during the last weeks of the test; that is, the high elongations showed the greatest deterioration. This is probably due to the fact that when the samples under greater tension began to crack the cracks opened wide, exposing fresh surfaces to bright light, whereas the cracks in samples under weak tension were not pulled wide open and the fresh surfaces at the bottom of the cracks were shadowed from direct sunlight. The more severe cracking at low elongations during the early weeks of exposure was striking and the order of intensity as determined by visual inspection was confirmed by the tensile results. This was the principal result of the first set of experiments.

Comparison of Sunlight with Geer and Bierer Aging Tests

The next step on a larger scale was a comparison of stretched and unstretched rubber in sunlight with the same compounds aged unstretched in the Geer oven and in the Bierer bomb. Several classes of compounds were treated by these methods, special emphasis being placed on the testing of treads and tubes. Here the general facts were found to be the same as in the first series of experiments. As the cracks deepen the measured thickness of the strips is greater than the actual thickness of the uncracked rubber and the tensile strength in kilograms per square centimeter is apparently less than it is actually. The tensile results

[1] Presented before the Division of Rubber Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

Table I—Physical Data on Tread Stock—Sunlight Aging

Time of Aging	Initial Stretch													
	0%		5%		10%		15%		30%		50%		100%	
	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.
Weeks	*Kg./sq. cm.*	*%*	*Kg./sq. cm.*	*%*	*Kg./sq. cm.*	*%*	*Kg./sq. cm.*	*%*	*Kg./sq. cm.*	*%*	*Kg./sq. cm.*	*%*	*Kg./sq. cm.*	*%*
0	283.71	646												
2	245.07	590	241.43	580	211.47	570	189.35	510	207.76	520	209.72	487	204.54	460
4	236.67	553	221.06	540	188.58	500	146.16	460	172.41	460	176.82	440	169.54	400
6	215.60	567	203.42	525	187.67	508	125.58	500	144.97	500	136.15	442	146.65	400
8	218.05	537	210.29	540	203.91	500	111.58	420	136.01	447	145.32	377	128.31	330
10	219.80	570	191.45	500	212.94	540	95.13	440	121.94	450	122.64	400	122.08	317
12	213.71	550	181.93	470	114.66	365	98.42	403	115.99	420	121.52	403	110.67	320
14	192.71	540	164.71	500	106.89	405	81.69	400	96.67	447	93.45	397	75.39	300
16	182.42	500	176.12	477	145.04	440	76.37	380	86.52	397	98.70	407	76.86	307
18	189.42	517	177.73	507	113.05	373	85.05	410	88.20	400	91.14	393	55.58	263
20	180.18	510	179 62	520	88.41	373	80.43	393	90.86	420	90.65	387	74.90	267
22	183.75	517	174.44	490	109.76	385	72.31	380	87.92	397	80.85	367	69.37	287
24	174.72	487	182.21	483	125.58	385	84.00	365	90.72	377	85.89	377	73.78	307

Table II—Physical Data on Shoe Upper Stock—Sunlight Aging

Time of Aging	Initial Stretch													
	0%		5%		10%		15%		30%		50%		100%	
	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.
Weeks	*Kg./sq. cm.*	*%*	*Kg./sq. cm.*	*%*	*Kg./sq. cm.*	*%*	*Kg./sq. cm.*	*%*	*Kg./sq. cm.*	*%*	*Kg./sq. cm.*	*%*	*Kg./sq. cm.*	*%*
0	201.81	520												
2	174.44	497	125.30	420	130.62	440	104.58	413	143.99	420	151.06	440	147.00	420
4	168.07	467	111.79	400	113.68	423	117.25	420	127.19	430	131.95	427	116.41	417
6	113.05	462	90.09	425	94.22	434	98.56	442	110.32	450	117.32	450	108.71	434
8	156.59	440	86.38	370	84.35	377	88.97	370	99.68	367	99.54	370	81.83	360
10	152.88	477	83.09	407	80.64	400	83.02	400	88.83	417	95.97	417	55.23	305
12	120.19	463	66.15	315	70.21	440	70.91	357	94.64	360	74.62	357	21.28	165
14	126.07	440	65.87	370	61.60	377	60.55	340	60.62	350	51.31	327	8.61	260
16	124.46	435	48.79	297	61.32	367	58.38	345	55.58	363	48.44	240	All strips stretched 100% were broken after 14 weeks' exposure	
18	113.68	420	84.00	380	84.07	370	64.12	340	58.17	357	26.46	160		
20	104.02	470	59.29	347	63.28	363	59.57	350	59.57	345	20.51	157		
22	139.86	477	52.99	310	61.67	365	45.71	310	52.50	330	20.79	159		
24	137.48	480	59.64	360	61.88	340	54.39	300	37.38	290	21.70	140		

based on the over-all thickness of the test strips, however, give a fairly accurate measure of the intensity of the cracking. The results were consistent with visual comparisons in each series of tests.

The compounds included in this series were tube stock, tread stock, bath cap, and brown shoe upper. An interesting comparison was brought out in this series of tests. The bath-cap stock hardened much more in sunlight and in the bomb than the other stocks. The bath cap was a fast-curing, relatively highly compounded stock, and hence should tend to harden with age. Natural aging in boxes of several caps made of the same stock produced a hardening of the surface. The Geer oven aging did not cause so great a hardening as the other methods. (Table III) No significant relation could be found between the results from the different types of aging tests in this series.

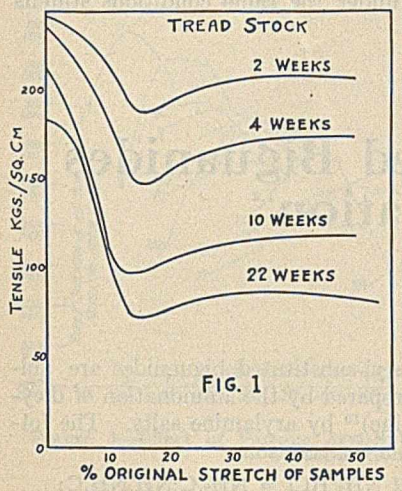


FIG. 1

Other Types of Aging Tests

The lack of significant data from the comparison of the aging of stretched rubber in sunlight with accelerated aging of unstretched samples in the dark suggested the examination of stretched rubber in other types of aging tests. One compound only was tested. This was a rubber-sulfur-accelerator mix in order to study the effect on a compound in which rubber was the principal ingredient. The strips, about $^1/_{32}$ inch (0.8 mm.) thick, were stretched 0, 50, 100, 200, 300, and 400 per cent. The stretched samples were placed in sunlight, in ultra-violet light (temperature 38° to 40° C.), and in a Geer aging oven at 70° C. The source of ultra-violet light was a quartz mercury arc placed 15 inches (38 cm.) from the samples. Samples from all methods were tested after 3 and 6 days' exposure. The curves in Figure 3 show the effect of sunlight on stretched rubber is to stiffen the compound, while ultra-violet softens it. The measurement of stress-strain relations showed profound differences between the effects of these two forms of accelerated aging, although the ultimate tensiles and elongations did not make a very clear distinction. The same series of tests shows that the oven test at 70° C. causes stiffening. Extended cracking over the surface occurred in both the sunlight and ultra-violet light tests. In the Geer oven, however, the cracks were localized along the edges of the test strips. The minimum stretch used in these tests is greater than that corresponding to maximum cracking in sunlight aging. Further work must be done, therefore, to ascertain whether deterioration takes place at a maximum rate in oven, bomb, and ultra-violet light at a definite percentage of stretch.

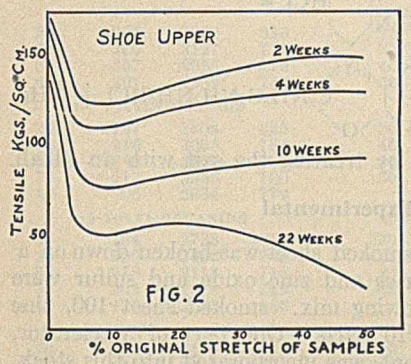


FIG. 2

Table III—Geer Oven Data

Time of Aging	Tread Stock		Shoe Upper	
	Tensile	Elong.	Tensile	Elong.
Days	*Kg./sq. cm.*	%	*Kg./sq. cm.*	%
Original	283.71	646	183.68	550
3	243.74	558	174.86	508
5	207.76	542	137.48	467
7	156.17	492	93.59	458
10	150.57	417	82.11	425
12	123.41	397		
14	99.12	358		

Sunlight aging is not satisfactory for quantitative work because the light intensity is never constant and the temperature and humidity of outside air vary. However, comparative tests against compounds of known quality are valuable if a compound is to be used outdoors. Often a compound which ages well in the oven and bomb tests will age poorly in sunlight. For other compounds the reverse is true.

Method

Dumb-bell strips were stretched and tacked to boards at the different elongations. The stretches were measured in the narrow portion of the strip where the break would occur, so that the measured portion was stretched the amount required. The strips were removed at certain periods and the tensile and elongation determined on the basis of cross-sectional areas, including the thickness of the cracked surface layer measured immediately prior to testing.

For sunlight aging the boards were placed on racks on the roof at an angle of 45 degrees facing southward. The Geer oven tests were run at 70° C. The Bierer bomb tests were run in pure oxygen at 70° C. under 300 pounds (20 atmospheres) pressure.

Summary

1—Sunlight aging under tension of many compounds including the following has been investigated: tire tread, shoe upper, tube stocks, golf ball thread, jar rubber, solid tire, bathing cap stock, channel rubber.

2—With some of these stocks the sunlight aging has been

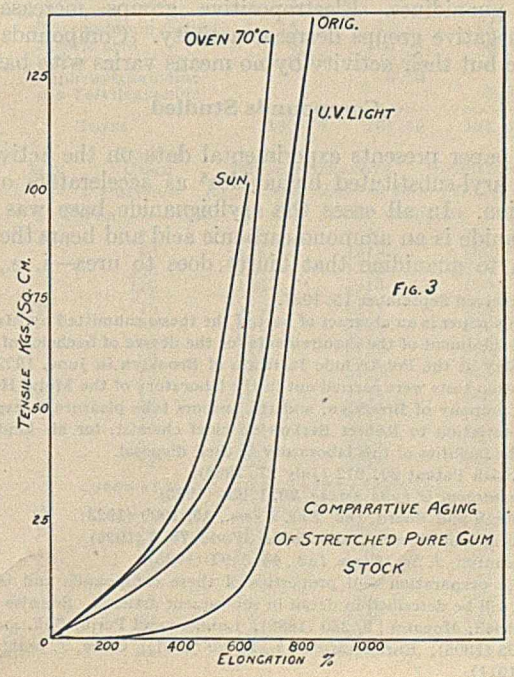


FIG. 3

compared with unstretched samples by Geer oven, Bierer bomb, and ultra-violet light methods.

3—The stretching of the test strips accelerates deterioration in sunlight, ultra-violet light, and Geer oven. Stretched samples have not yet been tested in the Bierer bomb.

4—The rate of deterioration was not proportional to the degree of stretch in any of the stocks in the early stages of exposure. In sunlight there is a critical elongation for each stock at which the deterioration progresses more rapidly than at any other in the early stages of aging.

5—No direct relationship was found between the results of sunlight aging and the other methods employed.

6—Stretched strips aged in ultra-violet light were found to give softer stress-strain curves than the unaged samples, whereas sunlight aging under the same conditions stiffens the stress-strain curve.

Activity of Certain Aryl-Substituted Biguanides as Accelerators of Vulcanization[1,2]

G. B. L. Smith and A. J. Weiss

Polytechnic Institute of Brooklyn, Brooklyn, N. Y.

As one chapter of a series of investigations in progress in this laboratory on the preparation and properties of aryl-substituted biguanides, their activity as accelerators of vulcanization of rubber was studied with the hope that some light might be thrown upon the relation between chemical constitution and accelerator action within this group of substances.

Substituted biguanides, α-phenylbiguanide or their carbonates or carbamates, have been patented as vulcanization accelerators.[3] Romani[4] studied the activity of α-phenylbiguanide and its salts, and concluded that, in general, the mechanism of accelerator action of these compounds was yet to be explained. Recently work has been carried out in the systematic examination of groups of pure substances as accelerators of vulcanization in order to extend the existing theories of acceleration by studying the relation between activity and the chemical constitution of the substituted radicals. The work on mercapto-benzothiazoles,[5] substituted guanidines,[6] and diaryl thioureas and diarylguanidines[7] are contributions to this subject. These studies have shown that activity increases, in general, with increase in molecular weight in homologous series and, among tolyl isomers, decreases from ortho to para derivatives in the case of the thioureas and from para to ortho derivatives in the case of the guanidines. Electropositive groups increase and electronegative groups decrease activity. Compounds must be basic but their activity by no means varies with basicity.

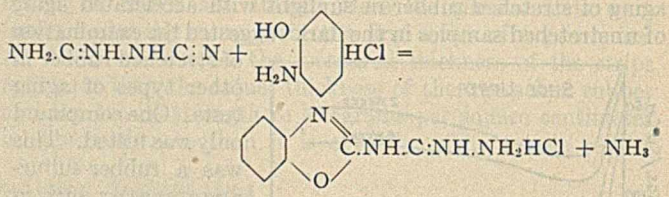
Compounds Studied

This paper presents experimental data on the activity of several aryl-substituted biguanides[8] as accelerators of vulcanization. In all cases the arylbiguanide base was used.

Biguanide is an ammono-carbonic acid and bears the same relation to guanidine that biuret does to urea—i. e., it is guanylguanidine. The aryl-substituted biguanides are ammono esters[9] and were prepared by the ammonation of dicyandiamide (cyanoguanidine)[10] by arylamine salts. The following equation represents the reaction:

$$NH_2.C{:}NH.NH.C{:}N + R\,NH_2\,HCl = NH_2.C{:}NH.NH.C{:}NH.NH\,R\,HCl$$

The base was obtained by treatment of the salt with an alkali, generally sodium hydroxide. Benzoxazoleguanidine was included in this study because of its close structural relationship to the biguanides and also to the benzothiazoles. The hydrochloride was prepared by the reaction between dicyanamide and *o*-aminophenol hydrochloride:



The base was obtained by treating the salt with an alkali.

Experimental

A selected batch of smoked sheet was broken down on a warm mill for 15 minutes and zinc oxide and sulfur were added to form the following mix: smoked sheet 100, zinc oxide 100, and sulfur 10 parts. One part of accelerator, on basis of rubber content, was incorporated into this stock. After allowing to stand for 24 hours, the uncured stocks were weighed into aluminum molds and cured in slab form at 302° F. (150° C.). The cured sheets were cooled in water immediately upon removal from the press vulcanizer.

Dumb-bell test specimens were cut out and tested 24 hours after curing according to Bureau of Standards specifications.[11] Four to six specimens from each cure were tested, and in the majority of cases results were obtained from two or more individual mixes made with different preparations of the same compound.

The compounds tested were compared with stocks containing no accelerator, and with stocks containing diphenylguanidine, hexamethylenetetramine, thiocarbanilide, and dicyandiamide. Table I records the tensile strength at break and the elongation. The results are shown graphically in Figure 1.

The activity of α-*o*-tolylbiguanide was further investigated in several typical commercial rubber stocks in order to obtain

[1] Received September 15, 1927.

[2] This paper is an abstract of part of the thesis submitted by Mr. Weiss in partial fulfilment of the requirements for the degree of bachelor of science in chemistry at the Polytechnic Institute of Brooklyn in June, 1927. The vulcanization tests were carried out in the laboratory of the Metal Hose and Tubing Company of Brooklyn, and the authors take pleasure in expressing their appreciation to Robert Berkowitz, chief chemist, for his kindness in placing the facilities of this laboratory at their disposal.

[3] British Patent 201,912 (July 27, 1923).

[4] *Caoutchouc & gutta-percha*, **20**, 12005 (1923).

[5] Sebrell and Boord, *Ind. Eng. Chem.*, **15**, 1009 (1923).

[6] Ellery and Powers, *India Rubber World*, **75**, 3 (1926).

[7] Naunton, *J. Soc. Chem. Ind.*, **44**, 549T (1925).

[8] The preparation and properties of these compounds and their derivatives will be described in detail in subsequent articles. See also Smolka and Friedrich, *Monatsh.*, **9**, 230 (1888); Lumiere and Perin, *Bull. soc. chim.*, [3] **33**, 205 (1905); Enrich, *Monatsh.*, **12**, 20 (1891); Cohn, *J. prakt. Chem.*, **84**, 394 (1911).

[9] Franklin, *J. Am. Chem. Soc.*, **44**, 492 (1922).

[10] Obtained from the American Cyanamid Company.

[11] *Bur. Standards, Circ.* **38**, p. 48.

some data as to the effects of numerous compounding ingredients upon the activity of a typical member of this class of accelerators. The general procedure was the same as that given for the tests in the high-zinc stock, except that cures were made at 40 and 20 pounds (2.8 and 1.4 kg. per

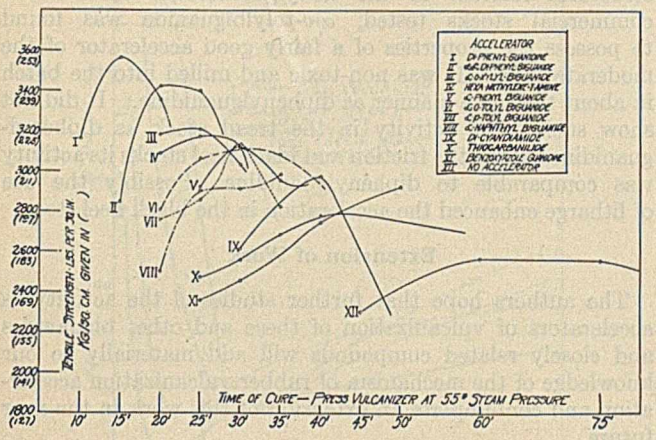


Figure 1—Effect of Various Aryl-Substituted Biguanides on Vulcanization

sq. cm.) steam pressure instead of the unusually high 55 pounds (3.9 kg. per sq. cm.). Comparisons of the activity of this compound were made with portions of the same stock containing (*a*) no accelerator, and (*b*) diphenylguanidine. The results are recorded in Tables II, III, and IV.

Table I—Cures at 55 Pounds (3.9 kg. per sq. cm.) Steam Pressure

Time of Cure Min.	Tensile Strength Kg./sq. cm.	Tensile Strength Lbs./sq. in.	Elongation Per cent	Time of Cure Min.	Tensile Strength Kg./sq. cm.	Tensile Strength Lbs./sq. in.	Elongation Per cent
α-PHENYLBIGUANIDE				BENZOXAZOLEGUANIDINE			
25	205	2920	830	25	163	2323	788
30	220	3127	771	30	172	2453	813
35	207	2955	779	40	193	2743	806
40	207	2959	745	50	205	2923	800
α-O-TOLYLBIGUANIDE				DICYANDIAMIDE			
20	197	2808	825	30	183	2613	733
25	215	3065	784	40	209	2973	725
30	218	3107	788	50	153	2185	700
35	217	3088	730	60	92	1299	500
40	206	2934	779				
α-P-TOLYLBIGUANIDE				HEXAMETHYLENETETRAMINE			
20	194	2736	850	20	217	3084	747
25	200	2852	765	25	223	3175	706
30	218	3118	718	30	220	3134	694
35	202	2878	719	35	149	2123	613
40	177	2522	686				
α(3,4)-XYLYLBIGUANIDE				DIPHENYLGUANIDINE			
20	223	3179	775	10	222	3161	775
25	225	3207	781	15	250	3561	756
30	213	3030	744	20	236	3355	716
35	184	2622	697	25	171	2435	607
α-NAPHTHYLBIGUANIDE				THIOCARBANILIDE			
20	176	2500	806	25	173	2470	800
25	204	2908	800	30	179	2552	786
30	204	2910	800	35	189	2681	800
35	210	2983	756	40	196	2778	775
				50	181	2578	800
				60	197	2797	800
α,α-DIPHENYLBIGUANIDE				NO ACCELERATOR			
15	172	2458	756	50	180	2565	780
20	241	3423	800	60	179	2559	791
25	239	3400	756	75	169	2405	750
30	184	2623	681	90	163	2320	726
				105	170	2428	738

Discussion of Results

This work shows that aryl-substituted biguanides are accelerators of the moderate class. α-Phenyl, α-*o*-tolyl, α-*p*-tolyl, and α(3, 4)-xylylbiguanides compared favorably with hexamethylaminetetramine in the stock used for testing purposes. α,α-Diphenylbiguanide possessed somewhat greater activity than the monoaryl derivatives, but α-naphthylbiguanide, having only a slightly lower molecular weight than the diphenyl derivative, did not show such great activity as the lower homologs. This was possibly due to its unstable character, and it was, moreover, the only compound tested which imparted odor during milling and vulcanization. With the exception of α-naphthylbiguanide, the activity of these aryl-substituted biguanides varied directly with the molecular weight of the substituted radical. α-*p*-Tolylbiguanide produced more rapid overcuring than α-*o*-tolylbiguanide, thus showing a tendency of the activity to decrease from para to ortho derivatives as in the case of diarylguanidines.

Table II—Tread Stocks

Material	A	B	C
Smoked sheets	100	100	100
Mineral rubber	5	5	5
Zinc oxide	5	5	5
Carbon black	40	40	40
Stearic acid	1	1	1
Pine tar	1	1	1
Sulfur	3	3	3
Diphenylguanidine		1	
α-*o*-Tolylbiguanide			1
Total	155	156	156

Mix	Time of Cure Minutes	Tensile Strength Kg./sq. cm.	Tensile Strength Lbs./sq. in.	Elongation Per cent
CURES AT 40 LBS. (2.8 KG. PER SQ. CM.) STEAM PRESSURE				
A	60	Undercured		
	75	Undercured		
	90	113	1607	713
	120	127	1803	688
	180	120	1700	617
B	30	226	3228	722
	45	246	3500	700
	60	248	3535	669
	75	240	3420	650
	90	227	3230	642
C	30	142	2030	713
	45	199	2845	700
	60	204	2907	682
	75	209	2983	688
	90	206	2930	675
CURES AT 20 LBS. (1.4 KG. PER SQ. CM.) STEAM PRESSURE				
A	No cures made			
B	60	Undercured		
	75	Undercured		
	90	176	2502	750
	120	189	2695	719
C	60	Undercured		
	75	Undercured		
	90	124	1760	725
	120	145	2066	708

Table III—Friction Stocks

Material	A	B	C
Smoked sheets	75	75	75
Whole-tire reclaim	25	25	25
Mineral rubber	5	5	5
Zinc oxide	5	5	5
Thermatomic carbon	15	15	15
Stearic acid	3	3	3
Sulfur	2.75	2.75	2.75
Diphenylguanidine		0.88	
α-*o*-Tolylbiguanide			0.88
Total	130.75	131.63	131.63

Mix	Time of Cure Minutes	Tensile Strength Kg./sq. cm.	Tensile Strength Lbs./sq. in.	Elongation Per cent
CURES AT 40 LBS. (2.8 KG.) STEAM PRESSURE				
A	75	106	1500	725
	90	135	1918	700
	105	120	1715	700
	120	120	1718	700
B	15	170	2421	763
	30	204	2910	750
	45	224	3188	719
	60	222	3167	700
	75	221	3143	650
C	15	151	2145	763
	30	209	2975	750
	45	233	3320	750
	60	234	3325	707
	75	229	3268	700
CURES AT 20 LBS. (1.4 KG.) STEAM PRESSURE				
A	No cures made			
B	45	162	2300	775
	60	173	2460	733
	75	183	2608	757
	90	196	2790	750
C	45	117	1670	725
	60	135	1920	700
	75	165	2343	713
	90	168	2388	725

Table IV—Black Heel Stocks

Material	A	B	C
Smoked sheets	22	22	22
Whole-tire reclaim	40.5	40.5	40.5
Litharge	1	1	1
Clay	20	20	20
Carbon black	8	8	8
Zinc oxide	5	5	5
Sulfur	2.5	2.5	2.5
Diphenylguanidine	..	1	..
α-o-Tolylbiguanide	..	..	1
Total	99.0	100	100

Mix	Time of Cure	Tensile Strength		Elongation
	Minutes	*Kg./sq. cm.*	*Lbs./sq. in.*	*Per cent*
	Cures at 40 lbs. (2.8 kg.) steam pressure			
A	15	108	1532	525
	20	108	1543	500
	30	114	1624	469
	45	104	1489	378
B	5	149	2125	507
	10	165	2343	475
	15	163	2328	400
	20	151	2045	350
	30	114	1628	238
C	5	150	2138	500
	10	166	2360	463
	15	161	2303	425
	20	151	2149	366
	30	123	1748	225
	Cures at 20 lbs. (1.4 kg.) steam pressure			
A		No cures made		
B	15	129	1835	525
	30	139	1975	463
	45	136	1938	416
	60	122	1740	375
C	15	140	1993	497
	30	153	2177	475
	45	150	2135	441
	60	135	1928	400

Since dicyandiamide was the substance from which these compounds were prepared, its acceleration properties were tested and confirmed.[12] Benzoxazoleguanidine was the least active of the compounds tested, probably owing to the presence of the electronegative oxygen in the molecule.

[12] British Patent 201,570 (July 27, 1923).

In some preliminary experiments it was found that, in the absence of zinc oxide as an activator, biguanides are very slow accelerators, as might be predicted from their close structural relation to the diarylguanidines. In the few commercial stocks tested, α-o-tolylbiguanide was found to possess the properties of a fairly good accelerator of the moderate type. It was non-toxic and milled into the batch in about the same manner as diphenylguanidine. It did not show such great activity in the tread stock as diphenylguanidine, but in the friction and black heel stocks its activity was comparable to diphenylguanidine. Possibly the use of litharge enhanced the acceleration in the black heel stock.

Extension of Work

The authors hope that further studies of the activity as accelerators of vulcanization of these and other biguanides and closely related compounds will add materially to our knowledge of the mechanism of rubber vulcanization acceleration and contemplate an extension of this work in the near future.

Conclusion

1—Aryl-substituted biguanides are rubber vulcanization accelerators of moderate activity.

2—The relation between the chemical constitution of the substituted radicals and the activity of the biguanides is, in general, about the same as found by other investigators for other types of accelerators.

3—α-o-Tolylbiguanide has a fairly great activity in certain commercial rubber stocks.

Effects of Ozone on Stretched Rubber[1]

F. H. Haushalter, Webster N. Jones, and J. W. Schade

The B. F. Goodrich Company, Akron, Ohio

It has been found that samples of vulcanized soft rubber under slight tension exposed to direct sunlight crack more severely than samples similarly exposed under somewhat greater tensions.[2] It has also been discovered that similar rubber compositions when stretched even a small amount in an atmosphere containing ozone (as low as 0.1 per cent) crack noticeably in a short time—a matter of seconds or minutes compared with a period of weeks to produce an equal degree of cracking in sunlight. As in sunlight exposure during its early stages, the degree of cracking in ozone decreases as the tension is increased beyond a definite value for each stock.

Methods of Bringing Ozone in Contact with Rubber

In the course of the experiments ozone was brought in contact with the rubber by two distinct methods.

Method I—By the first method 6 by 8 inch (15 by 20 cm.) sheets, $^3/_{32}$ inch (2.4 mm.) thick, were held at each end by a steel clamp; one clamp was fixed to a horizontal table, while loads were applied to the other clamp. A flat metal plate was placed under the sheet of rubber and a steel rod $^1/_4$ inch (6 mm.) in diameter was laid on the top side. The metal plate and rod were connected to the high-voltage terminals of a transformer. The voltage across the rubber sheet could be increased from 0 to 60,000 volts by means of a rheostat in the low-voltage circuit of the transformer. At 10,000 volts the oxygen of the air in the region of the top electrode (steel rod) was broken down and ozone produced. By accurately controlling the voltage and time of exposure, by working under constant atmosphere conditions, and by guarding the apparatus from air currents, very consistent results were obtained upon repetition of the tests. Dumb-bell test sections were cut from the treated sheets so that the cracked portion was in the constricted section. The effect was then determined.

Method II—The second method was by the use of an ozone machine made by the United States Ozone Company. Oxygen was bubbled through sulfuric acid into the ozonizer, where it was broken down by a voltage of 10,000. The ozonized oxygen then passed into a sealed box with a glass top. This box was 12 by 18 inches (30 by 45 cm.), and 12 inches (30 cm.) high, large enough to hold a special clamping device for stretching the samples of rubber several hundred per cent. The ozone entered one end of this box through three tubes; three small vent holes at the opposite end permitted movement of the gas through the box. Dumb-bell strips of rubber were tested at various percentages of stretch by this means under as uniform conditions of ozone concentration as could be maintained. Ozone concentrations in

[1] Presented by F. H. Haushalter and W. N. Jones under the title "Effect of Ozonized Oxygen on Stretched Rubber" before the Division of Rubber Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

[2] Kelly, Taylor, and Jones, *Ind. Eng. Chem.*, **20**, 296 (1928).

POLITECHNIKI ŚLĄSKIEJ

the box were checked at various times by potassium iodide titration. This concentration was found to be about 0.1 per cent. After considerable work by both methods the method of using high voltage in air proved preferable.

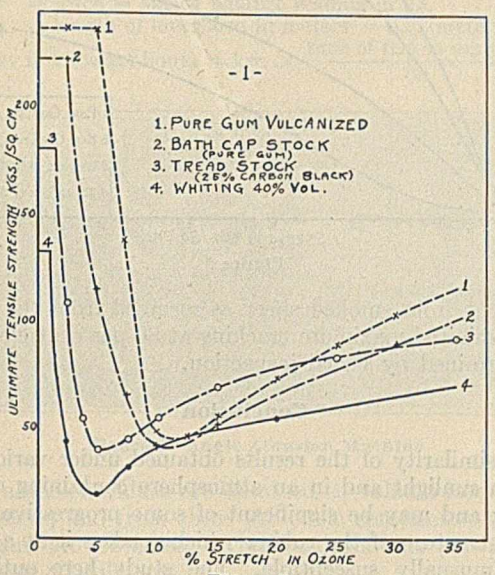


Figure 1

Tensile Tests

Where accurate comparisons were to be made on different stocks, two or three samples were clamped together in parallel in the clamping device, stretched a like amount, and subjected to ozone for a definite time, usually 1 minute. In determining the degree of stretch required to produce the maximum deterioration, samples were clamped together in parallel in the clamping device, one sample being stretched 2.5 per cent and the other 5 per cent. The next test would be made on one sample stretched 5 per cent and its companion 7.5 per cent; and so on. After exposure to ozone, strips were broken on the Scott rubber tester. All tensile values were calculated back to those for unstretched samples as a standard. The following machine tensiles and values calculated to the standard illustrate the method:

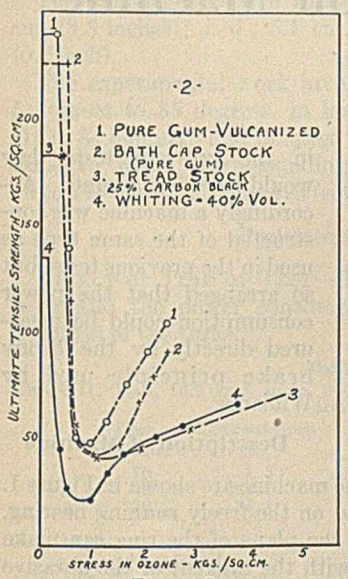


Figure 2

Stretch	Machine Values Expt. 1	Expt. 2	Expt. 3	Corrected Values Expt. 1	Expt. 2	Expt. 3
Per cent	*Kg. per sq. cm.*			*Kg. per sq. cm.*		
0	140			140		
2.5	111.2	105.60		111.2	112.0	
5		40	42.8		42.2	42.2
7.5			47.2			46.4

That is, the corrected figure for 5 per cent is 111.2/105.6 times the machine value of 40, and the corrected figure for 7.5 per cent is 42.2/42.8 times the machine value of 47.2. This method seemed to compensate for any slight changes in ozone concentration which may have occurred. The stress-strain relations (curve sheet 5) used for translating elongation values to tension values were plotted autographically on a machine in which the load was applied by means of a long calibrated coil spring. Near the top of the spring is a clamping nut, by which its length may be changed according to the cross-sectional area of the test strip. All curves are thus drawn autographically to the same scale.

The effect of the ozone treatment is shown on curves sheets 1 and 2. Comparison of the curves for various rubber compositions indicates that the maximum cracking takes place more nearly at a definite tension than at a definite elongation. It is interesting to note, however, from comparison of the data for pure gum and tread stocks (curve sheets 1, 2, 3, and 4) that changes in the degree of cracking and in hardness of the stretched stock seem to bear some relation to each other and to vary more nearly according to the amount of stretch than to the applied tension. The relative tension may, however, be closer in agreement with changes in hardness than the data indicate, because during the minute of exposure there is a decrease in the stresses due somewhat to the usual release in stretched rubber but more to that resulting from the cracking of the sample. In all cases the tensile figures checked the intensity of cracking as determined by visual inspection. The order in which the samples were placed on the basis of inspection was the same as that determined on the basis of tensile tests.

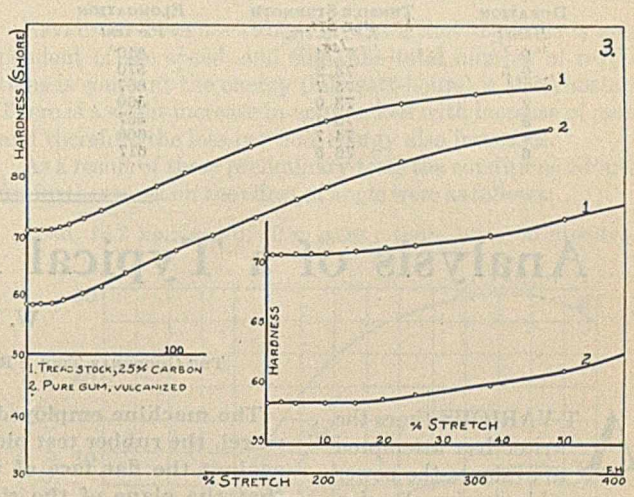


Figure 3

Hardness Tests

In measuring the hardness, a strip of rubber 1 inch wide, 5 inches long, and 0.25 inch thick (2.5 by 12.5 by 0.6 cm.) was clamped in the jaws of a tensile testing machine. The sample was stretched definite amounts—such as 2.5, 5.0, 7.5, and 10.0 per cent—the load recorded, and the hardness obtained by means of the Shore durometer. The sample was given a firm backing each time the instrument was applied. Sheets 0.6 cm. thick were used to avoid excessive thinning of the sample when stretched. The results indicate that the rubber does not at once increase in hardness as tension is applied; also, the tread stock (the stiffer of the two) begins to increase in hardness at a lower value of stretch than the pure gum stock.

The study indicates that in stretched samples there is a critical point at which the rubber is exceedingly sensitive to the oxidizing effect of ozone. As the hardness of the stock is increased by greater tension the effect of ozone is correspondingly diminished. This cracking does not occur in unstretched samples.

Effect of Ozone on Unstretched Rubber

A large number of compounds of various kinds have been subjected, unstretched, to higher concentrations of ozone,

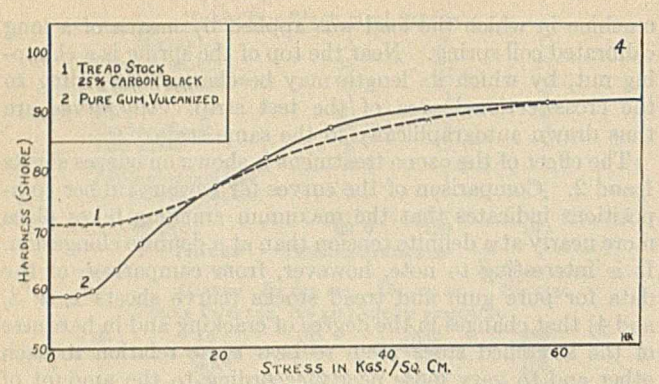


Figure 4

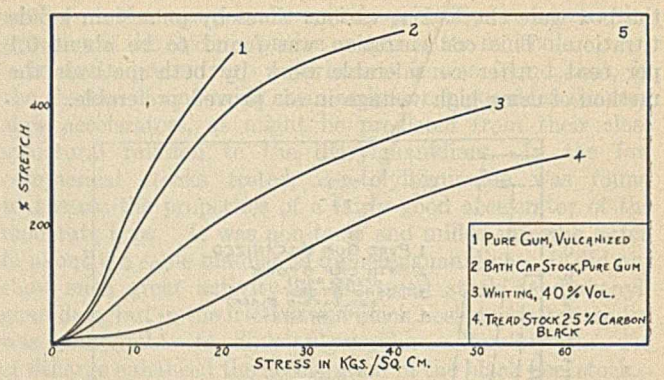


Figure 5

ranging from 2 to 5 per cent for 18 hours without showing any noticeable decrease in tensile strength. For example, dumb-bell test strips of linemen's protector shield stock were exposed, unstretched, at room temperature to ozonized oxygen which contained 0.5 to 1.0 per cent ozone. The strips were $^3/_{32}$ inch (2.4 mm.) thick and the test section 0.25 inch (0.6 cm.) wide. The lack of change is indicated in the following table:

Duration	Tensile Strength	Elongation
Hours	*Kg./sq. cm.*	*Per cent*
0	77.4	610
0.5	73.2	570
1	75.7	607
2	73.0	560
3	73.1	567
4	74.7	600
6	76.5	617

Strips cut from smoked sheet as received from the plantations exhibited maximum cracking at 30 per cent elongation as determined by visual inspection.

Conclusion

The similarity of the results obtained under various tensions in sunlight and in an atmosphere containing ozone is striking and may be significant of some progressive change in the structure of the rubber which renders it at a certain point unusually susceptible. The study here outlined is incomplete, but is presented in the hope that it may give other investigators an added method of studying problems connected with the structure or with the oxidation of rubber.

Analysis of a Typical Angle Abrasion Machine[1]

W. W. Vogt

The Goodyear Tire & Rubber Company, Akron, Ohio

The machine employed consists of a driven abrasive wheel, the rubber test piece in ring form being pressed against the flat face of the wheel in such a manner that the plane of the ring makes an angle with the tangent of the abrasive wheel at the spot of contact. Provision is made for measuring the power consumed in abrasion by a Prony brake method. This angle machine is essentially a constant-power machine. The relationships between abrasion loss and time, load, speed, angle, power consumption, etc., are given. An analysis of the forces involved is also given.

At various times the writer has attempted to evaluate the power consumed in causing abrasion of rubber. Two separate investigations were made; in both cases the abrasion machine used was of the angle type, wherein the periphery of a rubber ring was pressed against the flat surface of an abrasive wheel in such fashion that the plane of the ring was perpendicular to the face of the abrasive wheel and set at an angle to the tangent of the abrasive wheel at the point of contact. The power and energy figures were obtained from readings of the current supplied to the electric motor used to drive the abrasive wheel. On both occasions it was found that, for a wide variety of practical tread stocks, the differences in power consumption were less than the experimental error (which was not more than 5 per cent), even though the abrasion resistance of the stocks in question varied more than twofold. It was concluded that as a practical proposition the energy concept of abrasion was of little importance in differentiating various stocks.

Recently Williams[2] showed differences between stocks of such magnitude that it was believed that had they occurred in the previous tests they would have been found. Accordingly a machine was constructed of the same type as used in the previous tests, but so arranged that the power consumption could be measured directly by the Prony brake principle used by Williams.

Description of Machine

The essential features of the machine are shown in Figure 1. The test piece, *A*, is mounted on the freely running bearing, *B*, which can be set so that the plane of the ring can make any angle (0 to 90 degrees) with the tangent of the abrasive wheel at the point of contact of the ring. The point of contact is coincident with the axis about which the holder swings. The support arms can rotate freely on ball bearings around the shaft, *C*, of the turn table on which the abrasive wheel, *D*, is mounted. This is an alundum wheel, 36 grain. A flexible strap, *E*, is attached to an arc of proper radius, *F*, and the readings of the force are obtained from the spring balance, *G*, reading directly to $^1/_4$ pound.[3] The minimum load on the test rings is, of course, the weight of the attachment (6.72 kg. or 14.8 lbs.) and this can be increased by adding auxiliary weight *W*. The mechanism for rotating the abrasive wheel and air jets for cleaning its surface are not shown.

[1] Presented before the Division of Rubber Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

[2] *Ind. Eng. Chem.*, **19**, 674 (1927).

[3] All readings of force were taken in English units, but have been converted to the metric system to conform with the publisher's policy.

The Prony brake equation applies:

$$\text{Power in kilowatts} = \frac{2\pi NFL}{4564}$$

where N = r. p. m. of abrasive wheel
F = force = spring balance reading in kg.
L = length of lever arm in meters = 0.21 meters

$$\text{Energy in kilowatt-hours} = \text{kw.} \times \frac{\text{time of test in minutes}}{60}$$

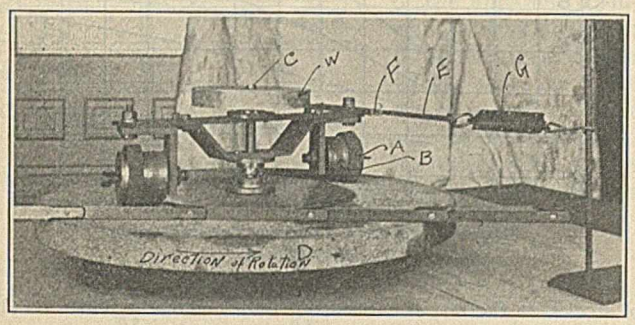


Figure 1—Angle Abrasion Machine

The abrasion values are obtained as volume loss in cubic centimeters, and from these the cubic centimeters per kilowatt-hour are obtained. These calculations are identical with those of Williams.

Description of Test Samples and Scope of Tests

Three stocks at their correct technical cure were used throughout this work; a sufficient number of rings were cured and all rings were aged at least one week before testing. Stock I is a first-grade black tread stock, stock II a second-grade tread, and stock III a third-grade stock.

The dimensions of the rubber test ring were: o. d., 8.9 cm. (3.5 inches); i. d., 5.1 cm. (2.0 inches); width, 1.8 cm. (0.7 inch).

The experimental work involves variations in angle from 5 degrees to 85 degrees, in load from 6.81 kg. to 24.5 kg. (15 to 54 pounds), and in speed from 36 to 112 r. p. m. of the abrasive wheel, corresponding to surface speeds of from 46 to 143 meters (150 to 470 feet) per minute.

Preliminary Tests

Effect of Time of Test—Table I shows that the rate of wear and the power consumption are independent of the duration of the test.

Table I

(Stock II; load, 16.2 kg.; angle, 20 degrees; speed, 80 r. p. m.; time, variable)

Time	Volume Loss	Rate of Wear	Power
Minutes	*Cc.*	*Cc./min.*	*Watts*
10	11.5	1.15	95
20	22.7	1.13	95
30	34.1	1.14	95

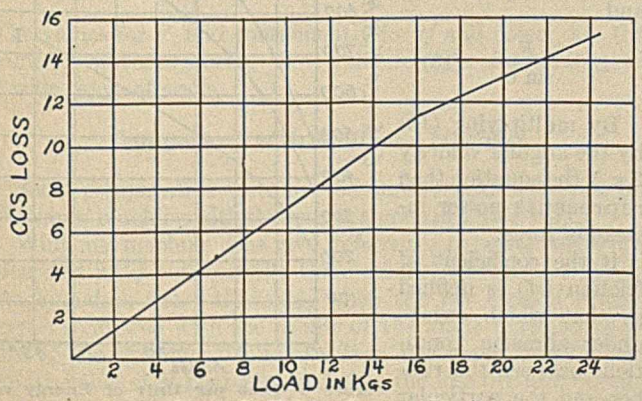


Figure 2—Volume Loss *vs.* Load

(Stock II; speed, 80 r. p. m.; angle, 20 degrees)

Effect of Load—The volume loss is practically proportional to the load, and the power consumption increases less rapidly than the load. (Table II and Figure 2)

Table II

(Stock II; time, 10 minutes; speed, 80 r. p. m.; angle, 20 degrees; load, variable)

Load	Volume Loss	Loss per kg. Load	Force	Power	Power per kg. Load	Loss per Unit Energy
Kg.	*Cc.*	*Cc.*	*Kg.*	*Watts*	*Watts*	*Cc./kw-hr.*
6.75	4.7	0.700	2.95	51	7.6	565
11.70	8.1	0.693	4.40	76	6.5	640
16.20	11.3	0.695	5.68	97	5.9	700
24.40	15.3	0.630	7.58	131	5.4	700

Table III

(Speed and time variable but constant (800) total revolutions)

Speed	Time	Force	Volume Loss	Energy	Loss per Unit Energy
R. p. m.	*Minutes*	*Kg.*	*Cc.*	*Watt-hours*	*Cc./kw-hr.*
STOCK II; LOAD 16.2 KG.; ANGLE, 20 DEGREES					
36	22.2	5.78	9.2	16.6	555
59	13.5	5.68	10.35	16.2	636
80	10.0	5.68	11.3	16.2	690
112	7.1	5.68	11.0	16.2	670
STOCK III; LOAD, 16.2 KG.; ANGLE, 25 DEGREES					
36	22.3	7.15	16.4	20.5	805
59	13.5	7.36	18.8	21.2	885
80	10.0	7.28	20.0	21.0	952
114	7.0	7.20	22.2	20.6	1070

Effect of Speed—Table III shows that the force is independent of the speed, and since the total number of revolutions is constant the energy (kilowatt-hours) is also constant. There is a slight increase in volume loss with increase of speed and therefore the loss per unit energy also increases.

As a result of these preliminary tests the conditions adopted for further work on the effect of angle were as follows:

Load, 16.2 kg.; speed, 80 r. p. m.; time, 10 to 30 minutes

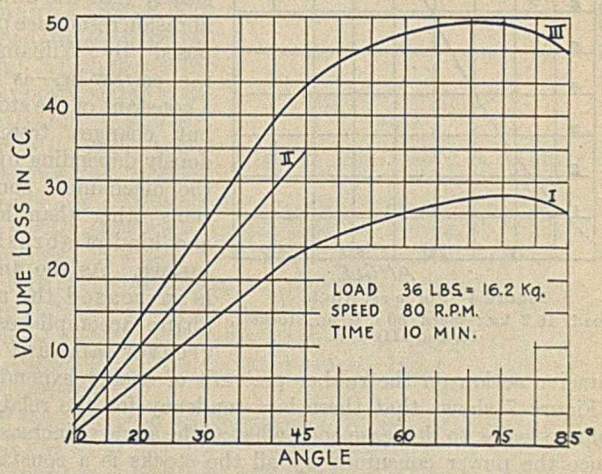


Figure 3—Volume Loss *vs.* Angle

Relation between Abrasion Loss and Angle

The data for the three stocks at various angles are given in Table IV. The longer time of run was used at the smaller angles, but all results are figured to a standard time (10 minutes).

These results are shown graphically. Figure 3 shows the relation of volume loss to the angle. The curves were extended to include some determinations made at very high angles. Between 10 and 45 degrees the volume loss is practically linear with respect to the angle. A few determinations indicate that at the 5-degree angle there is still a very slight but measurable abrasion taking place, but that at lesser angles the abrasion is negligible, leading to the conclusions that a certain slippage may take place without causing abrasion.

Table IV

Angle	Force	Power	Energy	Volume Loss		Loss per Unit Energy
Degrees	*Kg.*	*Watts*	*Watt-hours*	*Cc.*	*Per cent*	*Cc./kw-hr.*
			STOCK I			
10	2.36	41	6.8	1.45	100	214
15	4.00	69	11.6	3.65	100	317
20	5.78	100	16.6	7.20	100	434
25	7.50	130	21.7	10.80	100	500
30	8.65	149	24.9	14.10	100	562
45	11.60	200	33.3	24.50	100	736
			STOCK II			
10	Same as stock I			2.35	162	348
15				6.35	174	555
20				11.2	155	670
25				16.6	154	765
30				21.2	150	850
45				35.7	146	1070
			STOCK III			
5	Same as stocks I and II			0.35		
10				3.20	220	469
15				7.65	210	662
20				14.7	204	885
25				19.8 (?)	183 (?)	918
30				27.1	192	1090
45				45.0	184	1350

Figure 4 shows the force in relation to the angle. The points through which the curve is drawn indicate the maximum and minimum values for all three stocks. It can reasonably be said that the force, and therefore the power consumption, is identical for the three stocks.

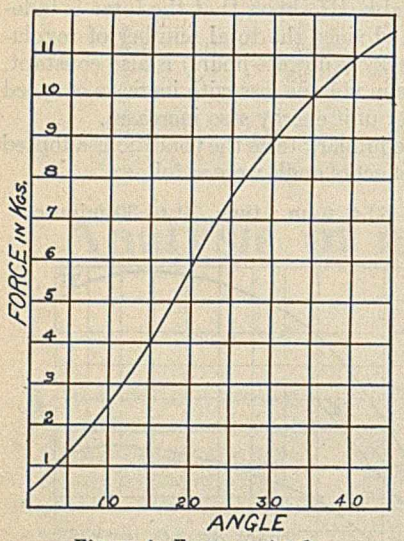


Figure 4—Force *vs.* Angle
(Load, 16.2 kg.; speed, 80 r. p. m.; stocks I, II, and III)

Although volume loss was for the most part determined at one load only, the readings of force were obtained for a large number of different loads at all angles. (Figure 5)

Figure 6 shows clearly that the unit of abrasion resistance proposed by Williams—i. e. cc./kw-hr.—is not a constant of the stock, but changes tremendously depending upon the mechanical conditions other than load and kind of abrasive surface. As the angle is increased the machine accomplishes a greater amount of abrasive action on the rubber per unit of energy expended.

Figure 7 shows that there is a tendency for the relative volume losses to decrease somewhat as the angle is increased. Since the power consumed by all the stocks is a constant, this chart also expresses the relationship between the three stocks based upon the values of cubic centimeters per kilowatt-hour.

Summary of Mechanical Behavior of Angle Machine

As a mechanical device for abrading rubber this particular form of angle machine is consistent in its behavior. The following points are noted:

(1) The volume loss is practically proportional to the load.
(2) The rate of wear is constant during the test.
(3) The loss is practically independent of the speed, an increase in speed of 300 per cent causing an increase in volume loss of about 20 per cent.
(4) The relationships between the three stocks are practically constant and independent of the load, the speed, the duration of the test, and depend only to a relatively slight extent on the angle.
(5) The over-all power is virtually a constant for a wide range of stocks, so the test is carried out under constant power conditions.

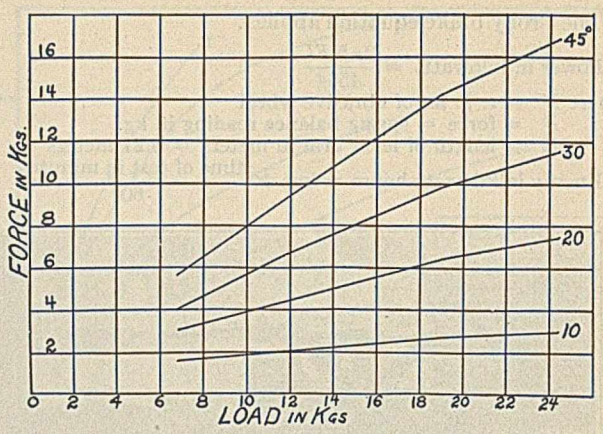


Figure 5—Force *vs.* Load for Various Angles
(Stocks I, II, and III; speed, 80 r. p. m.)

Mechanical Forces Involved

The mechanical forces involved in this type of machine have been analyzed. (Figure 8)

F = the total force as read on the spring balance (1)
L = length of the lever arm from the center of the abrasive wheel to the center of the spot of contact of the rubber ring (2)

F can then be resolved into

C = tangential component of abrading force (3)
D = axial component of abrading force (4)
Θ = angle between plane of ring and normal to L at point of contact (5)
A = component of bearing reaction normal to L (6)
X = component of bearing reaction parallel to L (7)
N = r. p. m. of abrasive wheel (8)
W = load on test piece (9)

By taking moments about the middle support,

$$FL = C \cos \Theta L + D \sin \Theta L \quad (10)$$

C can be evaluated by direct measurement when $\Theta = 0$

When $\Theta = 0$, $\cos \Theta = 1$, $\sin \Theta = 0$, $F = F_0$ (11)

Therefore, $C = F_0$.

Rewriting (10) $F = F_0 \cos \Theta + D \sin \Theta$ (12)

Experimentally, the value of C can be neglected for all but the very low values of Θ and

$$D = \frac{F}{\sin \Theta} \quad (13)$$

By multiplying (10) by the angular velocity $2 \pi N$ the equation then represents power instead of force.

If the coefficient of friction (cf) is defined as that which exists under abrasion conditions between the rubber and the particular abrasive surface used,

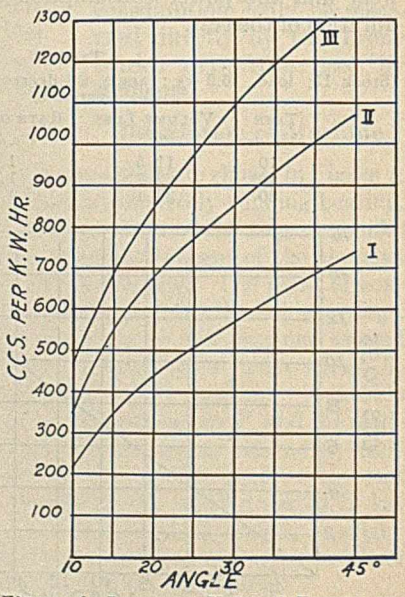


Figure 6—Loss per Unit of Energy *vs.* Angle
(Load, 16.2 kg.; speed, 80 r. p. m.)

Then $cf\ W = D$ (14)

Since $D = 0$ when W or $cf = 0$

and $cf = D/W$ (15)

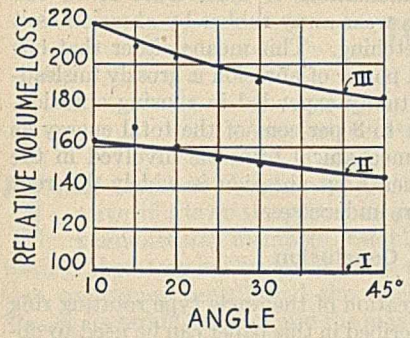


Figure 7—Relative Loss *vs.* Angle

Hence the measurement of F leads to values for the power consumption during abrasion, or to values of the apparent coefficient of friction under the abrading conditions which obtain. The same analysis can be applied to Williams' machine and in this case by taking moments $D = F$.

Table V

(Stocks I and III; angle $\theta = 0$; speed, 80 r. p. m.)

Load (W)	Force (F)	F/W
Kg.	*Kg.*	
6.75	0.14	0.0210
11.70	0.24	0.0206
16.20	0.34	0.0210
18.90	0.43	0.0220

Table V shows that F/W is analogous to the coefficient of rolling friction and is independent of the load within the limits studied.

Table VI

W	F	C	$C \cos \theta$[a]	$F_s = F - C \cos \theta$[a]	$F_s/\sin \theta = D$[a]	$D/W = cf$
Kg.	*Kg.*	*Kg.*				
6.75	3.95	0.14	0.12	3.84	7.70	1.14
11.70	6.60	0.24	0.20	6.38	12.70	1.09
16.20	8.65	0.34	0.29	8.35	16.60	1.03
18.90	9.65	0.43	0.36	9.25	18.50	0.98

[a] Based on values of W, F, and C in kg.

Table VI shows that cf is constant within 15 per cent over a variation of load of 300 per cent; it is also the same for the three stocks. The data are taken from Figure 4 for the 30-degree curve.

Table VII gives further data with respect to widely varying angles. Abrasion losses are figured as for 800 revolutions.

Table VII

(Stock III; load (W) = 16.2 kg.; speed, 36 r. p. m. for angles above 45 degrees, 80 r. p. m. for angles below 45 degrees)

Angle	F[a]	$C \cos \theta$[a]	$F - C \cos \theta$[a]	$\frac{F - C \cos \theta}{\sin \theta} = D$[a]	$D/W = cf$	Loss	Power	Loss per Unit Energy
Degrees						*Cc.*	*Watts*	*Cc./kw-hr.*
10	2.46	0.34	2.14	11.60	0.70	3.2	41	765
20	5.75	0.32	5.43	15.90	0.98	14.7	114	885
30	8.60	0.29	8.41	16.65	1.30	27.0	149	1080
45	11.80	0.24	11.56	16.40	1.01	45.0	204	1330
60	14.60	0.17	14.33	16.65	1.03	48.0	251	1150
75	15.40	0.10	15.40	15.90	0.98	51.0	267	1150
85	15.85	0.03	15.82	15.90	0.98	47.0	275	1020

[a] Based on values of W, F, and C in kg.

The values for F, and consequently for cf and power, are the same for all three stocks. The value for cf is about 1.00 over a wide range of angle.

Comparison with Williams' Machine

Some comparative tests on the three stocks were run on Williams' machine with the results shown in Table VIII.

Williams' machine does give differences in power consumption and in cf between the three stocks, whereas the angle machine does not. However, when the per cent of energy loss is compared with the results of the angle machine (Figure 7) the agreement is good. It is also noted that the absolute value of cf is greater and that the loss per unit energy is lower for Williams' machine.

Table VIII

(Load (W) = 3.74 kg.; time, 20 minutes; r. p. m., 37)

Stock	Volume Loss		Power	D	$D/W = cf$	Loss per Unit Energy	
	Cc.	*Per cent*	*Watts*	*Kg.*		*Cc./kw-hr.*	*Per cent*
I	1.37	100	15.4	6.36	1.70	268	100
II	1.86	136	14.0	5.75	1.54	402	150
III	2.14	156	12.9	5.35	1.43	495	185

There is no clear outstanding explanation of the differences in behavior between the two types of machine, particularly with reference to power consumption. The angle machine does not show differences in power consumption, but the relationships of volume loss of the three stocks are about the same as is obtained in the Williams machine by calculation of the cubic centimeters per kilowatt-hour.

A tentative explanation only can be attempted at the present time. It must be recognized that for both machines the measurement of power is an over-all measurement. In Williams' machine the abrasive action is a straight scrubbing action and the energy consumed is split as follows:

(1) That which appears as heat due to surface friction without causing abrasion.

(2) That which appears as heat due to hysteresis losses in the rubber.

(3) That which is actually consumed in dislodging particles of rubber.

In the angle machine the same three factors appear together with the additional one of rotational energy, the so-called C component which can be deducted leaving the D component (power consumed in axial scrubbing), which then must be apportioned as in the Williams' machine. Factor (3) is the one in which we are vitally interested, and the success which can be attained in evaluating the energy consumed in causing abrasion depends entirely on the extent to which we can make this factor approach 100 per cent of the total energy as measured. At present it seems very difficult, if not impossible, to evaluate the percentage of total energy expended in each of the three factors. However, some light may be thrown on the subject by the following experiment.

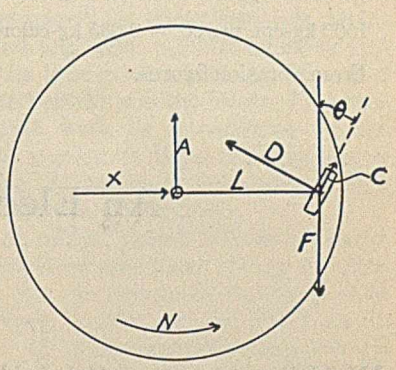


Figure 8—Plan View of Angle Machine

If the surface of the abrasive wheel is kept lightly covered with fine sand the energy consumption is decreased and the abrasion loss is decreased even more. By carefully controlling the amount of sand used, it is possible to maintain the energy consumption at any reasonably constant value and the abrasion loss can then be determined. Table IX gives some results on stock III.

Table IX

	Force	Power	Loss	Loss per Unit Energy
	Kg.	*Watt-hours*	*Cc.*	*Cc./kw-hr.*
Without sand	6.37	54.5	14.8	270
With sand	5.55	46.0	11.4	246
With sand	4.10	35.0	2.5	71
With sand	3.18	28.0	0.0	0

About 50 per cent of the energy is consumed in doing other things than causing abrasion.

Of course, it is obvious that the sand acts as a lubricant and cuts down the coefficient of friction between the rubber

and the abrasive wheel. This also takes place on the road. Furthermore, it may be argued that the loose sand, instead of abrading the rubber ring, abrades the abrasive wheel, and that the work expended is used up in that sort of abrasion. This cannot be denied, but in all probability part of the energy loss in an auto tire goes towards destroying the road material.

Still another line of reasoning leads to even more striking conclusions. The energy of resilience has been taken by Wiegand as an index of the abrasion resistance of a stock. The best possible tread stock has a value for energy of resilience of about 1200 foot-pounds per cubic inch or 1000 kg-cm. per cc. In stretching a piece of rubber to the break the test strip generally fails at one place. Little imagination is required to visualize a piece of rubber which when stretched would pull to a slightly higher value and then disintegrate into a fine powder, similar to that formed during abrasion. Let us assume a value of energy of resilience of 1500 kg-cm. per cc. for such a stock.

Now we can use the index of abrasion resistance as cubic centimeters per kilowatt-hour or kilowatt-hours per cubic centimeter. A good grade of tread stock on Williams' machine gives values of 270 to 400 cc. per kilowatt-hour and on the angle type from 200 to 670, depending on conditions.

From energy of resilience figures,

1500 kg-cm. per cc. = 0.035 kg-calories per cc.

From abrasion figures,

200 cc. per kw-hr. = 4.2 kg-calories per cc.
670 cc. per kw-hr. = 1.3 kg-calories per cc.

According to these calculations it takes from 35 to 120 times as much energy to wear away rubber by abrasion as it does to break it by stretching. This means either that our measurement of over-all power of abrasion is grossly misleading as to the energy actually expended in causing abrasion, this factor being from 1 to 3 per cent of the total energy as measured, or that the mechanical principle involved in the removal of rubber elements by abrasion is widely different from that causing rupture under stress.

Conclusion

The particular modification of the angle type rotating ring abrasion machine as described in this paper can be used to obtain a figure for the over-all energy consumed in causing abrasion of rubber. The writer is undecided as to whether or not the energy which actually goes towards causing abrasion is a large enough percentage of the total over-all energy consumption to warrant any belief that the energy of abrasion has yet been measured.

Acknowledgment

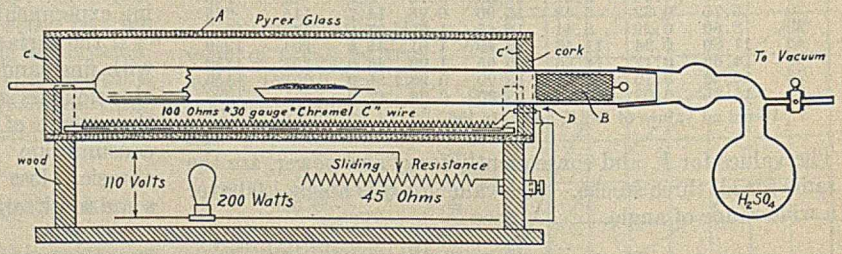
The writer desires to express his appreciation to R. B. Day for valuable contributions to the mathematical analysis of the forces involved, and to George Albertoni for assistance in the construction of the apparatus and in obtaining the experimental data.

An Electrically Heated Abderhalden Drier[1]

E. P. Clark

Bureau of Chemistry and Soils, Washington, D. C.

In the usual type of Abderhalden drier the tube to be evacuated is surrounded and maintained at the desired temperature by a jacket containing the vapors of a boiling liquid. Some features not possessed by this arrangement, but which are secured by an electrically heated apparatus, are the following: Any desired temperature may be approximately obtained by adjusting a rheostat; fire hazards are eliminated; condensing water is unnecessary, and the apparatus occupies a minimum amount of space. A unit featuring these advantages has been in use successfully for some time.



The construction of the apparatus is shown in the accompanying diagram, and is for the most part self-explanatory. The mantle, A, made of heavy Pyrex tubing, was furnished in the desired length by the Corning Glass Company. Potassium hydroxide, contained in a wire-gauze basket, B, in the cool part of the drying tube, removes moisture and acidic vapors, while the sulfuric acid removes alkaline and practically all organic vapors. The heating element is held in place by being laced to a 2-cm. strip of asbestos board which rests upon the bottom of the mantle. The leads from the coil pass through two pieces of glass tubing, D (D'), 1 mm. inside diameter tightly inserted in the end piece, C'. It is desirable to paint the board holding the heating coil, as well as the cork end pieces, C C', with a solution of sodium silicate.

The apparatus, wired as described, has been used at temperatures up to 125° C. with variations in any particular place within the tube not greater than 1° C. during the working day. There are, on the other hand, differences in the temperatures at various points throughout the tube. These are especially noticeable near C', which are due, for the most part, to end losses. Practically, these variations are of such a magnitude as to be unobjectionable for general work, especially if the material to be dried is placed sufficiently far from the cool end of the drying tube. For example, the difference between the temperatures of the ends of a boat 10-cm. long placed within the apparatus 15 cm. from C' was not more than 2° C. when operating at 75° C., or 3° C., when operating at 125° C.

[1] Received November 16, 1927.

Neon gas electric signs are now to be manufactured in Akron, Ohio. The Akron Neon Company as a subsidiary of the Daylo Sign Company, Akron, Ohio, has been organized. Samuel Weiss of New York is the holder of the patents for the signs.

Testing Laboratory of the American Gas Association[1]

Its Purposes and Accomplishments

R. M. Conner and F. E. Vandaveer

American Gas Association, Inc., Testing Laboratory, Foot East 62nd St., Cleveland, Ohio

THE American Gas Association, through coöperative efforts on the part of its gas company and manufacturer members, established a central testing laboratory in Cleveland, Ohio, on June 1, 1925. Gas companies contributed the funds necessary to finance its establishment, and the manufacturer members supplied a large share of its testing equipment. This laboratory was founded to insure the user and the public in general safe gas appliances, assist the appliance manufacturer in producing safe and efficient equipment, improve the art of appliance design, and eliminate forever from the market at the earliest possible moment appliances that do not meet proper concepts of substantiality, durability, and safety.

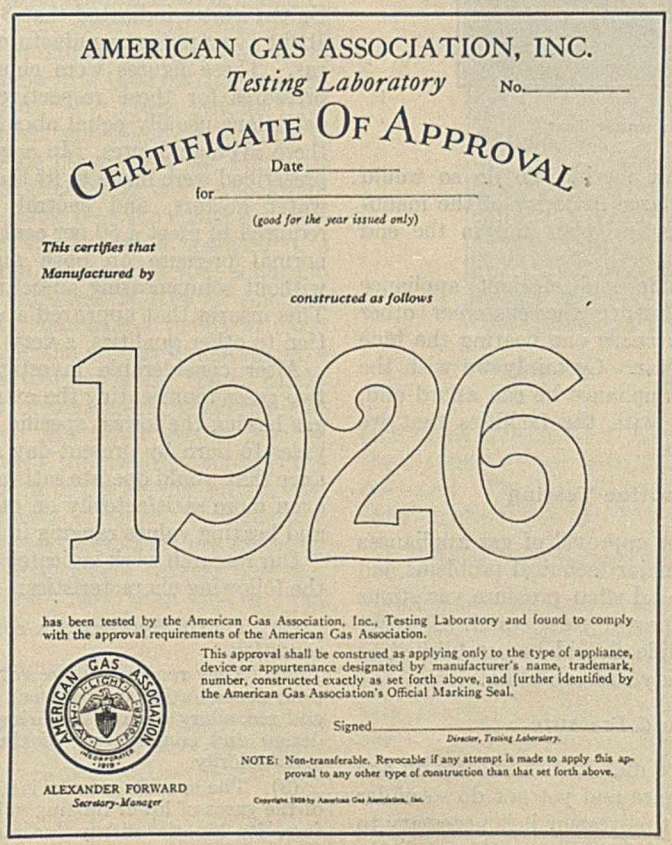
Laboratory Approval Seal

Considering the number of people served and the millions of appliances now in use, the gas industry as a whole has been remarkably free from accidents due to the operation of its appliances. However, since there has been a small percentage of accidents which might be attributed to imperfect appliance operation, the American Gas Association has decided to eliminate as nearly as possible the probability of such occurrences in the future.

The manufacture and use of gas appliances for heating is in many respects an old art. In 1850 James Sharp delivered a lecture on "Gastronomy" demonstrating gas cooking. In 1851 a Davis cooking stove was used in the United States. In 1876, the same year the American Chemical Society was founded, the Royal Baking Powder Company baked cakes on gas stoves at the Centennial Exhibition in Philadelphia. This apparently simple historical event marks one of the important milestones in the gas business. However, it was not until about 1895 that any great effort was made to popularize the use of gas for cooking and heating. Since that time cooking and heating with gas has become an accepted practice.

The fact that an appliance has been manufactured for fifty years does not necessarily mean it is the best possible product that can be made. There must always be progress and improvement—new features added, new conveniences provided—and it is in this field that a national testing agency can be especially helpful.

[1] Presented as a part of the Symposium on "Chemistry of Industrial Gas" before the Division of Gas and Fuel Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.



AMERICAN GAS ASSOCIATION, INC.

Testing Laboratory No._____

CERTIFICATE OF APPROVAL

Date_____

for_____

(good for the year issued only)

This certifies that

Manufactured by

constructed as follows

1926

has been tested by the American Gas Association, Inc., Testing Laboratory and found to comply with the approval requirements of the American Gas Association.

This approval shall be construed as applying only to the type of appliance, device or appurtenance designated by manufacturer's name, trademark, number, constructed exactly as set forth above, and further identified by the American Gas Association's Official Marking Seal.

Signed_____

Director, Testing Laboratory.

NOTE: Non-transferable. Revocable if any attempt is made to apply this approval to any other type of construction than that set forth above.

ALEXANDER FORWARD
Secretary-Manager

Copyright 1926 by American Gas Association, Inc.

Certificate of Approval Issued to Cover Approved Appliances

Our national gas-appliance testing program will be made effective largely by securing coöperation between the gas companies and appliance manufacturers. At the last American Gas Association convention, the gas company members pledged themselves to purchase and sell only A. G. A. approved ranges, space heaters, and tubing, since at that time other appliances had not been tested. Many appliance manufacturers have agreed to make only those which will receive A. G. A. approval. With such interest backing the movement and with coöperative advertising, the public will soon learn that an approved appliance is a quality product of proved merit, and the only safe thing to buy.

Establishment of Approval Requirements

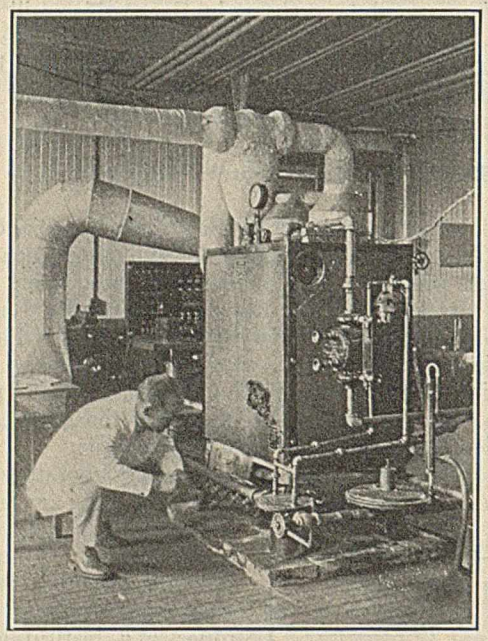
All official tests are made to determine compliance with approval requirements prepared by committee-men representing gas companies and appliance manufacturers as well as representatives from the Bureau of Standards, Bureau of Mines, U. S. Public Health Service, and the Master Plumbers Association. Such research work as is necessary in the preparation of the safety portion of these requirements is carried out by the Testing Laboratory of the American Gas Association and the U. S. Bureau of Standards.

The establishment of an official testing laboratory marks one of the most progressive steps ever taken by any industry in raising the standards of its public service. Contrary to the procedure adopted by most other approval laboratories and institutions, the work of the American Gas Association through its official testing agency is based almost entirely on public standards or specifications, in the preparation of which impartial experts outside of the industry coöperate actively and the results of which can be verified at any time by competent experts.

The approval requirements as they are drawn up are minimum requisites for satisfactory performance, substantial and durable construction, and safe operation. In their preparation sight was never lost of the necessity of providing every opportunity for manufacturers to improve their appliances and to embody individuality in their construction. It might be supposed that appliances constructed in accordance with certain requirements would

be the same, or essentially the same, regardless of the manufacture, the term "requirement" being easily capable of an interpretation conveying this thought. However, the requirements are so prepared that they are largely in the nature of laboratory performance requirements, with certain constructional restrictions that do not prevent the embodiment of ingenuity in design and improvement.

Not being familiar with our approval standards, there is a tendency on the part of some to misinterpret their meaning. As stated, they are minimum requirements and, what is more significant, they refer largely to the quality of performance, particularly its relationship to efficiency and safety, rather than to the manner in which an appliance shall be built. Our standards do insure reasonably durable construction, but they positively do not specify how many accessories shall be attached nor do they make any effort to classify approved



Gas Steam Boiler under Test

appliances in the order of their merit. To do so would react to the disadvantage of a large majority of the manufacturers coöperating in our testing plan and in the end result in endless controversies.

Our present plan insures safe and efficient appliance operation. To attempt to influence the customer other than to recommend that he purchase one bearing the blue star would be going much too far. Certainly we wish the customer to purchase the best appliance he can afford and, generally speaking, we believe with the facilities that we have provided that he will do so.

Conditions of Routine Testing

Before any routine testing for approval of gas appliances could be done nationally, two major technical problems had to be solved: (1) What gases and what pressure variations should be used in making approval tests; and (2) what concentration of carbon monoxide should be established as the maximum allowable under any test condition.

Kind of Gas and Pressure

It is obvious that an appliance may work perfectly on one kind of gas with a certain pressure and yet not do so under other service conditions. For this reason it is necessary to insist on a rather high degree of flexibility with respect to both variations in gas quality and the pressure at which it is supplied. To determine what gases should be used during our approval tests, duplicates of the natural gases served in Ohio, Pennsylvania, West Virginia, and Southern California were used. Manufactured gases similar to those distributed in Boston, New York, Philadelphia, Baltimore, Washington, Chicago, Denver, Tacoma, Portland (Ore.), San Francisco, and mixed gases similar to those distributed at that time in Los Angeles and Pittsburgh were duplicated. These gases are representative of those served in all our principal cities. Tests on them covered heating values from 400 to 1125 B. t. u. and specific gravity variations from 0.37 to approximately 0.7. The air required for complete combustion also varied from 3.5 to 11.2 cubic feet per cubic foot of gas burned.

At the present time the usual gases being delivered to the domestic customer vary in heating value from 400 B. t. u. to somewhat above 1200 B. t. u. per cubic foot and in specific gravity from 0.34 to 0.7. The pressure at which these gases are distributed when considered over the whole country may vary from 2 to 10 inches water pressure. These conditions naturally necessitate determining whether or not tests should be made on all or one kind of gas with the attendant variations in pressure. To prove conclusively how these conditions would have to be met, by attempting to anticipate every local condition, would have created such a complicated problem that it would have required years of research work to solve it. On the other hand, to find out what might be termed the worst conditions ordinarily encountered in service and to anticipate their effect on the appliance subjected to them is a more simple problem. The second procedure was selected and proved to be much easier and more satisfactory than expected. Therefore, as a result of these findings, tests are now made under the most severe conditions that appliances are ordinarily called on to meet with the knowledge that if they pass these tests they should prove even more satisfactory under average service conditions.

A rather careful survey of gas-pressure conditions over the United States indicated that 3.5 inches of water column was about average for manufactured gas and 7 inches for natural gas. These figures were chosen, therefore, as the normal pressures for these respective gases. Permissible pressure variations usually equal about 50 per cent either way from these average figures. In a general way the approval tests prescribed were made to fit these conditions. Space heaters, water heaters, and central house-heating appliances are required to meet a 50 per cent variation either way from the normal pressure on both manufactured and natural gas without compensating adjustments in the air or gas supply. This insures that approved appliances must possess, in addition to other qualities, a very high degree of flexibility.

After considerable investigation it was found that the two gases representing the extremes in heating value and the gas having the lowest specific gravity were the most difficult gases to burn by present-day appliances and that any appliance that would operate satisfactorily on them would perform even more satisfactorily on other gases with specific gravity and heating values ranging in between.

Our research work indicated that most natural gases possess the following characteristics:

(1) A high hydrocarbon content resulting in slow burning condition.

(2) They require a large volume of air for complete combustion, necessitating entrainment of greater quantities of primary and secondary air and requiring compensating provisions in the design and construction of the appliance used to burn them satisfactorily.

(3) The specific gravity is not very much greater than some of the gases of lower heating value, particularly coal gas; therefore, its kinetic energy for air entrainment is comparatively low.

A manufactured water gas of low heating value with a 0.7 specific gravity usually possesses the following characteristics:

(1) High hydrogen and carbon monoxide content, resulting in its being a rapid burning gas.

(2) A small volume of air required for complete combustion, necessitating entrainment of only a small amount of primary air.

(3) A high percentage of inerts (carbon dioxide and nitrogen) which flood the burner with inert gases and in general overcrowd the average gas range, water heater, or space heater burner, which is usually built for a higher B. t. u. gas.

Coke-oven gas of about 500 B. t. u. and 0.37 specific gravity generally has the following combustion characteristics:

(1) High hydrogen content, creating a comparatively fast burning long flame condition.

(2) Low specific gravity which does not give sufficient kinetic energy to the gas stream to inject large quantities of primary air.

Maximum Carbon Monoxide Concentration—Parallel with this investigation research on the establishment of a safety standard for completeness of combustion was conducted. This work was done jointly by the U. S. Bureau of Standards and our establishment.

Logically the first consideration in establishing a requirement for carbon monoxide is the maximum concentration human beings can breathe over a given length of time and feel no ill effects, and with this information in mind provide a factor of safety sufficiently large to insure safe operation under any reasonable service condition. According to such eminent authorities as Dr. Yandell Henderson[2] and Sayers, Meriwether, and Yant,[3] there are no deleterious effects on the human system when exercising or at rest when breathing an atmosphere of 0.03 of one per cent carbon monoxide for one hour.

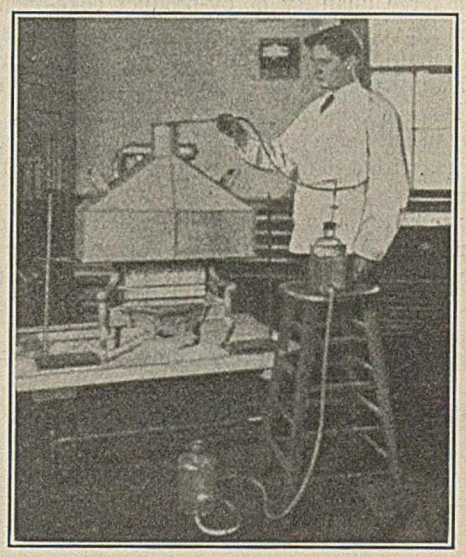
Accordingly a good gas appliance should produce no carbon monoxide, or at least such small quantities that it would have no effect on the human system. Consequently the limit permitted by the approval requirements of the A. G. A. for gas ranges under the most severe test conditions is one-third of the figure given by Henderson and Sayers, or 0.01 of one per cent concentration in a 1000-cubic foot room having four air changes per hour. For space heaters there are two requirements—one when the heater is burning in a normal oxygen supply, and the other when the appliance is burning in a room with a decreasing oxygen content. The second test is supplied in order that the customers may be safeguarded in cases where the heater is operated in a small and poorly ventilated room. Under the first condition the maximum allowable concentration is 0.02 of one per cent in the air-free products of combustion (0.002 to 0.005 per cent in the sample); under the second condition of a reduced oxygen supply, 0.05 of one per cent. These conditions figure out about one-tenth of the concentration required to produce any harmful effects. For water heaters, boilers, and furnaces, as such appliances are usually vented, the requirement is 0.04 of one per cent in the air-free products of combustion, giving a safety factor of about 5, under any usual service condition. These concentrations are probably lower than would be encountered where several men are smoking in a room, and certainly less than results from automobile exhaust on one of our busy streets.

Apparatus Used in Tests

In conducting its research and routine testing work, the American Gas Association's Testing Laboratory uses three types of apparatus for accurate determination of the completeness of combustion. Equipment ordinarily used for gas analysis—such as the Burrell, modified Orsat, Orsat, Haldane, pyrotannic acid, and canaries—is not sufficiently accurate for determination in the thousandths of one per cent. Three types of apparatus—the iodine pentoxide apparatus, the thermal conductivity, and the recording carbon monoxide apparatus—have been found very satisfactory. Successful development of the first two machines was accomplished by the U. S. Bureau of Standards; the third was perfected by the U. S. Bureau of Mines and the Mines Safety Appliance Company.

Determination of carbon monoxide by iodine pentoxide is based upon the reaction of carbon monoxide and iodine pentoxide, forming carbon dioxide and iodine. The iodine liberated is sublimed, collected in potassium iodide, and titrated with 0.001 N sodium thiosulfate. From the amount of thiosulfate used the percentage of carbon monoxide in the sample can be calculated.

In the thermal-conductivity apparatus the analysis of the gas is determined by the rate at which heat is carried by the gas under standard conditions. The recording carbon monoxide apparatus passes a measured amount of gas through a catalyst called Hopcalite (an intimate mixture of copper oxide and manganese dioxide) maintained at 100° C. by a steam bath, the carbon monoxide being selectively oxidized by the Hopcalite. The reaction liberates heat, which is transmitted to a thermopile imbedded in the Hopcalite. The electromotive force generated is recorded by a recording potentiometer which is calibrated in per cent carbon monoxide. All these apparatus are capable of an accuracy of 0.002 of one per cent. The laboratory makes between forty and sixty determinations per day to this degree of accuracy.



Sampling Products of Combustion from Space Heater

Certificate of Approval and Inspection System

When appliances pass the laboratory test the manufacturer is given a certificate of approval and permitted to display the laboratory approval seal, which is a blue star surrounded by two concentric circles containing the words "Testing Laboratory Approved." Where changes are made in the essential features of construction on any appliance during each year, the manufacturer must notify the laboratory of this change and, if it is one that affects combustion, resubmit this appliance to the laboratory for test.

An inspection system is also maintained to see that appli-

[2] *J. Ind. Hyg.*, **3**, 79, 137 (1921).

[3] *U. S. Pub. Health Service, Pub. Health Repts.* **37**, 1127 (1922), reprint No. 748.

ances bearing the laboratory seal of approval are being sold as approved. These inspections will be made at least once a year and more often if necessary. Where proper standards are being maintained, approval certificates will be issued covering each succeeding year, and once secured, are good indefinitely unless some changes are made that require additional tests.

Accomplishments to Date

During the past two years the laboratory has conducted research in the preparation of safety requirements for gas ranges, space heaters, water heaters, and central house-heating appliances, and also approved from test or inspection approximately 6000 gas ranges, 300 space heaters, 50 water heaters, 15 types of flexible gas tubing, and a number of central house-heating appliances. Considering that there are about 175 tests made on a gas range, 250 tests on a space heater, 200 tests on a water heater, and 150 tests on a central house-heating appliance, this demonstrates that an enormous amount of work has already been done.

Research on Mixing Gases

While the work of the testing laboratory is largely confined to routine testing, considerable research work has recently been done on mixing gases. This subject has become very important to every one in the gas industry. In some localities the natural gas supply is rapidly decreasing, necessitating mixing with the natural a manufactured gas of different heating value and different specific gravity. In other localities a large quantity of by-product coke-oven gas of low specific gravity is available, but there is not a sufficient quantity to supply the entire demand. Therefore, it is mixed with another gas, usually carbureted water gas of about the same heating value but much higher in specific gravity. The supply of oil, being somewhat doubtful, may necessitate mixing oil gas with coal or some other kind of gas as the price of oil increases.

The gas industry as a whole is interested in the question of how far it can go in varying specific gravities, or heating values, or both, and still maintain satisfactory appliance operation. It is an easy matter to manufacture and mix gases of different heating value and specific gravity, but the question arises as to how closely the mixing must be regulated without affecting the operation of gas appliances already in service. The laboratory is obtaining fundamental data on this subject. Although the whole investigation may not be finished for three or four years, the first phase of the work—that of finding out the effect of varying the specific gravity, the heating value remaining constant—will soon be completed.

Investment

At the present time the testing laboratory represents an investment of about $500,000 on the part of the gas industry, $125,000 of which was contributed by gas-company members; the remainder represents test fees that have been used partially to retire operating expenses and investments necessary on the part of appliance manufacturers to bring their equipment up to present standards.

Importance of Undertaking

With the hearty coöperation of every one concerned in this undertaking the testing laboratory is sure to succeed. It is founded by a great industry in the interest of better public service. It is raising the standards of construction and performance of gas-burning equipment and developing the art of appliance design. Already there are many signs of new developments, and a marked improvement can be seen in the approved ranges and space heaters being sold at the present time. The same can be said of water heaters and central house-heating appliances, when they are added to the approved list. This will also be true of other types of appliances submitted later for tests.

The gas industry appreciates the value of science in business. It realizes that it cannot with justice to the future of its business afford to shape its appliance policies after the customs and traditions of the past. The establishment of the Testing Laboratory was an epoch-making advance in the gas business and public evidence of the industry's consciousness of its moral responsibility to safeguard to the best of its ability the millions of people who are daily dependent on gas as one of the essential services of life.

Properties and Uses of an Edible Rice Cellulose[1]

E. R. Harding

Mellon Institute of Industrial Research, University of Pittsburgh, Pittsburgh, Pa.

A RECENT advance in food technology is the development of a process of recovery of an edible cellulose from the hulls of rice and other cereals. Cellulose is a natural constituent of practically all vegetable foods and is really an essential dietary constituent. By adding bulk and roughage to the intestinal contents normal elimination is promoted and constipation largely prevented.

In the development of a new ready-to-serve breakfast food milled rice was found to be the most desirable cereal base. Because of the low cellulose content of milled rice it was decided to reënforce the roughage content of the finished cereal by additions of a pure cellulose of suitable physical form. It was found that a satisfactory pure edible cellulose could be prepared from the hull of the rice, thus making the breakfast food an all-rice product. The cellulose of the hull is first isolated in a semifibrous form by a strong soda cook. A hydration treatment then reduces it to the proper physical form for use as an edible material.

[1] Received December 24, 1927.

A large plant for the production of this new form of pure cellulose has been in operation for some time. It is located at Lake Charles, Louisiana, adjacent to the largest rice mill in the world.

Rice cellulose as prepared for food roughage is a light, somewhat fluffy, fine, mealy material. It has a light cream color, but is easily bleached white if desired. It is odorless and tasteless. It has a mealy feel in the mouth, and although not intended to be eaten straight, when well moistened with saliva, can be swallowed without difficulty or irritation. Its ash content has been reduced to 1.0 per cent or less, although the original raw material contains about 18 per cent of ash that is largely insoluble silica. The washed product from the alkaline digestion may run as high as 99 per cent alpha-cellulose. In the finished product a part of the original compound or normal celluloses has been converted to simpler hydrated celluloses; but the freedom from impurities of non-cellulosic character entitles it to be called a practically pure cellulose.

Analyses of typical samples of rice cellulose which have been given the hydration treatment are given below:

	A	B	C	D	E
Alpha-cellulose	73.16	72.51	72.26	73.04	73.09
Hydrated cellulose	24.16	24.74	24.91	23.86	23.72
Copper number	8.91	9.16	8.65	9.32	9.04
Ash	0.74	0.86	0.83	0.97	0.68

Rice cellulose was primarily produced to supply moisture-absorbing roughage material for a ready-to-serve breakfast food. It is also suitable for enriching the roughage content of many other foods such as bread, muffins, pan cakes, crackers, thick soups, soft cheese, sandwich spreads, confections, etc. The use of substantially pure cellulose or hydrocellulose in foods in general and in prepared cereal foods in particular is protected by patents.[2]

The value of edible rice cellulose when used as a dietary roughage has been proved by a comprehensive series of practical tests. Using as subjects large groups of persons in two institutions—namely, an orphanage and a home for the aged—it was shown that when a rice-flake breakfast food containing a moderate percentage of purified cellulose was eaten regularly constipation was prevented or corrected in all except the most obstinate cases. There were no gastro-intestinal disturbances in these subjects. After feeding the cellulose for a long period to white rats its harmlessness was proved by autopsies on the animals, which showed no evidence of irritation to the digestive tract.

[2] U. S. Patents 1,495,789 and 1,547,582.

Formation and Solution of Calcium Hydroxide Crystals in Portland Cement[1]

Jasper O. Draffin

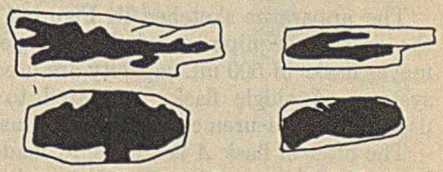
Department of Theoretical and Applied Mechanics, University of Illinois, Urbana, Ill.

When Portland cement is mixed with water it sets and finally hardens, and in so doing it liberates calcium, which later crystallizes from the solution as calcium hydroxide in the form of stout prisms and hexagonal plates. This calcium apparently comes from the di- and tricalcium silicates which hydrolyze under the action of the mixing water. During some studies on the hydration of tricalcium silicate it was observed that some of the crystals of calcium hydroxide which were formed in the solution were later dissolved in the solution from which they crystallized, the temperature remaining the same as when they formed.

The method of study was to mix some finely powdered tricalcium silicate, which contained only very small amounts of magnesium, aluminum, and iron oxides, with distilled water on a glass slide, cover it with an object glass, and cement around the edges with Canada balsam. This left the tricalcium silicate in water which could not evaporate and from which the air was excluded. The progress of hydration on these slides was observed by means of a petrographic microscope. About 12 hours after preparation many calcium hydroxide crystals could be observed and these reached their maximum size in 2 or 3 weeks. Many of these crystals had begun to corrode or dissolve at the end of 3 weeks, but this period was not constant; sometimes it was as early as 16 days; evidently it was related to the period of growth of the crystals. In many slides the crystals had dissolved completely in from 5 to 6 weeks, though the outlines were clearly defined after solution. Other slides showed some crystals dissolved while near them were crystals which were unaffected. The accompanying sketches show the manner in which the corrosion takes place. It generally begins on a prism face and not on a basal plane.

In searching for an explanation of the unusual action of a crystal dissolving in the solution from which it was formed, a number of possibilities were considered. One was a change to calcium carbonate. This was eliminated because the Canada balsam excluded the air and besides there was no trace of calcium carbonate on the slide. Another possibility was that of diffusion of the saturated solution from around the crystals to other parts of the slide, leaving unsaturated solution around the crystals. This was tested by preparing some slides with the tricalcium silicate concentrated at one side of the slide and other slides with the tricalcium silicate evenly distributed over the surface. No difference in action could be detected from this cause.

R. H. Bogue, research director of the Portland Cement Association Fellowship investigation, suggested that the soft soda-lime glass used in the slides and cover glasses might dissolve slightly and react with the calcium hydroxide in the solution. That would result in a gradual dissolution of the calcium hydroxide crystals and the reprecipitation of hydrated calcium silicate. It would account also for the skeleton outline of the crystals remaining after the completion of the reaction. Accordingly, some quartz object slides and fused-quartz cover glasses were obtained and experiments were carried on with these. No solution of crystals occurred with the quartz slides, though they were observed for 3 or 4 months. This indicates that the corrosion and solution of the crystals was caused by the soda-lime glass slides dissolving slightly, and it is believed that this is the correct explanation. The amount of solution of the slides is extremely small, so small that it cannot be detected with a microscope after the removal of the cover glass.



Sketch Showing Corrosion of Calcium Hydroxide Crystals. Shaded Portion Shows Part Dissolved

(Enlarged about 50 times)

The acceptance of this explanation raised the question as to what would be the effect on calcium hydroxide crystals in concrete when they were in contact with soda-lime minerals such as the feldspars. Experiments were therefore made in which finely powdered albite, labradorite, and anorthite were mixed with the tricalcium silicate on quartz slides, each mixture on a separate slide, to determine whether the feldspar would dissolve and cause the solution of the calcium hydroxide crystals. The addition of the feldspars did not cause corrosion of the calcium hydroxide crystals. Apparently the soda-lime glass is more susceptible to the action of calcium hydroxide than the soda-lime minerals.

Experiments with the feldspars mixed with the tricalcium silicate are being continued.

[1] Received January 28, 1927. Revised paper received January 6, 1928.

Determination of the Caustic Value of Lime[1]

Two Filtration Devices

W. M. Shaw,[2] W. H. MacIntire,[2] and J. E. Underwood[3]

THE UNIVERSITY OF TENNESSEE AGRICULTURAL EXPERIMENT STATION, KNOXVILLE, TENN., AND NATIONAL LIME ASSOCIATION, WASHINGTON, D. C.

Two tentative methods for the determination of the causticity of burnt and hydrated limes are given in the Methods of the Association of Official Agricultural Chemists.[4] These two methods and one other have been compared[5] with special reference to concordance between methods and to the effect of extraneous materials. Two modified procedures and filtration devices adapted to the determination of the causticity of calcium sucrate solutions are now proposed and the filtration procedure is compared with the modified Scaife procedure.

IN SPITE of its involved technic, the modified Scaife method has been widely used and by some it has been considered as standard in comparative studies. Although accurate for the clear solutions obtained from high-calcic limes, it is not accurate for the suspensions which are characteristic of high-magnesic limes. A much longer period than that prescribed is necessary to insure settling of suspended MgO-Mg$(OH)_2$, the presence of which precludes a positive titration end point. It therefore became necessary to devise a filtration apparatus which would eliminate all suspended matter in a CO_2-free atmosphere. In the course of collaborative work with the National Lime Association a device and technic were developed in this laboratory to insure rapid and accurate determinations of the CaO-Ca$(OH)_2$ value of any calcined commercial product with minimum exposure to carbon dioxide and negligible interference from impurities. The influence of impurities upon the accuracy of the procedure has been considered in another paper.[6] A different apparatus was evolved in the laboratories of the National Lime Association, but the two methods have in common the essential features of simplicity, speed, accuracy, and freedom from contaminating influences. Both devices will be described in this paper.

SHAW AND MACINTIRE DEVICE

Apparatus

The apparatus sketched in Figure 1 may be made from the ordinary equipment of the average laboratory. Erlenmeyer flasks of 500 ml. capacity are used to contain the lime system. A single flask, calibrated to deliver 500 ml., is used for all measurements of the aqueous-sucrose solvent.

The filter in flask *A* is a cone, *F*, made from a 25-ml. pipet by cutting the stem 2 to 3 cm. beyond the junction with the bulb. Two such cones can be made from one pipet. The periphery of the funnel is uniformly softened in a large flame and then curved inward by pressing down on a hard, flat surface. The cone is packed nearly full with cotton, which is then covered with a 2 to 3 mm. thickness of lightly compacted, macerated filter paper. For extremely fine suspensions a thicker filter-paper mat may be required, especially under the edges of the funnel. A fresh cotton-paper pad should be used for each determination. The stem of the cone is connected with a siphon, *B*, by means of thick-walled rubber tubing. If a large single filtrate or a number of filtration aliquots are desired, the face of the filter may be placed so near the bottom of the Erlenmeyer as to permit filtration of 95 per cent of the volume of the lime solution.

A number of receiving flasks, *m* and *n*, calibrated to deliver 50 and 100 ml., are most serviceable for collection of pilot and determination aliquots, respectively, when many determinations are to be made. Ordinary measuring flasks may be used, however, if the aliquot is delivered and the flasks then rinsed with CO_2-free distilled water. The inlet and outlet to the receiving flasks are made of evenly drawn-out tubing and fit into a No. 0 rubber stopper. The inlets should be just long enough to pass through the stoppers and bent slightly so that filtrates will run down the sides of the flask. The outlets should be long enough to permit adjustment to the meniscus mark on each receiving flask. The outlet from flask *n* is connected to flask *S*, to which is connected a soda-lime tube supplied with a stopcock, *D*, to permit equalization of pressure with CO_2-free air after filtration, and which is provided with a convenient suction attachment for removal of excess moisture from the cotton-paper filter.

Titration Buret

In using 0.5 *N* acid for titration, it is essential that the titration volume shall be accurately measured and that the standard acid be protected from the atmosphere. The authors used a 25-cc. overflow buret connected with a protected acid reservoir. A $^1/_4$-inch (6-mm.) bore, 3-way shellback buret 23 inches (58 cm.) long, $^7/_{16}$ inch (11 mm.) outside diameter, and calibrated to 0.05 cc. may be secured upon order and this buret enables readings to hundredths of a cubic centimeter.

Procedure

CHARGE—Grind the lime sample to pass a 100-mesh sieve and thoroughly mix by rolling before placing in a permanent container. The sample should be worked up in an atmosphere of minimum moisture and carbon dioxide content and protected against the breath of the worker. Transfer a portion of the sample to a weighing bottle. Withdraw charges by means of a polished, narrow-pointed spatula, calibrated to hold approximately 1.5 grams, and determine the exact weight by difference. Introduce the charge directly into a dry 500-ml. Pyrex Erlenmeyer flask, provided with a tightly fitting rubber stopper.

SUGAR SOLUTION—Prepare a sugar solution immediately before use by placing 25 grams of granulated sugar in a measuring flask calibrated to deliver 500 ml., and dissolve the sugar with cold CO_2-free water. Hold both the Erlenmeyer flask containing the charge and the measuring flask in a somewhat inclined position; insert the neck of the measuring flask a short distance inside the Erlenmeyer flask and carefully transfer the solution, agitating the flasks simultaneously and synchronously by a rotary motion to prevent granulation of the lime. Securely stopper the Erlenmeyer flask, and agitate. A quantity of clean, dry beads may be introduced, but they are seldom necessary. Six 1-minute agitations at intervals of 2 or 3 minutes will effect

[1] Received September 27, 1927.

[2] University of Tennessee Agricultural Experiment Station.

[3] National Lime Association. Present address, 206 Dickinson Ave., Swarthmore, Pa.

[4] Assocn. Official Agr. Chem., Methods, p. 35 (1925).

[5] Shaw, *J. Assocn. Official Agr. Chem.*, **8**, 344 (1925); **9**, 141 (1926).

[6] *Ind. Eng. Chem.*, **20**, 315 (1928).

complete solution of uncoated caustic lime. If any undisintegrated particles remain, they may be broken up easily by inverting the flask, trapping them in the space between the stopper and the neck of the flask, and crushing by careful twisting of the stopper. After 15 minutes' contact and the prescribed agitation, the sugar-lime solution is ready for filtration.

FILTRATION—Connect the filter cone with the siphon, *B*, and close stopcock *D*. Connect the receiving flasks, apply suction, and quickly connect the Erlenmeyer, *A*, containing the lime solution with the stopper, *E*. Filter 25 to 50 ml. of the solution; close stopcock *C* and open stopcock *D* to release suction. Replace the 50-ml. flask, *m*, containing the first fraction of the filtrate, with a dry 50-ml. flask. Close cock *D* and open *C*. To disconnect the system, close stopcock *C* and press down the outlet of the measuring flask gently to remove any excess of liquid above the meniscus and permit the intermediate connections to empty. Open cock *D* and remove the aliquots from the system. With two receiving flasks in series and each outlet in position, slightly above its meniscus mark, the attention of the operator may be safely diverted. Where the operator can give his entire attention to the determination, the system may be disconnected as soon as the first 50 ml. of solution has filtered and a dry 100-ml. flask substituted to be filled while the preliminary titration is being carried out.

Titrate the first 50-ml., or pilot, aliquot of the solution against 0.5 *N* hydrochloric acid with phenolphthalein indicator. Run twice the amount of this titration into a covered 200-cc. beaker; introduce the second, or 100-cc., aliquot into this acid; add phenolphthalein and complete the titration. Calculate the caustic value of the sample by the formula

$$\text{Per cent active CaO} = \frac{7A}{W}$$

where A = cc. 0.5 N acid per 100 cc. of lime solution and W = weight of charge.

Influence of Moisture Content of Filter Pad upon $Ca(OH)_2$ Concentration of Successive Portions of Filtrate

A small amount of water is retained by the freshly prepared cotton-paper filter pad after it is subjected to suction before introduction into the $Ca(OH)_2$ solution. The question arose as to the possibility of error induced by this amount of water. Each of three solutions of $Ca(OH)_2$ was therefore passed through a newly prepared cotton-paper filter pad. The siphon was also washed with water between filtrations. The titration values of three successive 50-cc. portions of 50 cc. each are shown in Table I.

Table I—Influence of Moisture Content of Homemade Filter Cone upon $Ca(OH)_2$ Determinations

Solution	0.5 *N* Acid per 50 cc. of Successive Aliquots of Sugar Solution: 1st or pilot	2nd	3rd
	Cc.	*Cc.*	*Cc.*
1	2.2	2.40	2.40
2	6.4	7.05	7.05
3	8.1	8.92	8.92

It will be seen that these filter pads quickly reached equilibrium with the lime solution and that a dilution error applies only to the pilot aliquot. If a more concentrated solution were filtered first, it would not be permissible to use the filter again for a less concentrated solution, because equilibrium in the reverse direction is not so easily established. For example, after the filtration of a 95 per cent calcium sucrate solution, which had an absolute titration of 95 cc., four successive 50-cc. washings of pure water gave titrations of 6, 0.6, 0.2, 0.1 cc. of 0.02 *N* acid. A new filter for each determination also precludes influence of reactive residuals from prior determinations. A fresh filter pad is therefore prescribed for each determination.

Concordance between Filtrate Replications

Four characteristic limes—two high-magnesic and two high-calcic—were used for five replications on filtrates obtained from each sample by this device. The concordance found is shown in Table II.

Table II—Concordance of Individual Causticity Determinations by Proposed Modification of Sugar Method

Lime	1	2	3	4	5	Av.	Max. Variation
	%	%	%	%	%	%	%
1	40.2	40.1	40.2	40.1	40.0	40.1	0.2
4	68.3	68.2	68.2	68.0	67.8	68.1	0.5
6	94.3	94.2	94.1	94.3	94.5	94.3	0.4
8	91.5	91.8	91.8	91.5	91.5	91.6	0.3

Comparison of Results by Scaife and Proposed Method

The caustic values of the same limes were determined by means of the modified Scaife procedure, in duplicate or triplicate, by three analysts in three different laboratories. A comparison of the average of these results (Table III) with those of Table II shows the agreement between results by the two methods, indicating no superiority for one method over the other on the score of absolute values when commercial products of high purity were analyzed. However, if equal merit be accorded the two methods on the basis of accuracy, as adapted to high-purity products, and the influence of impurities and adaptation to lower grade products be disregarded for the time being, the two procedures may still be compared on the basis of speed, facility, and general adaptation to ordinary analytical routine.

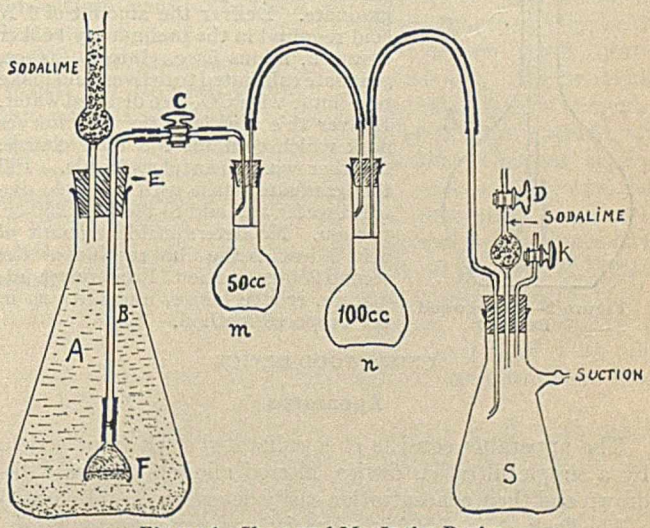


Figure 1—Shaw and MacIntire Device

Table III—Averages of Causticity Determinations Secured by Collaborators through Use of Modified Scaife Method

Lime	A	B	C	Av.	Max. Variation
	%	%	%	%	%
1	39.8	40.1	40.2	40.0	0.4
4	68.3	68.6	68.3	68.4	0.3
6	94.3	94.4	93.9	94.1	0.5
8	91.2	91.9	91.5	91.5	0.7

Advantages of the Filtration Procedure

(1) It is simpler and more expeditious.

(2) It is adapted to all forms of lime, eliminates delay incident to settling, insures a sharp end point, and affords replication aliquots.

(3) It requires only one charge and one manipulation to obtain both pilot and determination aliquots, whereas two complete manipulations are required by the Scaife method.

(4) The Scaife method is subject to the error incident to the delivery of a concentrated acid delivered from a large-bore buret. It requires two standard acids and consumes much more standard acid than is required by the modified procedure.

(5) The sugar method is adapted to the use of catch samples for CaO, whereas the modified Scaife makes use of such only at the expense of delay for extra computations between weighings and acid measurements.

(6) The modified Scaife requires heating and cooling and extra care to minimize exposure to atmospheric carbon dioxide, whereas the modified sugar method requires no heating or cooling and is carried out in a CO_2-free atmosphere.

(7) If glass beads are necessary to break up lumps, they may be introduced without volume correction.

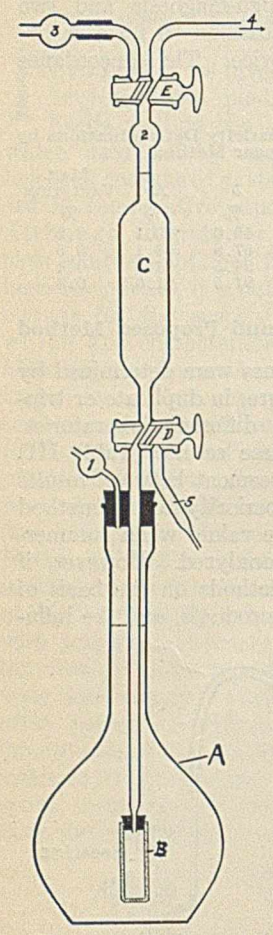


Figure 2—Underwood Device

Adaptation of Scaife Procedure to Filtration Device

If the principle of the Scaife method is preferred, the second stage of that procedure may be modified as follows to permit use of the filtration device, thereby eliminating interference of suspended $Mg(OH)_2$ and expediting manipulation.

Introduce the second charge into a 500-cc. Erlenmeyer flask instead of a graduate. Deliver the amount of 1 N acid required in the preliminary beaker titration, minus 5 cc., into a 250-cc. graduate calibrated to deliver, and make to volume with CO_2-free distilled water. Deliver this acid into the Erlenmeyer flask which contains the lime charge, together with clean glass beads. Fill the graduate again with CO_2-free distilled water and add to the first 250-cc. portion. No determinable amount of acid is lost as the film residue of the second 250-cc. portion. From this point, agitate, reduce lumps, and filter as in the proposed method.

UNDERWOOD DEVICE

Apparatus

The apparatus consists of a calibrated flask from which, by a simple filtration device, filtered aliquots can be withdrawn and their concentration easily determined. (Figure 2)

The flask, A, is of 500 ml. capacity and preferably of Pyrex, to reduce breakage. Its neck is enlarged above the graduation mark, as in the ordinary Kohlrausch form of sugar flask. This enlarged neck accommodates a two-hole rubber stopper which holds the filtering and measuring system in place, and also provides a means of access of air into A through bulb 1. The filtering medium, B, is attached directly to the longer tip of the modified pipet, C, by means of a 1-hole rubber stopper. The filter found to be most satisfactory for this purpose is a small alundum thimble[7] of sufficiently coarse texture and size to allow rapid filtration and effective removal of all suspended material. These thimbles are easily cleaned by a flow of hydrochloric acid and subsequent passage of water.

The filtered solution is measured in a 50-ml. delivery pipet, C. Suction is applied at 4, with the three-way stopcocks, D and E, in the positions indicated to draw the solution through filter B into the aliquot pipet. The bulb 2 allows an excess to be filtered for the filling of the outlet tube 5. The filtered solution is withdrawn from C by opening E to the air through 3 and turning D to deliver the filtrate through the outlet tube. The alkalinity of the solution is determined by neutralizing with 0.1 N hydrochloric acid, using phenolphthalein as indicator.

The bulbs 1 and 3 contain Ascarite or any other suitable carbon dioxide absorbing agent. An ordinary 50-ml. pipet may be used, but the same precautions against carbon dioxide contamination should be taken. Such an arrangement is not so satisfactory, inasmuch as the pipet must be taken from the system and the filter detached before the aliquot is obtained.

Procedure

Quicklime should be ground to pass a 100-mesh screen before a representative sample is taken, but no preliminary treatment is required for hydrated lime. Care should be taken to protect the oxide and hydroxide charges against carbon dioxide contamination. This applies to all parts of any procedure for the accurate analysis of these materials.

Weigh charges of approximately 1.4 grams and determine the exact weights by difference. Introduce the sample directly into the 500-ml. flask, A, and stopper immediately. Charges of quicklime should be completely slaked with a sufficient quantity of carbon dioxide–free water and brought to room temperature before addition of the sugar solution.

Prepare the sugar solution by dissolving pure, neutral cane sugar in carbon dioxide–free water. Add an amount containing about 25 grams of sugar to the freshly slaked quicklime or hydrated lime contained in A. The flask should be about three-quarters full and tightly stoppered. Shake this system (cold) intermittently for about 15 minutes. A definite number of glass beads may be introduced to expedite solution by the breaking up of any large particles, correction being made for their volume. After shaking bring the volume to the 500-ml. mark by the addition of more carbon dioxide–free water. After thoroughly mixing, the system is ready to be filtered.

Place the pipet with the alundum thimble in position as soon as the stopper in flask A is removed. Manipulate the stopcocks so that the filtered solution will be drawn into pipet C by suction at 4. Fill the pipet almost to the barrel of stopcock E. Turn stopcock D to the neutral position and adjust stopcock E to allow ingress of air through bulb 3. Permit the excess drawn into bulb 2 to fill outlet tube 5 and at the same time bring the contents to the calibration mark.

To determine the amount of 0.1 N hydrochloric acid necessary to neutralize the alkalinity of the filtered solution run the first 50 ml. into a small Erlenmeyer flask and titrate directly with the acid. Run subsequent aliquots into a slight excess of acid over that determined by this pilot run to minimize error from contamination by carbon dioxide. Back-titrate this excess of acid with 0.1 N sodium hydroxide to obtain the necessary value of acid equivalent to the calcium oxide content. Calculate the caustic value of the particular sample from the formula

$$\frac{A - B \times 1.4 \times 2}{W} = \text{per cent CaO}$$

where A = ml. 0.1 N hydrochloric acid, B = ml. sodium hydroxide, and W weight in grams of sample taken.

The filtration is generally so rapid that no time is lost between filtrations and titrations.

Adaptation to Scaife Procedure

This method of filtration may also be applied to the Scaife procedure to produce a clear aliquot for final titration. No other changes are necessary, although it is advisable to use a liter flask similar to the one just described.

[7] Thimbles, No. 13,471–Mixture R. A. 360, 50 mm. long, may be obtained from the Norton Company.

Effects of Certain Impurities upon the Determination of Causticity of Limes by Modifications of the Sugar and Scaife Methods[1]

W. M. Shaw and W. H. MacIntire

THE UNIVERSITY OF TENNESSEE AGRICULTURAL EXPERIMENT STATION, KNOXVILLE, TENN.

A study was made of the influence of the usual impurity components of caustic lime upon the accuracy of determinations of causticity values by the authors' modification of the sugar method and the modified Scaife procedure. Especial objectives were (*a*) to show the adaptation of a previously devised apparatus to the analysis of high-magnesic and slow-settling limes; (*b*) to determine the extent to which the different impurities may be expected to vitiate analytical results; and (*c*) to compare the two analytical procedures designated as tentative by the A. O. A. C. and A. S. T. M., respectively. The factors of magnesia, alone and in silicate combinations, interference of silica, neutral salt concentration of the titration system, and the formation of ternary compounds were considered.

THE modified sugar and modified Scaife methods are probably the most widely used for the determination of causticity of burnt and hydrated limes. Both methods have been adopted by the Association of Official Agricultural Chemists[2] as tentative for the determination of "calcium oxide in burnt and hydrated lime." The Scaife method is prescribed by the American Society for Testing Materials[3] as tentative for the determination of "available lime."

The term "available lime" has come into rather general usage in the industries. It is, however, somewhat indefinite and unscientific. It has one meaning when used with reference to soils and another in industrial practices. Calcium oxide, hydroxide, carbonate, and silicate are all of value when incorporated in soil, whereas only that amount of CaO which reacts under imposed conditions is considered as "available" in industrial usages. Haslam, Adams, and Kean[4] conclude that "for an availability test for lime to be of any great value the test must be based on the particular process in which the lime is to be used." Recently Blair[5] has stated, "available lime means nothing until it is known for what purpose it is available." It would seem that the uncombined CaO, or $Ca(OH)_2$, content of a commercial lime should be the basis on which the producer is entitled to compensation, irrespective of any lack of complete reaction arising from imperfect commercial utilization. The present authors, therefore, use the term "causticity," or "caustic value," in preference to "available lime."

Adaptability of Two Methods

It has been shown[6] that the sugar and modified Scaife methods give concordant determinations of the CaO-$Ca(OH)_2$ content of high-purity limes. Even the highest grade commercial lime, however, contains some extraneous materials. This is especially true of high-magnesic limes. The persistent suspension of finely divided magnesium hydroxide was a serious handicap to the accurate determination of causticity values by either method, in its original form. A study was undertaken to determine the extent to which this and any other factors influence the values given by the two methods. It became necessary, therefore, to eliminate all suspended material, with protection against carbon dioxide, immediately prior to final titrations. Two efficient and rapid filtration devices were perfected[7] in certain collaborative work. The homemade filtration device[7] reported by the present authors may be adapted to the modified Scaife procedure as well as to the sugar method. It was therefore used to obtain clear filtrates in the comparison of the systems produced by the two procedures. Unless otherwise stated, a constant charge of 1.4 grams was used in all the experiments.

Effect of Magnesia upon Causticity Determinations

Known amounts of "chemically pure" MgO were added to definite quantities of CaO. The two oxides were obtained by separate calcinations of "C. P." calcium and magnesium carbonates in an electric furnace for 5 hours at 950° C. No further loss in weight occurred when the oxides were again heated for 2 hours. The two oxides were then passed through a 120-mesh sieve, mixed, and bottled. Charges of lime and magnesia were weighed out separately to give the respective proportions of 10 and 40 per cent of MgO in CaO-MgO charges of 1.4 grams. The causticity of each charge of both materials, separately and in combination, was then determined. The results are given in Table I.

The value obtained for each mixture of the two oxides was greater than that for the corresponding charge of CaO alone, but in every case the actual determination for each CaO-MgO mixture was less than the summation of the two separately determined oxide values. The smaller amount of $Mg(OH)_2$ suspended alone in each of the two solvents was sufficient to produce a saturated solution, but the titration for the 40 per cent charge was about three times as great as that for the 10 per cent charge, in both sugar and aqueous calcium chloride solutions. These data indicated that the original magnesium carbonate contained some soluble alkali or alkali earth. The supposedly "C. P." $MgCO_3$ had been subjected to the usual oxalate procedure, and only a trace of CaO was obtained. The oxide was then extracted with boiling water and the alkalinity yielded by 10 grams in 500 cc. of water determined. The first water extraction gave a 47.5-cc. titration against 0.05 *N* acid. Three additional extractions of the moist oxide gave titrations of 5.5, 3.81, and 3.81 cc. The residue was again ignited and extracted three times. Considerable titratable alkalinity was developed by the second ignition, as shown by 0.05 *N* titrations of 29.0, 9.0, and 4.0 cc. A third ignition and two extractions gave titrations of 14.0 and 3.8 cc. Equilibrium was apparently

[1] Received October 24, 1927.

[2] Assocn. Official Agr. Chem., Methods, p. 35 (1925).

[3] *Proc. Am. Soc. Testing Materials*, **26**, 779 (1926).

[4] *Ind. Eng. Chem.*, **18**, 19 (1926).

[5] *Ibid.*, **18**, 389 (1926).

[6] Shaw, *J. Assocn. Official Agr. Chem.*, **9**, 141 (1926).

[7] Shaw, MacIntire, and Underwood, *Ind. Eng. Chem.*, **20**, 312 (1928).

established after the fourth ignition and extraction. The extracts from each of seven successive ignitions were combined and analyzed for calcium, by the oxalate method. This analysis gave a CaO content of 0.70 per cent, as against the 0.001 per cent given on the label. An occurrence of 0.70 per cent was also obtained by the use of the modified Stolberg method,[8] through the courtesy of G. E. F. Lundell, of the Bureau of Standards.

impurities being responsible for this discrepancy will be considered in succeeding paragraphs.

Effect of Silica upon Causticity Determinations

Silica is found as an impurity combined, or uncombined, in calcined products. The influence of this impurity was therefore studied by adding silica to give 10 and 30 per cent occurrences in the lime-silica mixture. The silica gel was made by the procedure of Holmes and Anderson.[9] The lime and silica were intimately mixed by repeated fractional grindings in a mortar and then passed through a 120-mesh sieve. These mixtures were then calcined in an electric furnace for 5 hours at 950° C. The calcined mixtures were again passed through a 120-mesh sieve and intimately mixed. The causticity values of filtrates obtained by both the sugar and the Scaife method are given in Table III.

Table I—Effect of Added Magnesia upon Causticity Values[a]

Composition of Charge	Modified Sugar Method			Modified Scaife Method		
	1	2	Av.	1	2	Av.
	%	%	%	%	%	%
10 PER CENT MAGNESIA						
A—Lime alone, 90% charge	88.65	88.65	88.65	88.43	88.43	88.43
B—Magnesia alone, 10% charge	0.35	0.35	0.35	0.30	0.33	0.32
C—Summation of A and B	89.00	89.00	89.00	88.73	88.76	88.75
D—Actual determination	88.75	88.75	88.75	88.50	88.25	88.38
Variation of determined value D from calculated value C	−0.25	−0.25	−0.25	−0.23	−0.51	−0.37
40 PER CENT MAGNESIA						
E—Lime alone, 60% charge	59.10	59.10	59.10	58.95	58.95	58.95
F—Magnesia alone, 40% charge	1.10	1.10	1.10	0.85	0.85	0.85
G—Summation of E and F	60.20	60.20	60.20	59.80	59.80	59.80
H—Actual determination	59.00	59.00	59.00	59.25	59.50	59.38
Variation of determined value H from calculated value G	−1.20	−1.20	−1.20	−0.55	−0.30	−0.42

[a] (Expressed as per cent CaO equivalent.) To afford uniform comparisons under experimental conditions the CaO equivalent was calculated from the total titration equivalent of the 500 ml. of solution in each instance and referred to the standard charge of 1.4 grams, regardless of the actual quantities used in the additions. Thus the 0.35 per cent CaO equivalent for a water extraction was derived from a titration of 0.70 ml. of 0.05 N acid per 100 ml. of the extract: $\frac{0.0014 \times 0.7 \times 5 \times 100}{1.4} = 0.35$.

The experiment was then repeated with the pure MgO thus prepared from the "C. P." hydrated carbonate. Table II shows the same titration value for the 10 and the 40 per cent charges of purified MgO. These data also show the same value for the lime alone, lime plus 10 per cent of MgO, and lime plus 40 per cent of MgO by the filtered sugar solution, even though the causticity value found for MgO alone by the sugar method was three times as great as that found by the modified Scaife method. Nevertheless, the causticity value registered by the Scaife procedure for the CaO-MgO charge which contained 10 per cent MgO was considerably less than that obtained for CaO alone. The disparity registered by the 40 per cent MgO inclusion was still greater. It therefore seems justifiable to conclude that the causticity value of CaO in high-magnesic limes is more accurately determined by the modified sugar method than by the Scaife procedure. The possibility of silica

These data show that a decided reduction in causticity resulted from the calcination of the lime-silica mixture. The reduction in alkalinity caused by the 30 per cent addition was 2.13 times that caused by the 10 per cent addition when measured by the modified sugar method. When measured by the modified Scaife method a corresponding ratio of 2.29 to 1 was obtained. This, of course, must be ascribed to silicates formed by reaction of a part of the added silica with CaO during calcination and with $Ca(OH)_2$ during the subse-

[8] Hillebrand, *U. S. Geol. Survey, Bull.* **700**, p. 143 (1919).

[9] *Ind. Eng. Chem.*, **17**, 280 (1925).

Table II—Effect of Further Purified C. P. Magnesia upon Causticity Values

Composition of Charge	Modified Sugar Method			Modified Scaife Method		
	1	2	Av.	1	2	Av.
	%	%	%	%	%	%
A—Lime alone, 1.40 grams	99.25	99.25	99.25	99.00	99.00	99.00
B—MgO alone, 0.14 gram	1.10	1.10	1.10	0.35	0.35	0.35
C—MgO alone, 0.56 gram	1.10	1.10	1.10	0.35	0.35	0.35
D—Lime, 1.4 grams + MgO, 0.14 gram	99.25	99.25	99.25	98.60	98.60	98.60
E—Lime, 1.4 grams + Mg, 0.56 gram	99.25	99.25	99.25	97.90	97.90	97.90
Variation of determined value D from summation of A and B	0.00	0.00	0.00	−0.40	−0.40	−0.40
Variation of determined value E from summation of A and C	0.00	0.00	0.00	−1.10	−1.10	−1.10

Table III—Effect of Silica Additions Followed by Calcination upon Causticity Values

Composition of Charge	Modified Sugar Method			Modified Scaife Method		
	1	2	Av.	1	2	Av.
	%	%	%	%	%	%
A—Lime alone, 90% of charge	88.65	88.65	88.65	88.43	88.43	88.43
B—Silica alone, 10% of charge	0.00	0.00	0.00	0.00	0.00	0.00
C—Summation of A and B	88.65	88.65	88.65	88.43	88.43	88.43
D—Actual determination	82.05	82.05	82.05	83.75	83.25	83.50
Variation of determined value D from calculated value C	−6.60	−6.60	−6.60	−4.68	−5.18	−4.93
E—Lime alone, 70% of charge	68.95	68.95	68.95	68.78	68.78	68.78
F—Silica alone, 30% of charge	0.00	0.00	0.00	0.00	0.00	0.00
G—Summation of E and F	68.95	68.95	68.95	68.78	68.78	68.78
H—Actual determination	54.90	54.90	54.90	57.50	57.50	57.50
Variation of determined value H from calculated value G	−14.05	−14.05	−14.05	−11.28	−11.28	−11.28

quent suspensions. It is evident that the full CaO-SiO_2 reaction registered by the differential titrations did not take place during calcination; but the extent of any reaction between $Ca(OH)_2$ and that part of the silica which did not react with CaO during calcination was not definitely established. Using the sugar method as an index in the larger proportion of 9 of CaO to 1 of SiO_2, the full CaO-SiO_2 reaction during calcination and suspension had accounted for 71 per cent of the added silica, as against 53 per cent by the modified Scaife method. The outstanding feature of this experiment is the consistently diverging difference between the sugar and the Scaife results with increase in quantities of silica in the lime-silica mixtures. In each case the sugar method shows a greater decrease in the causticity found as a result of the silica addition. The difference between the two methods was about 1.6 per cent CaO equivalence for the 10 per cent addition, whereas the corresponding difference for the 30 per cent addition is about 2.8 per cent. These differences may not be accounted for by assuming that the calcium silicate calcination product is less soluble in the lime-sugar solution than in the $CaCl_2$-$Ca(OH)_2$-H_2O system. The opportunity for further combination between $Ca(OH)_2$ and the uncombined silica residuals mentioned above must be taken into consideration. The results show that the calcium silicate impurities register as $Ca(OH)_2$ to a greater extent by the modified Scaife than by the modified sugar procedure.

Effect of Calcined Silica Gel upon Causticity of Aqueous-Sugar and $CaCl_2$-$Ca(OH)_2$-H_2O Systems

Several charges of a high-grade lime were completely dissolved in 5 per cent sugar solution and several others were partially dissolved in varying quantities of HCl, to obtain $CaCl_2$-$Ca(OH)_2$-H_2O systems of varying alkalinity. The solutions were all filtered free of suspended matter and the alkalinities of 50-cc. aliquots determined by 0.05 *N* acid. A 0.7-gram charge of calcined silica gel was then introduced into each filtrate. Each suspension was then shaken for 5 minutes, permitted to stand for 1 hour and for 18 hours, refiltered, and alkalinities again determined. The data of Table IV indicate appreciable reaction between the $Ca(OH)_2$ solution and the suspended ignited silica. It is interesting to note so extensive a reaction between the ignited silica gel and the approximately 0.0025 *N* $Ca(OH)_2$ solution obtained in simulating the conditions of the modified Scaife procedure. The speed of the lime-silica reaction increased with the concentration of $Ca(OH)_2$, and for dilute solutions of $Ca(OH)_2$ it had apparently reached equilibrium during the first hour or two. With $Ca(OH)_2$ concentrations of 0.01 normality, or greater, the reaction was more extended. With a $Ca(OH)_2$ concentration of approximately 0.01 normality the speed of reaction with the silica was practically the same as that determined for the calcium sucrate solution of tenfold alkalinity. This $CaCl_2$-$Ca(OH)_2$ concentration corresponds to a solution of high-grade lime by the Scaife method where the charge was almost neutralized by an addition of normal acid—5 cc. less than that required for complete neutralization of $Ca(OH)_2$—as determined by the preliminary determination. If these results are taken as criteria, it may be concluded that where the Scaife procedure is followed strictly as to incomplete neutralization of the charge there is to be expected no great difference between the results by that method and those by the sugar method, in so far as the interference of ignited silica is concerned. Should the residual alkalinity by the Scaife method be reduced beyond the prescribed normality of 0.01, silica impurities may be expected to cause appreciable differences in the results obtained by the two methods. These data emphasize the importance of making the titrations as soon as possible after solution is effected and the importance of filtration to admit of so doing, as contrasted to the unpermissible wait required to secure a clear solution by settling.

Table IV—Reactivity of Calcined Silica Gel (0.7 gram) in 400 cc. of $CaCl_2$-$Ca(OH)_2$ Solutions of Varying Concentrations

Expt.	1.4-Gram Lime Charge Unneutralized by HCl before Silica Gel Addition	Titration of 50 cc. Using 0.05 *N* Acid		Absorption of CaO by SiO_2 Gel	
		Before addition	After 1 hour	After 1 hour	After 18 hours
	%	*Cc.*	*Cc.*	%	%
1	2.5	2.70	0.95	1.75	1.85
2	5.0	4.90	1.50	2.40	2.50
3	10.0	9.80	5.70	4.10	5.70
4	20.0	18.60	12.20[a]	..	6.40
5	97.6[b]	97.60	93.70	3.90	6.00

[a] After 18 hours' standing.
[b] Calcium sucrate control.

Effect of Calcination of Silica-Magnesia-Lime Mixtures, as Indicated by Causticity Determinations

Calcination of high-magnesic limes affords opportunity for CaO-MgO-SiO_2 reactions. The conditions of such a calcination were simulated to show their effects upon causticity values recorded by the two methods. Silica gel, magnesia, and lime were mixed to give SiO_2-MgO-CaO proportions of 10, 40, and 50 per cent, respectively. The mixture was calcined, ground to fine powder, and sifted through a 120-mesh sieve, as in the preceding experiment. The causticity of the mixture and that of each component was then determined separately by both methods. The results are incorporated in Table V.

In spite of the large excess of magnesia over silica during calcination, the reaction between these two oxides was not complete. A part of the silica evidently combined with lime in both systems, as indicated by the reductions in causticity. The variable influence of impurities during the manipulations of the sugar and Scaife methods is again apparent. A decrease of 3.40 per cent in causticity was registered by the sugar method, as against 2.1 per cent by the Scaife method. The magnesium silicate fusion product runs parallel to the previously mentioned calcium silicate in showing a smaller solubility and causticity value by the sucrose solution than that recorded by the system created when carrying out the Scaife procedure.

Table V—Effect of Silica and Magnesia Additions Followed by Calcination upon Causticity Values

Composition of Charge	Modified Sugar Method			Modified Scaife Method		
	1	2	Av.	1	2	Av.
	%	%	%	%	%	%
A—Lime alone, 50% of charge	49.25	49.25	49.25	49.13	49.13	49.13
B—Magnesia alone, 40% of charge	1.10	1.10	1.10	0.85	0.85	0.85
C—Silica alone, 10% of charge	0.00	0.00	0.00	0.00	0.00	0.00
D—Summation of A and B and C	50.35	50.35	50.35	49.98	49.98	49.98
E—Actual determination	46.90	47.00	46.95	47.75	48.00	47.88
Variation of determined value E from calculated value D	−3.45	−3.35	−3.40	−2.23	−1.98	−2.10

Effect of Calcination of a Lime-Serpentine Mixture, as Indicated by Causticity Determinations

In balancing the CaO-MgO-CO_2 content of certain dolomites, it has been found necessary to assume the presence of magnesium silicate. It seemed desirable to determine what effect would follow from the ignition of such dolomites. Serpentine ($H_4Mg_3Si_2O_9$) was powdered and washed. A mixture of 10 per cent of this silicate and 90 per cent of lime was calcined, ground, and sifted through a 120-mesh sieve, as in the preceding experiments. The washed and ignited serpentine gave no determinable alkalinity when suspended alone in a 5 per cent sugar solution, nor by a Scaife-method control. Table VI shows the causticity value of the calcined CaO-serpentine mixture by both methods, as compared with that found for a corresponding charge of lime without serpentine. The causticity decreases of 2.05 per cent and 0.68 per cent by the modified sugar method and the modified Scaife method, respectively, may be attributed to the interchange between CaO and the magnesia of magnesium silicate during the period of ignition.

Table VI—Effect of Additions of Magnesium Silicate Followed by Calcination upon Causticity Values

Composition of Charge	Modified Sugar Method			Modified Scaife Method		
	1	2	Av.	1	2	Av.
	%	%	%	%	%	%
A—Lime alone, 90%	88.65	88.65	88.65	88.43	88.43	88.43
B—Serpentine alone, 10%	0.00	0.00	0.00	0.00	0.00	0.00
C—Actual determination	88.65	88.65	88.65	88.43	88.43	88.43
D—Summation of A and B	86.50	86.50	86.50	87.75	87.75	87.75
Variation of actual determination D from calculated value C	−2.05	−2.05	−2.05	−0.68	−0.68	−0.68

These two experiments establish the fact that the presence of a large excess of magnesia over SiO_2 does not insure a complete tie-up between silica and magnesia during the ignition of CaO-MgO-SiO_2 mixtures, and the further fact that both calcium and magnesium silicates are formed when a dolomitic lime containing silica is calcined.

Effect of Calcium Silicate

Calcium silicate may result from reactions between silica impurities and CaO during the process of calcination and may also be formed readily when finely divided silica is suspended in aqueous solutions of $Ca(OH)_2$, hence it was essential to determine the effect of calcium silicate upon the procedures followed in the two methods. Calcium silicate was prepared by the addition of a solution of calcium chloride to one of sodium silicate. The silicate was washed, dried, and ignited. Two charges, 0.070 and 0.140 gram, were shaken with 500 cc. of each of the following media: water, 5 per cent aqueous sugar solution, 0.5 per cent and 1.0 per cent $CaCl_2$ aqueous solutions, and the same $CaCl_2$ solutions plus sufficient calcium hydroxide to give an alkalinity of 0.095 N. The systems were shaken 1 hour and then allowed to stand for 24 hours. Aliquots of 100 cc. of the clear solutions were then titrated with 0.05 N HCl and the alkalinities expressed as per cent of the lime charge, as in Table VII.

Table VII—Solubility of Prepared and Ignited $CaSiO_3$ in Aqueous, $CaCl_2$, and $CaCl_2$-$Ca(OH)_2$ Systems

(Expressed as CaO in a hypothetical charge of 1.4 grams)

$CaSiO_3$	In H_2O	In 5% Sugar Solution	In 1% $CaCl_2$	In 0.5% $CaCl_2$	0.0095 N $Ca(OH)_2$ Containing:	
					1.0% $CaCl_2$	0.5% $CaCl_2$
Gram	%	%	%	%	%	%
None	...	...	...	...	9.4	9.5
0.070	0.4	0.40	0.3	0.30	8.4	8.8
0.140	0.5	0.45	0.4	0.35	7.7	8.3

It is apparent that the solubility of $CaSiO_3$ in water alone is almost identical with that found for water containing 5 per cent of sugar. The addition of both 1.0 and 0.5 per cent $CaCl_2$ considerably depressed the solubility of $CaSiO_3$. The $Ca(OH)_2$ in the $CaCl_2$ solution resulted in practically complete insolubility of the $CaSiO_3$ addition. Conversely, the $CaSiO_3$ addition caused a diminution in the original $Ca(OH)_2$ concentration. The chemistry of this phenomenon is of sufficient importance to warrant further investigation. It is apparent that not only the concentration of $Ca(OH)_2$, but also the total concentration of calcium ions, is a factor in the repression of the alkalinity induced by the $CaSiO_3$.

The experiment with $CaSiO_3$ was repeated with the lime of Table I, using both the modified sugar and modified Scaife methods. The usual time of contact, 20 to 30 minutes, was allowed. The results are given in Table VIII.

Table VIII—Effect of Additions of Precipitated and Ignited $CaSiO_3$ upon Causticity Determinations

Composition of Charge	Modified Sugar Method			Modified Scaife Method		
	1	2	Av.	1	2	Av.
	%	%	%	%	%	%
Lime only	91.8	91.5	91.7	91.6	91.8	91.7
Lime + 5% $CaSiO_3$	91.8	92.3	92.0	91.8	91.5	91.7
Lime + 10% $CaSiO_3$	91.3	91.5	91.4	91.5	91.5	91.5

It is evident that neither the 5 nor the 10 per cent addition of $CaSiO_3$ had any effect upon the CaO value obtained by either of the two methods. These results are in apparent contradiction to those of Table VII, which were obtained by the addition of the $CaSiO_3$ to solutions of $CaCl_2$-$Ca(OH)_2$. It was assumed that the difference in time of contact was responsible for this apparent discrepancy, since in the experiment with the pure $Ca(OH)_2$ solutions the contact period was 24 hours, whereas with the lime charges it was only 30 minutes. The residual lime solutions were therefore again titrated after 24 hours, and it was found that the solid-phase $CaSiO_3$ had brought about a decreased concentration of $Ca(OH)_2$ during the longer period. This proved true for both the modified sugar and modified Scaife methods. The resultant decreases in values were from 1.0 to 1.5 per cent of the charge. It may therefore be concluded that the presence of $CaSiO_3$ in the lime sample has a tendency to produce a minus error by both methods. When contact extends for only 20 to 30 minutes the error attributable to calcium silicate is negligible. Since the magnitude of this error depends upon the period of contact, further emphasis as to the desirability of insuring rapidity through filtration is thus obtained.

Because of the decided reduction in the $Ca(OH)_2$ concentration caused by the presence of added prepared calcium silicate during an extended period, there arises the question of the actual composition of the calcium silicate. The phenomenon may be due to: (*a*) the absorptive properties of the pulverulent $CaSiO_3$; (*b*) reaction between $Ca(OH)_2$ and any slight excess of uncombined SiO_2 in the prepared product; or (*c*) the formation of dicalcium silicate upon standing.

Influence of Impurities of Al_2O_3, Fe_2O_3, and $CaSO_4$ upon Causticity Determinations

Alumina, ferric oxide, and calcium sulfate are present in varying quantities in all limes. It has been shown[10] that after $Ca(OH)_2$ has reacted with Al_2O_3 and Fe_2O_3 to form $3CaO(Al_2O_3)$ and $3CaO(Fe_2O_3)$, respectively, further reaction with $CaSO_4$ ensues to form $3CaO.Al_2O_3.3CaSO_4.33H_2O$ and $3CaO.Fe_2O_3.3CaSO_4.nH_2O$. The taking up of $CaSO_4$ to form the ternary systems does not affect the amount of $Ca(OH)_2$ fixed, but it produces a crystalate which has properties different from those of calcium aluminate. The conditions imposed were not the same, however, as those encountered in carrying out the determination of caustic values by either of the methods.

Some reaction undoubtedly occurs between CaO and Al_2O_3 during calcination of limestone, and it is very probable that most, if not all, of the alumina content of a commercial lime will have combined with the excess of CaO during that process.

Aluminates so formed are stable in concentrated solutions of $Ca(OH)_2$, but they readily hydrolyze in concentrations of less than 0.01 normality. Consideration was therefore given to the effect produced by such compounds while carrying out the two analytical procedures with both high-calcic and high-magnesic limes.

Table IX—Effect of Additions of Al_2O_3 upon Causticity Determinations

Sample	Al_2O_3 Added	Modified Sugar Method		Modified Scaife Filtrates	
		Found	Decrease	Found	Decrease
	%	%	%	%	%
High-calcic	None	93.9	...	93.9	...
	2.5	93.2	0.7	93.3	0.6
	5.0	92.2	1.7	92.8	1.1
	10.0	91.2	2.7	92.0	1.9
High-magnesic	None	54.2	...	54.4	...
	2.5	52.8	1.4	53.9	0.5
	5.0	52.0	2.2	53.4	1.0
	10.0	51.2	3.0	52.7	1.7

The vitiating influence exerted by 2.5, 5.0, and 10.0 per cent additions of Al_2O_3 upon causticity values is shown in Table IX. A definite decrease for each addition was registered for each type of lime by both methods. The decrease caused by the 2.5 per cent Al_2O_3 addition to the high-calcic lime was 0.7 per cent and 0.6 per cent for the modified sugar and modified Scaife methods, respectively. Corresponding decreases of 1.7 and 1.1 per cent were obtained with the same lime by the two methods when the Al_2O_3 addition was 5 per cent of the charge, whereas still further respective decreases of 2.7 and 1.9 per cent were caused by the 10 per cent Al_2O_3 additions. Similar diminutions in causticity were also obtained from the high-magnesic lime by both procedures. An Al_2O_3 occurrence of 2.5 per cent is, however, more than would be expected in commercial limes, and the results from the two large additions may therefore be considered mainly as of academic interest. It is, nevertheless, plain that the full potential causticity of a lime having a high content of Al_2O_3 cannot be determined accurately by either of the two methods. It is also evident that the killing off of the larger part of the $Ca(OH)_2$ before filtration, as in the Scaife method, results in a diminished reaction between calcium hydroxide and alumina. This was true for both types of lime.

Effect of Calcium Aluminate Present before Analysis

It has been pointed out that calcium aluminate may be present in the original lime as a result of calcination reactions. It may be that the CaO so combined is of value under some conditions, but the object of the methods proposed is the determination of uncombined CaO. The effect of calcium aluminate *per se* upon the two analytical procedures was therefore studied by means of 2, 5, and 10 per cent additions.

The results of Table X show that some causticity is derived from the hydrolysis of the added calcium aluminate. It further appears that the increase in causticity found by the sugar method is in proportion to the amounts of calcium aluminate added, whereas with the Scaife method the difference between the increase from the 2 and the 10 per cent additions was only 0.3 per cent. Again, however, the increases in causticity found by the two methods are practically the same for the 2 per cent addition, which would represent the maximum calcium aluminate occurrence for a commercial product.

Table X—Effect of Additions of Calcium Aluminate upon Causticity Determinations

Combination	Modified Sugar Method				Modified Scaife Method			
	1	2	Av.	Increase	1	2	Av.	Increase
	%	%	%	%	%	%	%	%
Lime alone	91.8	91.5	91.7	...	91.6	91.8	91.7	...
Lime + 2% $CaAl_2O_4$	92.5	92.4	92.5	0.8	92.8	92.0	92.4	0.7
Lime + 5% $CaAl_2O_4$	...	93.8	93.8	2.1	92.7	92.5	92.6	0.9
Lime + 10% $CaAl_2O_4$	...	96.3	96.3	4.6	93.0	92.4	92.7	1.0

The foregoing results indicate that the added calcium aluminate underwent considerable hydrolysis in the two analytical procedures. The solubility of the added calcium aluminate was, therefore, determined for (*a*) aqueous, (*b*) 5 per cent sugar, (*c*) neutral $CaCl_2$ solutions, and (*d*) $CaCl_2$ solutions containing $Ca(OH)_2$ to the extent of 0.0095 normality—a value corresponding to that of the Scaife method after the preliminary addition of hydrochloric acid.

The results in Table XI show that the solubility of the aluminate is in approximate proportion to the charge, for the pure-water solution, the 5 per cent sugar solution, and the neutral $CaCl_2$ solution. There was only a slight hydrolysis in either the 0.5 or the 1.0 per cent $CaCl_2$ solution in 0.0095 *N* $Ca(OH)_2$ and no marked increase in the hydrolysis was induced by doubling the amount of calcium aluminate. This indicates a repression of hydrolysis of the aluminate and a diminished dissociation of the hydroxide as a result of the excess of calcium ions in the chloride and hydroxide combination.

Table XI—Effect of Certain Concentrations of $Ca(OH)_2$ and $CaCl_2$ upon the Solubility of Calcium Aluminate, in Terms of CaO

$CaAl_2O_4$ Added	In Water	In 5% Sugar Solution	Aqueous Solution		In 0.0095 *N* $Ca(OH)_2$[c]	
			Per cent $CaCl_2$ in solvent			
			0.5	1.0	0.5	1.0
Gram	%	%	%	%	%	%
None	0.0	0.0	0.0	0.0	9.5	9.3
0.070[a]	2.8	2.8	2.0	1.5	9.8	9.7
0.140[b]	5.3	5.5	3.3	2.5	10.0	9.7

[a] 5 per cent of charge.
[b] 10 per cent of charge.
[c] Simulating usual alkalinity and $CaCl_2$ content of solution at end of Scaife method titrations of high- and low-calcic limes.

Correction

In my article entitled "Bromocresol Green as an Indicator in the Manufacture of Grain-Curd Casein" [*Ind. Eng. Chem.*, **20**, 15, (1928)] the next to the last line in the second paragraph should read "(0.05 per cent solution)" instead of "(0.5 per cent solution)."

ANNE G. BENTON

[10] MacIntire and Shaw, *Soil Science*, **19**, 125 (1925).

Application of the U. S. P. Methanol Test[1]

Wm. L. O. Whaley

PROHIBITION LABORATORY, U. S. INTERNAL REVENUE SERVICE, NEW ORLEANS, LA.

Observations of the result of applying the U. S. Pharmacopeia method[2] for detection of methanol to distillates from flavoring extracts, perfumes, etc., collected for the purpose of determining the alcoholic strength of these substances

THE purpose of this paper is to point out the result of applying this test for methanol to some preparations in daily use, to show the effect of concentration of alcohol upon the sensitiveness of the reaction, and to point out the necessity of using caution in interpreting such tests when applied to material other than that upon which the method was worked out and commended. The method as given is to be applied to alcohol. If it is desired to use this test on other material, it must be modified to meet the new conditions.

These observations are the outcome of experimental work to discover if certain flavors and so-called medicinal preparations, brought to our attention by the extremely favorable price quoted on the lots in question, were compounded from cleaned or purified denatured alcohols.

Application to Fluid Extract of Ginger

To determine the alcoholic strength of fluid extract of ginger a 10-cc. sample was diluted to 100 cc.[3] and approximately 100 cc. of distillate were collected and made exactly to the 100-cc. mark. Both the specific gravity and the refractive index were determined on a number of these distillates, and the alcoholic percentages corresponding to these two values looked up from suitable tables. There was usually a wide discrepancy between these two values, and in consequence a number of these distillates have been submitted to tests for methanol.

Several distillates from fluid extract of ginger, when tested for the presence of methanol, gave a faint bluish violet coloration with the modified Schiff reagent. Three laboratories tested the same sample. One reported methanol present, and another reported methanol absent; so that the writer was in doubt as to whether this color was due to methanol or to some other normal constituent of the ginger.

Ten cubic centimeters of the ginger were then diluted to 50 cc. with distilled water, made alkaline with 0.1 *N* caustic soda, treated with magnesium oxide and fuller's earth, and filtered. The filtrate and precipitate were washed till there resulted a volume of 100 cc. filtrate and washings. Distillate from this material gave a faint positive reaction.

Some of the straight ginger extract was diluted to contain 5 per cent alcohol, and subjected to the test. A deep green color appeared. Another portion was diluted with 50 per cent alcohol, saturated with sodium chloride, and extracted with ether. The ether extract gave no color reaction with the modified Schiff reagent after oxidation, but the salt water–alcohol portion gave a bluish green color on testing for methanol in alcohol.

Comparison of the colorations just described with those under similar conditions using alcohol alone, alcohol with methanol, and ginger extract with added methanol, led to the conclusion that in this instance the color had been caused by some constituent of the preparation. Ginger ale concentrates have shown a similar development of a violet tinge upon being subjected to the test.

Sensitiveness and Effect of Alcoholic Concentration

So great a tendency to develop a coloration readily confused with the formaldehyde reaction in the methanol test was shown by such a large number of the samples investigated that the following procedure was carried out to get some limits for the methanol test:

In testing a sample of alcohol under normal conditions one will find 2 per cent methanol or find it absent. However, we suspected that in our samples every effort had been made to remove the methanol, if ever present, and accordingly it was desirable to know the smallest amounts that could be shown, as well as the intensity of the color under various concentrations.

Two concentrations, listed in Table I as *A* and *B*, show the effect of the concentration of total alcohols as well as the amounts of methanol that may be detected. *A* was prepared by measuring 1 cc. of chemically pure methanol, 4 cc. of refined absolute ethanol, and distilled water to make 100 cc.; *B* was prepared from 1 cc. of methanol as in *A*, but 49 cc. of ethanol and distilled water to make 100 cc. Thus, while the content of methanol is the same in both cases, the total alcohol concentration in *B* is just ten times that of *A*. A solution of 5 per cent ethanol was also prepared by measuring 5 cc. of absolute alcohol and making up to 100 cc. with distilled water, to be used in making the final volumes to 5 cc. as called for in the test.

Solution *A* has 5 per cent total alcohols and 1 per cent methanol.
Solution *B* has 50 per cent total alcohols and 1 per cent methanol.
The 5 per cent ethyl alcohol solution we will for convenience call *C*.

Since the tests were made by taking the shown amounts of *C* and using in parallel series with both *A* and *B*, we have a series with not only steadily increasing amounts of methanol but in the case of *B* a corresponding increase and also an increase in total alcohol concentration.

Table I—Sensitiveness of Methanol Test

No.	Solution *C*	Solutions *A* and *B*	Methanol Indication and Time Required: Solution *A*		Solution *B*	
	Cc.	*Cc.*				
1	0.5	4.5	Neg. 30 min.	? 2 hours	Neg. 30 min.	Neg. 2 hours
2	1.0	4.0	Neg. 30 min.	Pos. 2 hours		
3	1.5	3.5	? 30 min.	Pos. 2 hours		
4	2.0	3.0	Pos. 30 min.	Pos. 2 hours		
5	2.5	2.5	Pos. 15 min.	Pos. 2 hours		
6	None	5.0	Pos. 5 min.	Pos. 4 days		

Since *A* only had 1 per cent methanol in No. 1, the methanol concentration in the solution tested was only one-tenth of the original or 0.1 per cent; in No. 2, one-fifth the original or 0.2 per cent, etc. We see that with the specified concentration of total alcohols one-half of 1 per cent will in a reasonable time give a positive reaction. With 1 per cent the color will hold for 4 days (possibly much longer). In

[1] Received September 16, 1927. Published by permission of the head of the Technical Division of the Bureau of Prohibition.

[2] U. S. Pharmacopeia X, p. 39.

[3] Method of the Chemical Division of the Bureau of Prohibition, Washington, D. C.

case of *B*, even in the sixth test, where there was 1 per cent methanol but 50 per cent total alcohols, no color had developed within 2 hours. A faint color did appear after about 4 hours, but it was gone the following morning. In the *B* series the influence of increasing the amount of methanol was entirely offset by the increase in total alcohols.

Modifications of the Test

In order to test the smallest concentrations of methanol that could be detected, two modifications were made in the test as given in the U. S. Pharmacopeia. For convenience the methods have been designated as follows: No. 1, the original from the Pharmacopeia; No. 2, exactly the same except that the materials were first distilled (25 cc. in 100) and distillates used; No. 3, 50 cc. of the solution diluted to about 200 cc., placed in a distilling apparatus, and oxidized at room temperature for 10 to 15 minutes with 5 cc. of 85 per cent phosphoric acid and 10 cc. of 3 per cent potassium permanganate solution. Should any pink color remain at the end of the time, it is discharged by sufficient 10 per cent oxalic acid solution, and then a flame applied and the distillate collected in a tube containing the modified Schiff reagent.

Note—It was found necessary to remove the oxidizing influence of the permanganate prior to heating; otherwise pure alcohol is so much attacked as to cause the similar color of acetaldehyde.

In the test shown in Table II the 5 per cent ethanol previously described was used with sufficient of the other ingredient to bring the total concentration to the 5 per cent, in the amounts indicated.

Table II—Results with Modified Procedure

Added Ingredient		5% Ethanol	Observed Reaction for Methanol after 10 Minutes		
			No. 1	No. 2	No. 3
	Cc.	*Cc.*			
Nothing		5.0	Neg.	Neg.	? (fleeting)
Methanol[a]	0.5	4.5	Pos.	Pos.	Pos.
Glycerol	0.5	4.5	Pos.	Neg.	Pos.
Acetaldehyde	0.5	4.5	Neg.	Neg.	Pos.[b]
Acetaldehyde	1.0	4.0	? [b]	? [b]	Pos.[b]
Sucrose	0.5 g.	4.5 and 0.5 water	Neg.	Neg.	Pos. (faint)
Invert sugar	0.5 g.	4.5 and 0.5 water	? (faint)	Neg.	Pos.
Methanol[a]	0.5	4.5 of 50% alcohol	Neg.	Pos.	Pos.

[a] Methanol 5 cc. and distilled water to make total volume of 100 cc.
[b] Fleeting; acetaldehyde when in sufficient concentration produces a purple color closely approximating in shade that of the formaldehyde compound. It appears under these conditions much more rapidly than does the formaldehyde color and is not permanent, always disappearing in from 5 to 10 minutes.

In the first and last sets we again find the same amount of methanol failing to be shown when the total alcohol strength has been increased. The preliminary distillation is therefore the procedure that in most cases must be used. This is undoubtedly true of practically all the substances under investigation in the next series of results.

Color Tests

The phenomenon of giving a color reaction similar to that of methanol by distillates from fluid extract of ginger has already been noted. It was thought of interest to examine a larger number of preparations under conditions of the methanol test and to note the resulting color.

The distillates obtained for the estimation of the alcoholic strength were used. They were distilled from the material made to dilutions according to the supposed alcoholic strength from the declared formulas, and after determination of the alcohol percentage they were diluted to correspond to the specified 5 per cent of the test. The resulting colors are described as closely as names could be selected for the colors and shades observed. (Table III)

No attempt was made to apply the tests on the raw material, consequently tests No. 2 and No. 3 are the only ones to report.

Discussion

The modification of the U. S. P. procedure of testing for methanol, mentioned in this article as method No. 3, was undertaken in order to increase the sensitiveness of the test. However, it appears to give more interference from substances other than methanol than does the usual procedure. Thus oxidation and subsequent heating seem to cause decomposition in some instances, as in the case of sugars. Taggart[4] has shown that in high concentrations of sugars under conditions encountered with sugarhouse products, temperatures above 115° C. alone are sufficient to produce formaldehyde from all these products.

Table III—Color Tests

Substance under Examination	Color Developed in 30 Minutes	
	No. 2	No. 3
Hair tonic	Deep green	Yellowish green
Bay rum (from S. D. 39D)	Yellow	Yellowish green
Extract of almond	Yellow	Yellowish green
Extract of lemon	Yellow	Deep green
Extract of orange	Yellowish green	Green (apple)
Sarsaparilla extract[a]	Orange-yellow	Yellowish green
Compound extract of vanilla	Yellow	Yellowish green
Orange coloring	Yellow (lemon)	Greenish yellow
Yellow coloring	Yellow	Pale amethyst
Red coloring	Yellow	Deep green
Antiseptic (containing oil of peppermint)	Yellow	Green
Blackberry cordial	Yellow	Deep green
Eau de cologne	Pale green	Deep green
Headache remedy	Orange-yellow	Deep green
Same with 1% added methanol	Violet	Violet
Same with 3% added methanol	Intense purple	Intense purple
Same with 0.05% added methanol	Yellow	Pale violet
Eau de cologne (as above) with 0.05% added methanol	Greenish yellow	Pale violet
Perfume, "extract" (from S. D. 40M)	Greenish violet	Greenish yellow
Hair dressing	Pale green	Green
Toilet water	Greenish yellow	Green
Artificial strawberry flavor	Greenish yellow	Greenish violet
Pure lemon extract	Yellow	Green
Orange flavor, imitation	Yellow	Pink
Essence of peppermint	Yellowish green	Yellowish pink
Grape compound	Yellow	Yellow
Grape flavor base	Yellow	Green
Imitation extract of pineapple	Pale violet	Pale violet
Aromatic extract of ginger	Orange-yellow	Greenish violet
Ethyl alcohol alone (control)	Lemon-yellow	Lemon-yellow

[a] The sarsaparilla was known to contain oil of wintergreen. It was declared in the formula and was also readily detected by the odor. However, there was no reaction for methanol and the sample had been treated with magnesium oxide and filtered prior to distillation, in order to remove oils, for the alcohol determination. Accordingly 50 cc. of the extract were diluted to 150 cc., made decidedly alkaline with 0.1 *N* caustic soda solution, digested at 100° C. for 1 hour under a reflux condenser, then distilled and the first 50 cc. of the distillate separated into two portions. One of these was diluted and tested straight, the other was diluted, treated with fuller's earth, filtered, and then tested. Both gave a violet color at once.

Methyl esters seem to be far less liable to cause complications than esters of the higher alcohols. It has been the experience of the writer that amyl esters very readily give oxidation products which are inclined to develop a violet color.

The contributions of Georgia and Morales[5] give the most advanced and complete information upon limitations of the method and interfering substances. The writer has found the reagent prepared from rosaniline salt to be more sensitive and more convenient than that prepared from fuchsin. The tests in this article were nevertheless made with the fuchsin reagent.

Several additions might be made to the list of interfering substances[5] given by Georgia and Morales. The writer has found that glycerophosphates and vanillin do not give the test. In the procedure for alcohol determination used in our examples one must exercise care even in the interpretation of the results of Georgia and Morales. The conclusions of Haley,[6] though applicable under the specific conditions cited, are certainly not applicable to a large variety of materials which might be suspected of containing methanol.

So prone are certain substances to produce shades suggesting traces of methanol, that a neglect of the precaution to prepare the sample of 5 per cent alcoholic strength caused

[4] *Ind. Eng. Chem.*, **2**, 260 (1910).
[5] *Ibid.*, **18**, 304 (1926).
[6] *Ibid.*, **18**, 1312 (1926).

a sample of completely denatured No. 5 to get through the test with no indication of the 2 per cent of methanol which it contained.

Conclusions

When the procedure is strictly followed the findings are authentic for the materials for which the test was intended. By proper interpretations of the difficulties and suitable modifications, the test can be used on many other materials.

While under certain conditions confusing findings occur, these can usually be verified or eliminated by testing some of the same material to which a small quantity of methanol has been added.

A method is suggested with a sensitiveness so high as to meet any requirements, but the advantages are offset by its ready response to the effect of interfering substances. The use of both methods on a sample will probably result in the detection of any methanol present, and if both give a positive indication methanol is very likely present.

Universal Tank Calibration Chart[1]

A. K. Doolittle

THE SHERWIN-WILLIAMS CO., CHICAGO, ILL.

THE accompanying chart (Figure 2) was prepared to facilitate the work of inventorying the various liquid-storage tanks used by one of the large manufacturers of nitrocellulose lacquers. After having calibrated a number of these tanks individually, laboriously integrating the volume in the end bulges by plotting the cross sections on coordinate paper and counting the squares, the writer determined to prepare a chart that would be applicable to all cases.

Use of Chart

By use of this chart it is possible to read, with an accuracy closer than 1 per cent, the volume of liquid at any depth in a cylindrical tank, whether horizontal or vertical, of diameter 2 to 10 feet and length 1 to 50 feet. The correction for the spherical end bulges on large tanks is also plotted on the same chart.

To use the chart for horizontal tanks, start at the left margin with the depth (inches) of the liquid above the bottom of the tank. Move horizontally to the right till the curve corresponding to the diameter (feet) of the tank is reached. Then move vertically till the line corresponding to the length (feet) of the tank is reached, thence horizontally to the right margin where the volume in the cylindrical portion of the tank will be read in gallons.

To determine the volume in the end bulges, use the curves on the top portion of the chart. Starting at the left with the depth in inches (same as above), move horizontally to the right till the diameter curve is reached, then vertically to read the volume (both ends) on the top scale. The end-bulge correction is added to the volume in the cylindrical portion to give the total volume of liquid in the tank.

To use the chart for vertical tanks, consider the depth of the liquid the length of the tank. Use the full diameter of the tank, disregarding entirely the values on the left margin.

The volumes in tanks of diameters or lengths not in even feet can be readily interpolated from the chart.

Preparation of the Chart

The main portion of the chart was prepared by plotting on logarithmic paper two sets of curves to the same abscissa. The first set of curves were plotted to:

$$A = f(h);\ D = 2r = \text{constant}$$

where A = area (square feet), h = depth (inches), and D = diameter (feet).

This function may be integrated from:

$$A = \int_0^h 2x\,dy;\ x = \sqrt{r^2-(y-r)^2} \text{ to}$$

$$A = \left[(h-r)\sqrt{r^2-(h-r)^2} + r^2 \sin^{-1}\frac{h-r}{r} - \frac{3\pi r^2}{2}\right]$$

but the values are more readily plotted from the data in handbooks on segment areas.

The second set of curves were plotted to:

$$V = 7.4805\,AL;\ L = \text{constant}$$

where V = volume (gallons), A = area (square feet), and L = length (feet).

It will be noted from the above that the abscissas common to both sets of curves represent the area of the segmental cross section of the liquid.

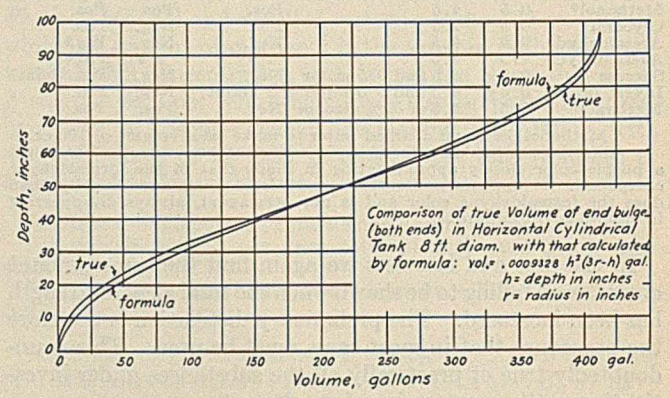


Figure 1

The construction of the curves for end bulge was more interesting from the mathematical point of view. In standard tank practice the end bulge is designed to represent a segment of a sphere of radius equal to the diameter of the tank. As the integration of the volume considered as a segment of a sphere is too complex to admit ready calculation of the values, this volume was integrated as an ellipsoid of revolution.

$$V = \int_0^h \pi x y\,dz \quad \text{(both ends)} \tag{1}$$

where $x = \frac{a}{r}\sqrt{r^2-(z-r)^2}$; $a = r(2-\sqrt{3})$; $y = \sqrt{r^2-(z-r)^2}$.

Integrating

$$V = \frac{2-\sqrt{3}}{3}\pi h^2(3r-h) \tag{2}$$

[1] Received July 2, 1927.

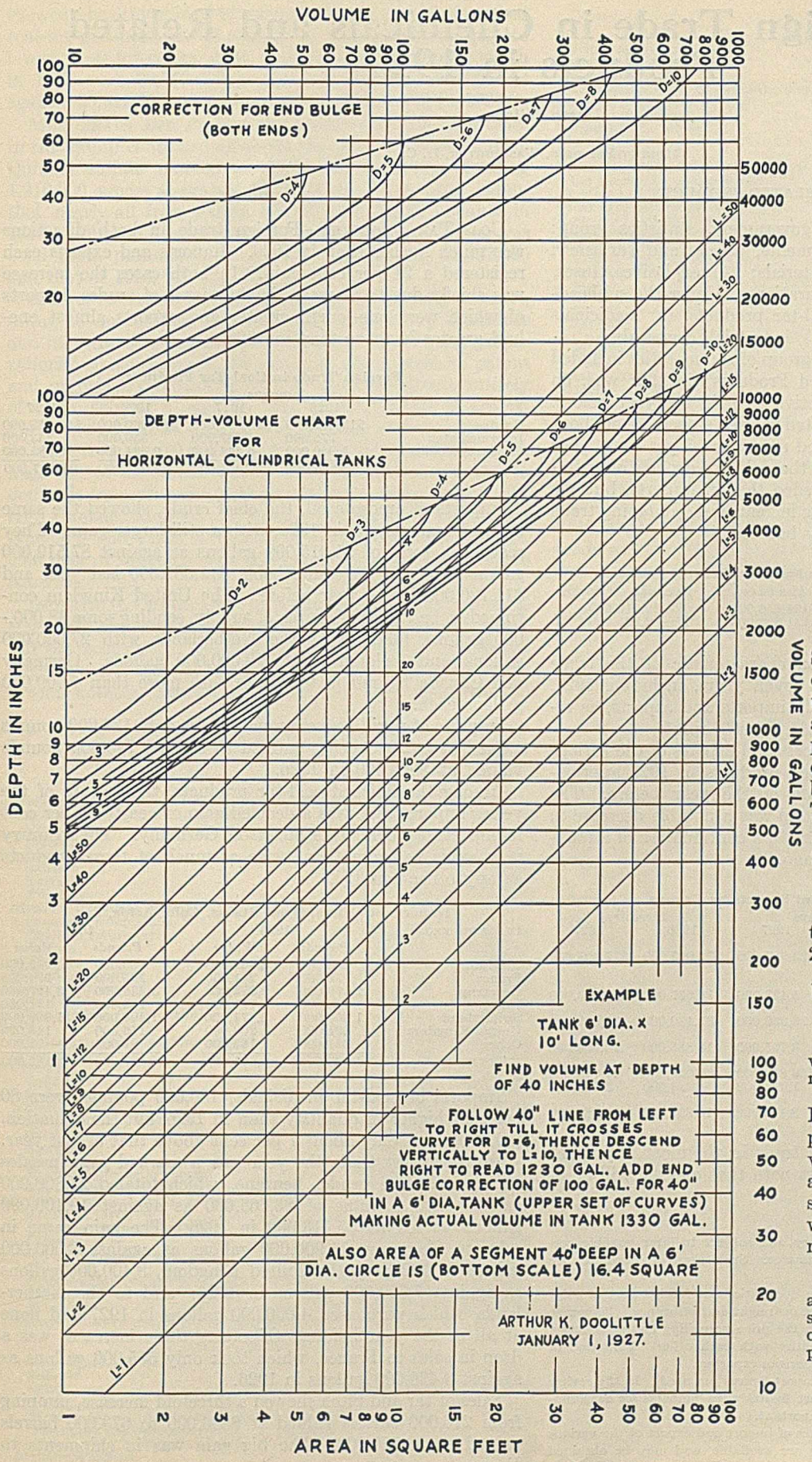


Figure 2

The full volume of end bulge according to the above formula ($h = 2r$) is

$$V = \frac{2-\sqrt{3}}{3}\pi 4r^3 \qquad (3)$$

The true full volume (both ends), considering same as segments of sphere, is:

$$V_t = 2\int_{\sqrt{3}r}^{2r} \pi y^2 dx, \text{ where } y^2 = 4r^2 - x^2 \qquad (4)$$

Integrating,

$$V_t = 2\pi\left(\frac{16}{3} - 3\sqrt{3}\right)r^3 \qquad (5)$$

Dividing equation (5) by equation (3), we find:

$$\frac{V_t}{V} = \frac{2\pi\left(\frac{16}{3}-3\sqrt{3}\right)r^3}{\frac{2-\sqrt{3}}{3}\pi 4r^3} = \frac{16-9\sqrt{3}}{4-2\sqrt{3}} = 76.7 \text{ per cent}$$

Since all variables cancel out, equation (2) can be reduced by the constant ratio 76.7 per cent and represent a very close approximation to the true value of the volume in the end bulges at all depths.

The corrected equation (2)

$$V = 0.767\,\frac{2-\sqrt{3}}{3}\pi h^2(3r-h) \qquad (6)$$

therefore becomes (dividing by 231 to reduce to gallons)

$$V = 0.0009328\, h^2(3r-h) \text{ gallons} \qquad (7)$$

(both ends)

where h = depth (inches), r = radius of tank (inches).

How closely this function approximates the true value of the volume of the end bulges is apparent from Figure 1, which shows that the error is well within the limits of accuracy of reading the logarithmic chart.

NOTE—Blue prints of the above calibration in full detail, size $19^1/_2 \times 35$ inches, can be obtained from the author, postpaid, upon receipt of $1.00.

Our Foreign Trade in Chemicals and Related Products in 1927[1,2]

Otto Wilson

MUNSEY BUILDING, WASHINGTON, D. C.

CHEMICALS AND RELATED PRODUCTS

UNDER this heading government statistics group: (1) chemicals; (2) pigments, paints, and varnishes; (3) fertilizers and materials; (4) explosives, fuses, etc.; (5) soap and toilet preparations. Under the subheading "chemicals" are: (*a*) coal-tar products, (*b*) medicinals and pharmaceuticals, and (*c*) industrial chemicals.

Foreign trade in the general group of commodities included under "Chemicals and Related Products" in 1927 was, on the whole, somewhat more active than in the year before. The total value of goods imported showed a decrease of about 4 per cent, while exports gained more than 5 per cent. For the first time in several years the value of exports of chemicals and chemical wares exceeded that of imports, but the difference was so small that the incoming and outgoing trade may be said to be practically balanced.

U. S. Foreign Trade in Chemicals and Related Products

Year	Imports	Exports	Balance of Trade
1926	$134,766,000	$124,856,000	−$9,910,000
1927	129,643,000	131,828,000	+ 2,185,000

This even balance has been characteristic of the trade for many years. In the last seven years, including 1927, for example, the average yearly imports and exports, as reported, have been less than $1,000,000 apart.

For the most part both imports and exports of the various groups of chemicals and related products in 1927 approximated fairly closely the trade of the year before. The greatest change in any one group was a notable decrease in imports of fertilizers and materials, a continuation of a tendency which began two years ago.

Chemical Imports and Exports by Groups

	Imports		Exports	
	1926	1927	1926	1927
Chemicals:				
Coal-tar products	$19,806,000	$23,987,000	$14,093,000	$17,097,000
Medicinal and pharmaceutical preparations	5,891,000	5,423,000	19,677,000	20,103,000
Industrial chemicals	28,294,000	28,369,000	31,130,000	35,689,000
Pigments, paints, and varnishes	3,821,000	3,755,000	18,888,000	20,906,000
Fertilizers and materials	69,239,000	58,842,000	20,040,000	17,724,000
Explosives, fuses, etc.	1,165,000	1,093,000	4,223,000	3,455,000
Soaps and toilet preparations	6,551,000	8,173,000	16,806,000	16,854,000

A comparison of last year's trade in the most important articles of each of these groups with that of 1926 will be of interest.

[1] Received February 8, 1928.

[2] All 1927 figures are preliminary and subject to later possible correction by the Department of Commerce. Such changes, however, are usually few and of minor importance.

Valuation of imports is based on declarations at foreign port of shipment, and does not include cost of ocean freight and insurance. "Average valuation" is not to be confused with the price prevailing in this country, although the two fluctuate in sympathy with each other. Valuation of exports is based on declarations by American exporters.

In the present review general import figures are used. In the review published in the February issue import figures were "imports for consumption." The differences are seldom important.

In most cases more detailed figures of import and export of the various commodities than can be given here are available, and may be obtained through the writer.

Chemicals

COAL-TAR PRODUCTS—Foreign trade in both directions was much livelier than in 1926. Imports and exports each registered a 21 per cent gain. In both cases the increase was chiefly due to increases in shipments of crudes, imports of which were one-fourth greater and exports almost one-half greater in value than in 1926.

Foreign Trade in Coal-Tar Products

	Imports		Exports	
	1926	1927	1926	1927
Crudes	$13,072,000	$16,296,000	$7,060,000	$10,359,000
Intermediates	775,000	1,147,000	339,000	353,000
Finished products	5,959,000	6,544,000	6,694,000	6,385,000
Total	19,806,000	23,987,000	14,093,000	17,097,000

Imports of creosote oil, the chief crude, showed the same upward tendency as in 1926, with a still larger gain. They reached a total of 95,915,000 gallons as against 87,519,000 gallons in 1926, the value being $15,381,000 last year and $11,720,000 in the year before. The United Kingdom continued to be the chief source of supply, sending some 38,000,000 gallons, followed by the Netherlands with 27,000,000 gallons and Belgium with 19,000,000 gallons. Germany and Canada figured in the trade with more than 4,000,000 gallons each.

Imports of pyridine were much lower, only 136,000 pounds valued at $42,000 being entered as against 743,000 pounds valued at $366,000 in 1926.

Among the finished coal-tar products, the feature of the year's import trade was a decided gain of nearly 50 per cent in imports of colors, dyes, etc., from Germany. That country now sends us more than twice as much of these products as any other country.

Imports of Colors, Dyes, Stains, Color Acids, Etc.

Imported from:	1926		1927	
	Pounds	*Value*	*Pounds*	*Value*
Belgium	236,000	$367,000	180,000	$242,000
France	178,000	241,000	235,000	274,000
Germany	2,179,000	2,323,000	3,238,000	3,427,000
Italy	93,000	111,000	113,000	131,000
Switzerland	1,865,000	2,171,000	1,494,000	1,869,000
United Kingdom	201,000	203,000	146,000	148,000
Other	221,000	185,000	91,000	91,000
Total	4,973,000	5,601,000	5,497,000	6,182,000

Imports of coal-tar medicinals, 130,000 pounds, were 80 per cent higher in quantity than in 1926, but the valuation, $277,000, was only about 7 per cent above that of last year.

In the export trade the year saw a marked gain in sales of the principal crude, benzene, which totaled 25,800,000 gallons with a value of $6,665,000 as against 19,100,000 gallons valued at $5,513,000 in 1926. The gain came in sales to Germany, 11,900,000 gallons as against 8,000,000 gallons in 1926; to the United Kingdom, 8,400,000 gallons as against 7,500,000 gallons in 1926; and to the Netherlands, which purchased 4,600,000 gallons in 1927 and none at all in the year before. Offsetting these increases was a drop in sales to France, which took only 555,000 gallons as against 3,420,000 gallons in 1926.

Sales of tar and pitch showed a threefold increase, jumping from 216,000 barrels valued at $883,000 to 673,000 barrels valued at $3,256,000. The big gain was in shipments to France.

Exports of intermediates, amounting to 2,400,000 pounds, showed a healthy gain of 40 per cent. Sales abroad of finished coal-tar products fell off slightly in value, owing largely to lower prices for colors, dyes, and stains, shipments of which in 1927 were 26,766,000 pounds valued at $5,491,000, as against 25,812,000 pounds valued at $5,950,000 in 1926.

MEDICINALS AND PHARMACEUTICALS—Imports of articles in this group continued at about the same levels as in 1926. Quinine sulfate entered in increased quantities, totaling 1,916,000 ounces as against 1,584,000 ounces in 1926. Menthol, nearly all from Japan, fell off from 459,000 pounds in 1926 to 369,000 pounds last year, and the drop in value was even more pronounced, the 1927 figure being $1,332,000 and that of 1926, $2,842,000.

Sales of American medicinals abroad rose slightly in value, owing to an increase in patent and proprietary medicines and in antitoxins, serums, and vaccines. The "other preparations" classification in the statistics which includes patent and proprietary medicines and is made up almost entirely of them, showed a value in 1927 of $17,839,000 as against $17,509,000 in 1926. Antitoxins, serums, and vaccines rose in value from $1,440,000 in 1926 to $1,730,000 in 1927. The huge sale of the former article, as in past years, was due to demands from all parts of the earth, with the near-by countries Canada, Mexico, and Cuba, together with the United Kingdom and Latin American lands, leading as customers. The bulk of the antitoxins go to buyers in North and South America.

INDUSTRIAL CHEMICALS—Imports and exports of industrial chemicals are shown in detail in the accompanying table. For the most part, it will be noted, the trade of 1927 followed fairly closely that of the previous year. But there were several notable changes.

Foreign Trade in Industrial Chemicals

		1926 Pounds	1927 Pounds
IMPORTS			
Acids and anhydrides:			
Arsenious acid, or white arsenic		15,407,000	25,034,000
Citric		138,000	117,000
Formic		2,315,000	3,220,000
Oxalic		1,567,000	1,844,000
Sulfuric		55,937,000	34,869,000
Tartaric		1,565,000	2,854,000
All other		12,873,000	12,964,000
Alcohols, including fusel oil	*value*	$436,000	$830,000
Ammonium compounds, n. e. s.:			
Chloride (muriate)		15,812,000	14,279,000
Nitrate		8,344,000	11,218,000
All other		1,161,000	1,769,000
Barium compounds		24,477,000	14,649,000
Calcium carbide		21,845,000	4,561,000
Cobalt oxide		333,000	370,000
Copper sulfate (blue vitriol)		2,559,000	1,979,000
Lime:			
Chlorinated, or bleaching powder		3,767,000	2,712,000
Citrate of		3,371,000	166,000
Glycerol:			
Crude		27,564,000	14,785,000
Refined		10,880,000	8,268,000
Iodine, crude		711,000	926,000
Magnesium compounds		29,997,000	21,054,000
Potassium compounds, n. e. s.:			
Cyanide		104,000	340,000
Carbonate		11,523,000	13,192,000
Hydroxide (caustic potash)		12,969,000	14,762,000
Nitrate, crude, or saltpeter	*tons*	9,416	3,550
Bitartrate, crude, argols, or wine lees:		25,570,000	24,906,000
Cream of tartar		259,000	291,000
Chlorate and perchlorate		12,537,000	13,392,000
Other, n. e. s.		11,409,000	9,817,000
Sodium compounds, n. e. s.:			
Cyanide		31,804,000	32,559,000
Ferrocyanide (yellow prussiate)		815,000	1,787,000
Nitrite		1,927,000	292,000
All other	*value*	$1,312,000	$1,602,000
Radium salts and radioactive substances	*value*	$549,000	$394,000
EXPORTS			
Acids and anhydrides:			
Sulfuric		9,224,000	7,513,000
Other		16,382,000	14,247,000
Alcohols:			
Methanol, pure and denaturing grades	*gallons*	417,000	311,000
Other pure and denatured	*gallons*	425,000	477,000
Ammonia and compounds (except sulfate)		4,878,000	4,338,000
Aluminum sulfate		44,063,000	42,258,000
Baking powder		4,501,000	4,747,000

Foreign Trade in Industrial Chemicals (*Concluded*)

	1926 Pounds	1927 Pounds
EXPORTS		
Calcium compounds:		
Acetate of lime	18,589,000	11,634,000
Calcium carbide	4,534,000	4,873,000
Chlorinated lime, or bleaching powder	20,858,000	16,689,000
Copper sulfate (blue vitriol)	4,799,000	6,207,000
Dextrine or British gum	22,200,000	24,659,000
Formaldehyde (formalin)	2,387,000	2,240,000
Glycerol	768,000	699,000
Petroleum jelly	5,095,000	5,275,000
Disinfectants, insecticides, fungicides, and similar preparations and materials	13,190,000	.....
Nicotine and tobacco extracts	.....	2,307,000
Other agricultural insecticides, etc.	.....	4,396,000
Household insecticides, etc.	.....	14,983,000
Potassium compounds, n. e. s.	3,356,000	2,930,000
Sodium compounds, n. e. s.:		
Bichromate and chromate	8,527,000	8,907,000
Cyanide	1,883,000	1,299,000
Borax	28,610,000	73,908,000
Soda ash	39,533,000	40,802,000
Silicate (water glass)	48,345,000	54,886,000
Sal soda	12,653,000	12,742,000
Caustic soda	103,295,000	100,889,000
Bicarbonate	19,339,000	18,287,000
Other	83,854,000	79,826,000
Washing powder and fluid	4,935,000	5,488,000
Blacking and polishes:		
Metal polishes	2,285,000	2,402,000
Shoe polishes	3,393,000	3,512,000
Other	3,500,000	3,380,000

Our purchases of arsenious acid were more than 60 per cent higher in quantity than in 1926. In value the gain was even more notable, imports being $922,000 in 1927 and $510,000 in 1926, or an 80 per cent increase. Last year's trade was the highest in many years. In 1923 it was 20,000,000 pounds, in 1924, 17,700,000 pounds, and in 1925, 18,600,000 pounds. The average value of these imports has fluctuated widely, last year's figure of 3.7 cents per pound comparing with 3.3 cents in 1926, 5.8 cents in 1925, and 8.9 cents in 1924. The three leading countries in the trade—Mexico, Canada, and Japan—all increased their shipments to us last year.

The considerable decrease of 37 per cent in the quantity of sulfuric acid imports was accompanied by an even larger decrease, 41 per cent, in total value of shipments, which amounted to $198,000 in 1927 as against $338,000 in 1926. Canada sent almost the whole amount in 1926, with some small shipments coming from Mexico and Belgium. In 1927, however, the entire importation came from Canada.

There is a considerable exportation of sulfuric acid, although it is much smaller than the importation. This trade also fell off in 1927. It is widely scattered, the greater part of the shipments going to Latin-American buyers, particularly Mexico and Cuba.

Imports of tartaric acid were second in value only to arsenious acid. They almost doubled in value, totaling $644,000 against $330,000 in 1926. The value of formic acid imports rose with the quantity, being $231,000 in 1927 against $164,000 in 1926; the unit value in each year was about 7 cents.

The increase in value of imported alcohols was due directly to the gain in methanol imports. Neither the increased duty (18 cents per gallon instead of 12 cents) which went into effect December 27, 1926, nor the starting of the manufacture of synthetic methanol in this country, prevented shipments from abroad from far surpassing those of any previous year. They totaled 1,714, 000 gallons valued at $718,321, as against 1926 imports of 755,000 gallons valued at $345,000, and 1925 imports of 508,000 gallons valued at $231,000. The heavier shipments were accompanied by a lower average valuation, which for 1927 stood at 41.9 cents per gallon against 45.7 cents in 1926 and 45.4 cents in 1925.

Figures of imports by months show that shipments in the first half of the year were particularly heavy, but that they fell off sharply in the second six months. In the last quarter total valuations (at foreign port of shipment) dropped rapidly, and for December imports averaged less than 30 cents per gallon.

Imports of Methanol by Months in 1927

	Gallons	Value		Gallons	Value
January	313,000	$141,000	July	102,000	$45,000
February	67,000	29,000	August	95,000	42,000
March	146,000	61,000	September	53,000	24,000
April	164,000	68,000	October	88,000	32,000
May	316,000	139,000	November	77,000	23,000
June	199,000	87,000	December	94,000	27,000
1st 6 months	1,205,000	525,000	2nd 6 months	509,000	193,000

All but two or three small shipments of imported methanol came from Germany.

With strong competition from Germany in our own markets it was to be expected that the demand for American methanol in other foreign countries would be affected. The influence of the German competition is seen in reduced exports of methanol from the United States, showing a loss of 25 per cent. The value of the exports fell from $312,000 to $263,000. Last year's exports were less than half those of three years before. The average valuation of exports, however, was 84 cents per gallon in 1927 as compared with 74 cents in 1926.

Among other noticeable changes in the import trade in industrial chemicals was the sharp drop of 80 per cent in calcium carbide shipments, nearly all of which came from Canada. The value decreased in about the same ratio, from $847,000 to $171,000. This was a much lower figure than for many years back. Large declines are also to be noted in shipments of citrate of lime, glycerol, and crude potassium nitrate. Among the exports, sales of borax to foreign countries increased almost threefold in quantity, although the total value was only doubled, being $2,422,000 in 1927 as compared with $1,257,000 in 1926. Borax sales are very widely scattered, the largest buyers being European countries and Japan.

Pigments, Paints, and Varnishes

The year was marked by increased exports of paints and related materials, with slightly decreased imports. In total value our sales to foreign countries were 10 per cent above those of 1926 and our purchases some 2 per cent less.

Foreign Trade in Pigments, Paints, and Varnishes

	Imports		Exports	
	1926	1927	1926	1927
Mineral-earth pigments	$1,538,000	$1,631,000	$1,006,000	$1,132,000
Chemical pigments	1,463,000	1,400,000	7,984,000	8,574,000
Paints, stains, and enamels	742,000	680,000	7,858,000	8,590,000
Varnishes	78,000	44,000	2,040,000	2,610,000
Total	3,821,000	3,755,000	18,888,000	20,906,000

Imports of iron oxide and iron hydroxide pigments fell off about 14 per cent, totaling 24,050,000 pounds valued at $588,000 against 27,987,000 pounds valued at $667,000 in 1926. Trade in ochers and siennas, 20,872,000 pounds, was practically the same as in the year before. Zinc pigments, of which 18,787,000 pounds were imported, were 1,000,000 pounds under 1926, but their value, $886,000, was slightly higher. There was a decrease of about 12 per cent in imports of paints, stains, enamels, and varnishes.

In the much more important export trade the largest class of commodities, chemical pigments, showed a gain of 7 per cent. The chief of these is carbon black, exports of which showed a substantial increase of 40 per cent in quantity in 1927, the total being 54,431,000 pounds valued at $4,600,000, against 39,210,000 pounds valued at $3,623,000 in 1926. As usual the United Kingdom was the leading buyer, increasing its purchases from 11,000,000 to 13,200,000 pounds. But the biggest gains were in the trade with Germany, which more than doubled its purchases, taking 9,300,000 pounds as against 4,300,000 pounds in 1926, and in that with Canada, which took 9,000,000 pounds against 4,700,000 pounds in the previous year. France, Italy, Japan, and Australia, the other leading buyers, substantially increased their purchases.

Exports of zinc oxide, as usual, went to a wide range of countries in all parts of the globe. Shipments to the United Kingdom fell off sharply, registering only 6,800,000 pounds against 10,600,000 pounds in 1926. Canada, however, raised her purchases from 8,500,000 pounds to 11,000,000 pounds and took first place in the trade. France more than doubled her 1926 purchases, but Germany's total was less than half that of the previous year. Total shipments to all countries were 28,900,000 pounds against 29,300,000 pounds in 1926.

Exports of enamels and ready-mixed paints were well above those of 1926, the total shipments being: enamels, 480,000 gallons in 1927 and 432,000 gallons in 1926; other ready-mixed paints, 2,634,000 gallons in 1927 and 2,208,000 gallons in 1926. There was also a slight gain in sales of varnishes abroad, which amounted to 1,284,000 gallons as against 1,108,000 gallons in 1926, but there was a change in the character of the trade, oil varnishes giving way to lacquers and other sorts.

Fertilizers and Fertilizer Materials

The most notable change in the fertilizer trade of the year was the large decline in Chilean nitrate imports. The decrease in value was even more marked than in quantity, amounting to 30 per cent as against 18 per cent.

As stated above, this decline is a continuation of the steady downward tendency shown by the import trade since 1925. During the abnormal war years imports averaged about 1,173,000 tons annually. In 1921 they reached the low mark of 369,000 tons, rising to 542,000 tons in 1922, 892,000 tons in 1923, 987,000 tons in 1924, and 1,112,000 tons in 1925. That was the peak of recent years, the 1926 shipments falling to 914,000 tons valued at $42,781,000, and last year's shipments to 749,000 tons valued at $30,132,000.

In spite of the decline, Chile's trade in nitrates with this country is yielding only slowly to the advance of synthetic nitrogen. Our 1927 imports of nitrate were still 40 per cent heavier than in pre-war years, and we paid 70 per cent more for them.

The gradual post-war change in the general nitrate situation is reflected more clearly in the changing values than in quantities shipped. The average valuation of Chilean nitrate per ton reached its peak in 1921, when it stood at $48.73. The next year it was $48.25, and then for three years it fluctuated between $47 and $48. In 1926 it fell to $46.79, and last year dropped to its lowest mark since the war, $40.24.

Of the other nitrogenous fertilizers, a large gain in imports of ammonium sulfate–nitrate is to be noted. The 1927 imports of 44,659 tons, valued at $2,631,000, compare with 1926 imports for consumption (nearly the same in this instance as general imports) of 16,245 tons valued at $1,099,000. Average valuation of these imports at port of shipment in 1927 was $58.90 and in 1926, $67.65. Imports of straight sulfate of ammonia also showed a large increase, 17,153 tons being brought in, valued at $780,000, against 8386 tons valued at $468,000 in 1926. Calcium cyanide imports were 109,730 tons valued at $4,353,000, as against 88,373 tons valued at $4,193,000 in 1926.

There was a marked decrease in the volume of potash imports, but higher prices prevented a proportionate fall in total value.

Imports of Potash Fertilizer

	1926		1927	
	Tons	Value	Tons	Value
Chloride, crude (muriate)	199,000	$6,196,000	164,000	$5,739,000
Sulfate, crude	70,000	2,823,000	69,000	2,948,000
Kainite	182,000	1,215,000	103,000	815,000
Manure salts	316,000	3,391,000	278,000	3,677,000
Other potash-bearing substances	48,000	498,000	9,000	245,000
Total	815,000	14,123,000	623,000	13,424,000

Bone phosphate imports show an increase of 17 per cent, amounting to 54,586 tons valued at $1,541,000 against 46,716 tons valued at $1,380,000 in 1926.

In the export trade in fertilizers, sulfate of ammonia dropped from 181,000 tons valued at $9,824,000 to 140,000 tons valued at $6,827,000 in 1927, a falling off of 22 per cent in quantity and 30 per cent in value. The big decrease occurred in the trade with Japan, although there was a general decline in shipments to the Far East, which takes the great bulk of these exports.

Phosphate rock and acid phosphates showed a substantial gain in exports, but a fall in values in the trade in high-grade rock kept the total returns for that article some 25 per cent under those for 1926. Total shipments of phosphate rock were 918,000 tons valued at $4,733,000, whereas in 1926 they were 749,000 tons valued at $4,436,000. Superphosphates were sent abroad to the extent of 107,000 tons valued at $1,614,000 in 1927 and 64,000 tons valued at $937,000 in 1926. As in past years, all but scattering shipments went to Canada and Cuba.

Explosives, Fuses, Etc.

Our yearly purchases of these goods from abroad are small, amounting last year to a value of $1,093,000, which compared with $1,165,000 in 1926. The chief item was firecrackers, valued at $835,000, slightly more than in the year before. China is the largest source of supply.

A drop of 25 per cent in the most important export of this group, dynamite, was largely responsible for a decrease in value of exports of the group as a whole, which reached $3,455,000 as against $4,223,000 in 1926. Total dynamite shipments stood at 12,110,000 pounds valued at $1,808,000 in 1927. In the previous year they were 16,221,000 pounds valued at $2,331,000. Smokeless powder exports were less by two-thirds than in 1926, and electric and other blasting caps sent abroad were about one-half the 1926 exports in number although the value, $373,000, was about 4 per cent greater than in the year before.

Soaps and Toilet Preparations

This is essentially an export trade, our sales abroad aggregating twice the value of our foreign purchases. Soaps make up the largest item of export.

The largest single item last year, as usual, was laundry soap, whose value, $3,878,000, was 6 per cent under 1926. Mexico and other Latin-American countries, Canada, and the Philippines are the heaviest buyers. Sales of toilet or fancy soaps abroad were nearly 10 per cent less than in 1926, totaling 8,186,000 pounds valued at $2,801,000 as against 8,975,000 pounds valued at $3,038,000 in 1926. As usual these exports were scattered among practically all the countries of the globe.

Sales of dental cream in 1927 showed a healthy gain over the previous year, aggregating 3,828,000 pounds with a value of $3,357,000 as against 3,119,000 pounds valued at $3,021,000 in 1926. Talcum and other toilet powders, 3,254,000 pounds valued at $1,621,000, and creams, rouges, and other cosmetics, 2,958,000 pounds valued at $1,707,000, showed no great change from 1926. Trade in these articles also seeks out every corner of the earth.

Imports of toilet goods are mostly perfumery and perfume materials, chiefly from France. The average valuation of these materials admitted free in 1927 was nearly $100 a pound, twice that of 1926. The total quantity of imports was 18,468 pounds valued at $1,796,000 as against 25,390 pounds valued at $1,183,000 in 1926. Dutiable imports under this class were valued at $2,533,000 in 1927 and $1,616,000 in the year before.

MATERIALS RELATED TO CHEMICAL INDUSTRIES

Aside from the above articles, included in government statistics under the classification "Chemicals and Related Products" (Group 8), a number of commodities classified with other groups are of interest to the chemical industry. Imports and exports of the more important of these are reviewed below.

Mineral Oils

Our total exportation of mineral oils set a new mark in 1927, shipments of crude and refined together being greater than in any previous year. As compared with 1926 all classes showed an increase except illuminating oil (kerosene), which was 12 per cent less in quantity.

Exports of Mineral Oils (Barrels of 42 Gallons)

	1926		1927	
	Barrels	*Value*	*Barrels*	*Value*
Petroleum, crude	15,406,000	$28,496,000	15,843,000	$25,944,000
Gasoline, naphtha, and other light products	42,480,000	263,200,000	43,436,000	210,370,000
Illuminating oil	22,016,000	100,353,000	19,280,000	78,874,000
Gas and fuel oil	34,516,000	45,354,000	43,019,000	49,944,000
Lubricating oil	9,256,000	86,415,000	9,623,000	88,827,000

In point of value, however, exports fell considerably below those of 1926. Last year's exports of petroleum and products were valued at $486,143,000 against $554,534,000 in the year before, a decrease of 12 per cent. The lower value was in evidence in all classes except gas and fuel oils and lubricating oils, and even with them the average value per barrel was lower than in 1926.

Canada, Cuba, and Japan, which between them consume some 95 per cent of our crude petroleum exports, all increased their purchases last year. In the trade in gasoline, naphtha, etc., the two largest buyers, the United Kingdom and France, both bought considerably less in 1927 than in 1926, while shipments to Canada, Australia, and New Zealand, among others, showed good increases.

The drop in kerosene shipments was due largely to a falling off in the trade with the Far East (Japan as well as China taking considerably less), with British India, and with France. The United Kingdom slightly increased its purchases. Japan took 4,419,000 barrels of gas and fuel oil, more than double its 1926 figure, and Panama, the largest buyer, also increased its purchases, but the United Kingdom took less. South America figures heavily in this trade.

Not included in the above figures of exports was bunker oil laden on vessels in foreign trade, which totaled 50,051,000 barrels in 1927 as against 46,662,000 barrels in 1926. This oil last year was valued at $72,967,000 and in 1926 at $71,045,000.

Offsetting these exports of oil were imports of crude petroleum amounting to 58,383,000 barrels valued at $78,609,000 in 1927, which compares with 60,382,000 barrels valued at $79,308,000 in 1926, and refined oils totaling 13,281,000 barrels valued at $33,638,000 in 1927 against 20,902,000 barrels at $44,597,000 in 1926. Mexico furnished only 44 per cent of the crude oil imports last year against 67 per cent in 1926, heavier shipments from Colombia, Venezuela, and Peru making up most of the difference.

Sulfur

Exports of sulfur were much heavier in 1927, totaling 789,000 tons valued at $16,269,000 as against 577,000 tons valued at $10,918,000 in 1926. France, Germany, the Netherlands, Canada, and Australia, the leading buyers, all took increased amounts.

Vegetable, Animal, and Essential Oils

Exports of cottonseed oil advanced to a marked extent in 1927, totaling 67,982,000 pounds as against 40,901,000 pounds in 1926. The greatest gain was in shipments to Canada, the largest buyer.

Edible animal oils and fats sent to foreign countries fell off considerably in 1927 both in quantity and value. Oleo oil exports totaled 78,781,000 pounds, valued at $9,599,000, whereas in 1926 they were 96,902,000 pounds valued at $11,785,000. The Netherlands, which bought about 30 per cent of the total, took first place in the trade in 1927 from Germany, whose purchases fell off about one-fourth.

Exports of lard were 681,300,000 pounds, valued at $92,-035,000, comparing with 698,961,000 pounds valued at $108,600,000 in 1926. The United Kingdom and Germany, leaders in the trade, both took reduced quantities. Neutral lard, however, rose from 18,116,000 pounds in 1926 to 20,-397,000 pounds last year, the value falling off slightly, and lard compounds fell from 10,581,000 pounds to 8,988,000 pounds.

Imports of edible vegetable oils, very largely olive oil, rose in value from $13,925,000 in 1926 to $17,635,000 in 1927. Of the oils classed as inedible, coconut oil from the Philippines was imported to the extent of 293,369,000 pounds valued at $22,900,000 as compared with 245,129,000 pounds valued at $22,088,000 in 1926. Chinese wood oil, 89,650,000 pounds valued at $11,810,000, and palm oil, 159,911,000 pounds valued at $11,040,000, both increased materially over 1926. Linseed oil imports were much lower, dropping from 15,041,000 pounds in 1926 to 946,000 pounds in 1927.

Imports of Essential and Distilled Oils

		1926		1927	
		Pounds	*Value*	*Pounds*	*Value*
Cassia and cinnamon		322,000	$474,000	378,000	$488,000
Geranium		222,000	526,000	186,000	469,000
Otto of roses	*ounces*	34,000	364,000	26,000	297,000
Bergamot		76,000	418,000	104,000	628,000
Citronella and lemon grass		1,320,000	745,000	1,466,000	612,000
Lavender and spike lavender		198,000	509,000	323,000	927,000
Lemon		508,000	974,000	400,000	723,000
Orange		209,000	506,000	204,000	495,000
Sandalwood		5,000	13,000	4,000	16,000
Other		3,432,000	2,044,000	3,496,000	1,794,000
TOTAL		...	6,573,000	...	6,449,000

Exports of essential and distilled oils reached a value of $2,118,000 as compared with $1,695,000 in 1926. Peppermint oil made up about 65 per cent of the total last year.

Dyeing and Tanning Materials

Quebracho extract, the chief imported tanning material, was brought from abroad last year, to the extent of 112,-000,000 pounds, valued at $4,930,000, an increase of about 9 per cent over 1926. Imports of quebracho wood almost doubled, rising from 32,000 tons to 60,900 tons, the value rising from $510,000 to $1,068,000. Logwood imports were 32,200 tons, a 30 per cent gain, and myrobolans fruit came in to the amount of 27,400 tons, double the 1926 amount.

Rubber

Crude rubber imports rose slightly in amount but fell off sharply in total value. The 1927 shipments were 954,-817,000 pounds having a value of $339,875,000, whereas in 1926 the imports stood at 925,878,000 pounds valued at $505,818,000. The average value in 1927 was 36 cents, as compared with 55 cents in 1926. From the Netherlands East Indies we received 169,551,000 pounds as against 156,-555,000 pounds in 1926. The amount received from British plantations, direct and through the United Kingdom, also increased.

Naval Stores, Gums, and Resins

Exports of articles grouped under this heading fell off slightly in value, amounting to $34,326,000 as compared with $36,865,000 in 1926. The decrease occurred in the chief export, rosin, which registered a total of $23,074,000 in value as compared with $24,633,000 in 1926. The quantity, however, 1,382,000 barrels, was well above that of the year before, 1,094,000 barrels.

Turpentine exports also rose in quantity and fell in value, the figures being: 1927, 15,810,000 gallons valued at $9,-505,000, and 1926, 11,587,000 gallons valued at $10,636,000.

Imports of gums, resins, and balsams fell from a value of $34,046,000 in 1926 to $32,536,000 in 1927. Shellac is the largest article in this group. It dropped from 31,296,000 pounds in 1926 to 25,102,000 pounds last year, the value, however, showing only a slight loss. Chicle imports were about the same as in 1926, the total being 12,167,000 pounds valued at $6,156,000. Natural crude camphor fell from 2,019,000 pounds in 1926 to 1,690,000 pounds in 1927, while refined rose from 1,170,000 pounds to 1,481,000 pounds, and synthetic was about the same in 1927 as in the year before, imports amounting to 2,934,000 pounds against 2,944,000 pounds in 1926.

The Higher Coal-Tar Hydrocarbons. By ARTHUR ERNEST EVEREST. 334 pages. Longmans, Green & Co., New York and London, 1927. Price, $7.00.

This book is a valuable compilation of the most important available information on the higher hydrocarbons of the cyclic series. It includes information from both scientific publications and patent records. It deals with the hydrocarbons of the acenaphthene, fluorene, phenanthrene, and other miscellaneous groups, as well as the known derivatives of these hydrocarbons. The author has done a very difficult task well.

The chapters on the acenaphthene, fluorene, and phenanthrene groups present a complete picture of our present knowledge of these hydrocarbons and their derivatives. The book is particularly valuable because of the large number of citations to patents on derivatives of the higher hydrocarbons. It is shown that certain derivatives of acenaphthene have already assumed a prominent position as intermediates for dyes. Particularly is this true of acenaphthenequinone. Condensations with indoxyl and its halogen derivatives give vat dyes producing various hues of violet on cotton. Condensations with other intermediates, such as hydroxy thionaphthene and related products, give very important vat dyes capable of dyeing unmordanted cotton different colors. Some of these vat dyes are of very great commercial importance. In several instances the author points out the lack of information on certain derivatives of these hydrocarbons and suggests lines for future research.

In the chapter on fluorene the author points out that fluorene of suitable purity can be obtained in large quantities without much difficulty from coal tar, but that up to the present there has been no commercial demand for the product. A large number of derivatives have been studied and many of them patented, but few are of commercial importance. Practically nothing is known of the possible fluorene quinones. This is virgin field for future research.

Considerable space is given to the discussion of phenanthrene and its derivatives. The presence of the phenanthrene nucleus in alkaloids suggests many attempts at synthesis. The section dealing with the work that has been done to utilize phenanthrene as an intermediate for dyes is particularly thorough and interesting. The chapter on perylene points out the growing importance of this hydrocarbon and its possibilities in the syntheses of vat dyes. It is the nucleus of some of the most important vat dyes.

In general, the book is a valuable contribution to the literature on cyclic hydrocarbons and their derivatives.

M. L. CROSSLEY

PERKIN MEDAL AWARD

At the meeting of the American Section of the Society of Chemical Industry in New York City, on January 13, the twenty-first award of the Perkin Medal was made to Irving Langmuir, assistant director of the Research Laboratory of the General Electric Company, in recognition of his valuable work on atomic hydrogen and its application to welding.

L. V. Redman, chairman of the section, presided over the meeting. An interesting account of the early life of the medalist was given by Ellwood Hendrick, who emphasized the inherited qualities and early training which contributed to the personality which Doctor Langmuir has so successfully dedicated to the service of science and his fellowmen. W. R. Whitney, the medalist's long-time associate in the General Electric Company, continued the tale of his progress and this vivid story of his accomplishments is given below.

The medal was then presented by William H. Nichols, who opened his remarks with the following brief history of the award:

The Perkin Medal was founded in 1906 to commemorate the fiftieth anniversary of Sir William Perkin's discovery of mauve. As part of the commemoration of this jubilee, Sir William and his family were invited to visit this country as the guests of the American chemists, that we might be enabled to express in some adequate manner the great admiration we had for him and his epochal work. Among other provisions of the celebration, a banquet was served at Delmonicos—now, alas! only a memory—to a large gathering of chemists and their friends, all wearing mauve neckties. During the succeeding exercises I had the honor of presenting the first Perkin Medal to Sir William himself as a testimony of America's appreciation of the fundamental value of his work, pointing the way as it did to the great organic chemical industry of today and the future.

Since that occasion the medal has been awarded annually by a jury of a representative character, and has been received by many men who have contributed greatly to the benefit of mankind. It has become one of the great honors which while not sought is, I am sure, especially appreciated by those who have been selected from year to year as the recipients. Among the rules covering the matter is one which provides that the senior American past president of the Society of Chemical Industry should present the medal. For many years Doctor Chandler, who was the first American president, was able to be with us, and year after year he acted in the capacity for which he was so well qualified. Doctor Chandler has left us and, as his successor in the list of American presidents, it is my duty and privilege to act tonight.

Doctor Langmuir accepted the award with a few words of appreciation and then told the history of some of his work in the address which will be found in these pages.

The previous recipients of the Perkin Medal were as follows:

Date of Award	Awarded to	Principal Fields of Inventions
1907	Sir W. H. Perkin	Discoverer of first aniline color
1908	J. B. F. Herreshoff	Metallurgy; contact sulfuric acid
1909	Arno Behr	Corn products industry
1910	E. G. Acheson	Carborundum; artificial graphite
1911	Charles M. Hall	Metallic aluminum
1912	Herman Frasch	Desulfuring oil and subterranean sulfur industry
1913	James Gayley	Dry air blast
1914	John W. Hyatt	Colloids and flexible roller bearings
1915	Edward Weston	Electrical measurements; electrodeposition of metals; flaming arc
1916	L. H. Baekeland	Velox photoprint paper; Bakelite and synthetic resins; caustic soda industry
1917	Ernest Twitchell	Saponification of fats
1918	Auguste J. Rossi	Development of manufacture and use of ferrotitanium
1919	Frederick G. Cottrell	Electrical precipitation
1920	Charles F. Chandler	Noteworthy achievements in almost every line of chemical endeavor
1921	Willis R. Whitney	Development of research and application of science to industry
1922	William M. Burton	Achievement in oil industry; efficient conversion of high-boiling fractions into low-boiling fractions
1923	Milton C. Whitaker	Great constructive work in field of applied chemistry
1924	Frederick M. Becket	Process for extraction of rare metals from ores; manufacture of calcium carbide; processes for reduction of rare metals and alloys
1925	Hugh K. Moore	Electrochemical processes for caustic soda, soda, and chlorine; production of wood pulp; hydrogenation of oils, etc.
1926	R. B. Moore	Radium, mesothorium, and helium

Langmuir's Work

W. R. Whitney

General Electric Company, Schenectady, N. Y.

I CANNOT expect to do justice to the subject of Doctor Langmuir's accomplishments. Conventional sentences seem unsatisfactory, for the truth, if properly told, would animate and stimulate young men. I know his interest in young men and his unbounded faith in science. These are so great that I want my brief address to help students of physics and chemistry to see the pleasure and excitement of research without special reference to the financial rewards and the honors which exist for first-class scientific contributions.

Above everything I place his published scientific work, because it is the kind on which he and others will continue to build serviceable structures, and we know that such mental and spiritual advances as its marks are superior to technical ones. His published researches on fundamental physical and chemical subjects comprise one hundred and twelve papers, all on new knowledge. They cover such widely different fields as chemical reactions at low pressures; conduction, convection, and radiation of heat; vapor pressures of metals; new vacuum pumps and vacuum gages; crystal structure, atomic structure; electronic and ionic currents; high-power vacuum tubes; theories of absorption, of evaporation, of passivity, etc. They are all subjects for which he has combined rare insight with unusual practical experience.

Second to his published scientific work I place that equally unmeasurable thing which, not only in a research laboratory, but in all organizations of men, determines results. This is his willingness and ability to work with, assist, guide, or direct others. These seem less tangible, but more valuable than the material accomplishments which I shall consider next.

Langmuir has accomplished great things in the electrical industry. The average citizen might cry out here—don't say it with flowers, tell us in dollars! Perhaps after expressing it in millions of something or other, I can then peacefully proceed to a finer appreciation. Doctor Langmuir was the first to apply

argon and nitrogen to tungsten lamps, and thus reduced by 50 per cent the cost of more than half the light we all buy. The total number of tungsten lamps sold in America last year—vacuum, gas-filled, and miniature—was 538 million. Nearly a third of the lamps now sold are gas-filled. There have been made in the United States nearly a 1000 million of these new type lamps. More than 100 million of them are made annually. One way to express the value of this improvement of putting gases into the tungsten lamp is to say that it saves to the American public more than a million dollars a night on its lighting bill of over a billion dollars a year.

But Langmuir also carried out successful work on the vacuum lamp, and this too might be expressed in millions. He would wish me to say, however, that the discoveries of others, quite necessary at the time for first-class lamps, were conjoined in the finished products. The same may be said of radio tubes. While these came into use through the consecutive efforts of Edison, Fleming, and de Forest, Langmuir's work seems to have been absolutely essential to the production of radiotrons; and these, too, are now made by the million.

His long study of atomic hydrogen, referred to later, led him to the atomic hydrogen flame, which now welds the evaporators of all our refrigerators. This is a development not yet expressible in millions, but it may be, and if this kind of welding should replace riveting in buildings we could at least speak of millions of rivets which will be quietly omitted.

Doctor Langmuir has already received medals for some of his accomplishments, and listened to corresponding addresses of appreciation, so I may be brief and embarrass him less by recalling that he twice received the Nichols Medal, once for work on chemical reactions at low pressures, and again for work on atomic structure. The Hughes Medal came to him for researches on molecular physics, and the Rumford Medal for thermionic researches and for the gas-filled lamp.

I shall not attempt a systematic outline of the sixteen years of Langmuir's inquisitive experimental study which I have witnessed. Scores of his researches continue to weave together into fabric of ever increasing value and interest. I can but picture a few things as I see them, and let the reader imagine how his methods of thought and action are applied in other cases.

Study of the Atom

To him the atom had long been a really existent thing, just as the boldest chemists pictured it, but he did not hesitate to dissect it and construct it anew in much finer detail. He weighed the advanced theories of matter and pushed hard with the foremost speculators, for he was actively interested in principles of elementary physics and chemistry. In 1916 he wrote a long article which described only the beginning of extensive researches on the constitution and fundamental properties of solids and liquids. He had been incited by the Bragg work on crystal structure. This work led him to other studies and to such other publications as "The Adsorption of Gases on Plane Surfaces," "The Shapes of Group Molecules," "The Surfaces of Liquids," The Interior Structure of Atoms and Molecules," "The Octet Theory of Valence," "Isomorphism, Isosterism, and Covalence," etc. None of these are particularly edible without cooking, but his experimental work made them palatable. It is characteristic of him to advance a new hypothesis, but still more characteristic to prove it by exhaustive experiment.

Improvement of Incandescent Lamp

Before Doctor Langmuir joined our research staff everyone, from Edison down, had sought to improve the vacuum of the incandescent lamp. Will it stay better if initially made better, or does glass leak, even a little? Is the glass some sort of sponge which slowly gives off absorbed gases? Is it perhaps like some hydrated mineral, such as mica or basalt, slowly yielding water of composition to the vacuum? To what extent does the carbon or the metal filament carry within itself gases which later cause deterioration? What are the possible diseases of a lamp and how lengthen its expectation of life? Langmuir not only asked these questions and others, but he even seemed to see in the lamps the kinds of gases and their individual atoms. In his bold and speculative mind he saw molecules all arranged in proper places and oriented even to single atomic layers. Carbon monoxide, dioxide, water, air, etc., were present in glass because it had once been liquid and in equilibrium with all the gases of the glass furnace.

Such foresight, on the strength of pure knowledge and reasoning is free to anyone, but some are more successful with it than others. The successful are those who have profound knowledge of their field and who carry on intelligent and extensive experiments. But there is admittedly in Langmuir something more. It is a very unusual analytical mind. In his vacuum study he exhausted empty lamp bulbs and bulbs containing filaments, at all possible temperatures. He operated lamps for days under liquid air, and he included a scheme for exhausting lamp bulbs, heated close to their melting point, which had vacuum both inside and outside, because otherwise the external pressure flattened them completely. He and his co-workers spent many years doing such work. They also revised the experiments and turned them upside down and inside out. Extensive experiments were made in which the merest traces of various gases were put into the most perfectly evacuated bulbs, and their reactions, absorptions, and distributions studied. This work has really never stopped. The original, complicated exhausting apparatus, with its numerous bulbs of gases, special vacuum pumps, gages, and various devices, all securely welded together in one continuous glass system, has been in use by him or his assistants every day for the past fifteen years and is probably destined to contribute still further to atomic and electronic physics. So it is his persistent, investigative method, its continuity and coherence that I like to think about.

Atomic Welding Arc

His discovery of the atomic welding arc of last year is a product of cultivated growth and illustrates this patient, persistent process. The atomic-hydrogen welding torch is a combination of a jet of hydrogen gas through which an electric current is being sent. The electrical energy dissociates the hydrogen molecules into atoms. These not only exert great chemical reducing power but, by their interreaction, give a localized, extreme heat suited for reducing and welding most of our refractory metals. The device, so simple in appearance, did not result from carelessly throwing together in some single, snappy experiment the various parts which now constitute it. New knowledge which seemed at first useless, remote, and merely mathematically pure, was being collected for fifteen years before this welding arc was conceived. The published series of relevant data tells the story. Years ago Langmuir showed that thermal losses from tungsten filaments in hydrogen at high temperatures deviated from the law for gases in general, even including hydrogen at low temperatures. Thermal losses were usually proportional to the 1.9^{th} power of the absolute temperature. In case of hydrogen, however, the losses were much greater and the deviation increased rapidly with temperature.

Here was a new fact, or a discovery. He saw in it the separation of the atoms of hydrogen, and so sought a determination of the energy involved. He found this to be 98,000 Calories, which is more than that for the combination of hydrogen and oxygen. This meant to him that unusually high temperature should result from the reunion of the hydrogen atoms, and he found he could even melt tungsten thereby. While carrying out this study, with other researches under way, he published articles on the dissociation of hydrogen in 1911, 1912, 1914, and 1915. Still

more came out in 1916, and hydrogen continued so to interest him that the process called atomic-hydrogen arc welding only became complete and was described in 1926. Thus, this is a natural outcome of a long series of researches. His production is not sporadic, sudden, and accidental, but has an almost predictable certainty about it.

Other Lines of Work

The same continuity of events appears in other lines of his published work. For example, his treatment of thermionics, in one form or another, is sprinkled through our chemical and physical literature from 1915 to date, and radio tubes are still being improved by it. A similar growth of knowledge of mercury-arc characteristics is shown in his writings, as well as such speculative concepts as the Lewis-Langmuir octet theory of atoms. While these purely scientific researches were under way he found time to develop one of the most efficient vacuum pumps known. This was described under the title, "A High Vacuum Mercury Pump of Extreme Speed," and these pumps were at once put into the factories to meet the severe requirements of radio and x-ray tube production.

The Mind of Langmuir

I like to think of the Medalist as an example of what a good scientific education may do when it has first-class raw material to work upon. Langmuir's is not a case of weak exposure to some mental contagion which clung to him, but a case of virile acquisition and constructive use of a stock of modern science which he has always kept increasing. It is only in recent years that scientists or engineers working in industry have been both technically productive and active in publishing new scientific data. Langmuir has done much to encourage others in this way. He has averaged seven publications each year for sixteen years. I have been interested to note the persistence with which he has continued along each of his chosen paths of research. In his publications he discloses the daily accretions to his knowledge, and he never loses interest in a subject, for knowledge of it is never complete.

Doctor Langmuir is endowed with such an unusual analytical and sharp focusing mind that it would be foolish to say that anyone could have done his work who was merely persistent, thoughtful, optimistic, and energetic. I don't know how analytical minds become endowed. But I know that good education at least helps. Many young men lose inquisitiveness and acquire a fear-complex or some satisfying polarization before they reach the happy level of sustained and exciting flight. My sixteen years of observation of Langmuir convince me that an analytical mind, supported by optimistic, single-minded devotion to Nature's old cross-word puzzles and novelties, accounts for much of his success, and that perhaps none of these necessary attributes need be exclusively his. I don't like the word "superman" in this connection, and as he is a fearless speculator he is not supersensitive. The word "supersensible" seems to fit the occasion.

Radio Tubes

When we come to radio tubes, Langmuir's apparent natural fertility is most marked. To recite even the titles of his publications would be exhausting. From the very first experiment, where he was studying the emission of negative current from the old-time carbon filaments and trying to check up the Richardson equation, down to the new radio tubes of today, he seemed to have a clear preview of the phenomena. When he first talked of pure thermionic emission no one believed in it. All measured results had consisted of mixed gas-ion and electronic conductions. I doubt if the laws of electron emission would have been proved for years but for his work on the tungsten filament. Starting from the first proof of discharges in vacua as determined strictly by filament temperature (which was the basis of his first radio tubes), he proceeded to find out quantitatively how traces of gases affected the currents. He had developed the now well-known conception of space charge in case of the electrons, and then was able to understand better the ionic conduction which has also found application in so-called gas tubes. His work on the electron emission of thoria and other elements as components of tungsten filaments led to enormous increases in efficiency of radio tubes. I will not analyze the extensive group of tubes which came from this work, but I must list here the kenotron, the pliotron, the magnetron, the axiotron, the thyratron, the dynatron, and the pliodynatron, which he and his co-workers developed for places in the growing radiotron family.

A Modern Crystal Gazer

When Langmuir first told me he thought he could make a better tungsten lamp by putting gases into it than by trying to further exhaust it, I thought he was dreaming. And so he was. But it was the kind of dream he could make come true. Nothing had seemed more improbable a few months earlier. Through his study of conduction and convection of heat by gases, combined with the laws of radiation of energy from hot filaments, he decided that a filament could be made large as a light giver and relatively small as a heat loser. He had already determined the beneficial effect of gases in reducing the rate of evaporation of tungsten at high temperatures, and so, by coiling the fine tungsten wire into a helix, so that its entire surface gave light, while the heat losses were only those of the short cylinder defined by the wire, he was enabled to make the reduction in the cost of light previously mentioned.

There is something in Langmuir's work that suggests, by sharp contrast, an oriental crystal gazer seated idly before a transparent globe and trying to read the future without doing anything about it—a hopeless philosophy. In my picture an equally transparent and more vacuous globe takes the place of the conventional crystal sphere. It is a lamp bulb, a real light source. Langmuir boldly takes it in his hand, not as some apathetic or ascetic Yogi, but more like a healthy boy analyzing a new toy even as Langmuir himself studied and fixed the complex watch of his boyhood days, but seeing visions, too, of many new things. There might have been nothing in that vacuum, but he was driven by insatiable curiosity to investigate and learn for himself.

Thus he peopled that empty space with new and strange little beings or personalities which he had first dreamed of, then devised, and finally endowed with real character—and all this solely to make his various dreams come true. He first dreamed that tungsten atoms were being carried by disreputable foreign atoms (oxygens) from the filament to the glass to obstruct the light. These were parts of disobedient water molecules which had not come out when commanded. They were divorced by the filament and were bootlegging tungsten in the one place in the world where a dry law was absolutely necessary. He dreamed of banishing or imprisoning these bootleggers. When Langmuir made this dream come true we got good, clear, long-lived tungsten lamps.

Still he dreamed, with both eyes on the ball, of a greater light. Therefore he populated the lamp bulb with new beings, rare gases of dependable character, like nitrogen or argon. His divorced water molecules had taught the danger of affinities, so he chose for this new lamp investion a great horde of argon molecules. These had no affinities and are never divorced because they never marry. By this method the light he foresaw in the bulb became just twice as great as it was before, and all of us now easily see it, and the world is glad to pay for it.

Gazing into the same sphere again, he dreamed about disembodied electricity, and soon the reliable little electrons were tamely obeying special laws—laws that had never been known

before and that most men do not yet understand. He gazed again and saw outlaw atoms coöperating with his electrons, so that he was able to add to the thermionic servants of the radio sphere accurately controlled groups of electrical helpers in the shape of gas ions, and thus he continually improved radio tubes.

Here lies the difference between the ancient and the modern seers or prophets. The modern prophet is a doer. No one can fix the best ratio between thinking and doing. The pure thinker is apt to think too much and the active man to be too active. Evidently that Mendelian law which determines mutations and produces increased strength by cross-breeding explains why a certain mixture of thinking and acting yields greatest product. I know of no one who seems to combine these two characteristics in better balanced ratio than Langmuir.

. . . . . .

Atomic Hydrogen as an Aid to Industrial Research

Irving Langmuir

General Electric Company, Schenectady, N. Y.

I BELIEVE the primary object of the Perkin Medal is to do honor to the memory of Sir William Perkin, that pioneer who devoted himself to pure scientific research after having led in the industrial applications of research for fifteen years. This object is best attained by encouraging the kind of research that he valued so highly. The medal should thus be regarded, not as a reward for accomplishment nor as a prize to stimulate competition in research, but rather as a means of directing attention to the value of research and to the methods of research that are most productive. Having this in mind, I am going to tell you, although somewhat reluctantly, the history of some of my own work, in so far as it illustrates a method of industrial research that has proved valuable.

Two Types of Industrial Research

The leaders of industries are frequently conscious of the need of improvement in their processes, and even of the need of new discoveries or inventions which will extend their activities. It is thus logical, and often extremely profitable, to organize research laboratories to solve specific problems. Efficiency requires that the director shall assign to each worker a carefully planned program. Experiments which do not logically fit in with this program are to be discouraged. This type of industrial research, which should often be called engineering rather than research, has frequently been very successful in solving specific problems, but usually along lines already foreseen.

This method, however, has serious limitations. Directors are rare who can foresee the solutions sufficiently well to plan out a good compaign of attack in advance. Then, too, the best type of research man does not like to be told too definitely what must be the objects of his experiments. To him scientific curiosity is usually a greater incentive than the hope of commercially useful results. Fortunately, however, with proper encouragement, this curiosity itself is a guide that may lead to fundamental discoveries, and thus may solve the specific problems in still better ways than could have been reached by a direct attack; or may lead to valuable by-products in the form of new lines of activity for the industrial organization.

Of course, no industrial laboratory should neglect the possibilities of the first and older method of organized industrial research. I wish, however, to dwell upon the merits of the second method in which pure science or scientific curiosity is the guide.

History of the Gas-Filled Lamp

I first entered the Research Laboratory of the General Electric Company in the summer of 1909, expecting in the fall to return to Stevens Institute, where I had been teaching chemistry. Instead of assigning me to any definite work, Doctor Whitney suggested that I spend several days in the various rooms of the laboratory, becoming familiar with the work that was being done by the different men. He asked me to let him know what I found of most interest as a problem for the summer vacation.

A large part of the laboratory staff was busily engaged in the development of drawn tungsten wire made by the then new Coolidge process. A serious difficulty was being experienced in overcoming the "offsetting" of the filaments, a kind of brittleness which appeared only when the lamps were run on alternating current. Out of a large number of samples of wire, three had accidentally been produced which gave lamps that ran as well with alternating as with direct current, but it was not known just what had made these wires so good. It seemed to me that there was one factor that had not been considered—that is, that the offsetting might possibly be due to impurities in the wire in the form of gases. I therefore suggested to Doctor Whitney that I would like to heat various samples of wire in high vacuum and measure the quantities of gas obtained in each case.

In looking through the laboratory I had been particularly impressed with the remarkably good methods that were used for exhausting lamps. These methods were, I thought, far better than those known to scientific research workers. My desire to become more familiar with these methods was undoubtedly one of the factors that led me to select for my first research an investigation of the gas content of wires.

After starting the measurements that I had planned, I found that the filaments gave off surprisingly large quantities of gas. Within a couple of weeks I realized that something was entirely wrong with my apparatus, because from a small filament in a couple of days I obtained a quantity of gas which had, at atmospheric pressure, a volume 7000 times that of the filament from which it appeared to have come; and even then there was no indication that this gas evolution was going to stop. It is true that in the literature—for example in J. J. Thomson's book on the "Conduction of Electricity through Gases"—one found many statements that metals in vacuum give off gases almost indefinitely, and that it is impossible to free metals from gas by heating. Still I thought that 7000 times its own volume of gas was an entirely unreasonable amount to obtain from a filament. I spent most of the summer in trying to find where this gas came from, and never did investigate the different samples of wire to see how much gas they contained. How much more logical it would have been if I had dropped the work as soon as I found that I would not be able to get useful information on the "offsetting" problem by the method that I had employed.

What I really learned during that summer was that glass surfaces which have not been heated a long time in vacuum slowly give off water vapor, and this reacts with a tungsten filament to produce hydrogen, and also that the vapors of vaseline from a ground-glass joint in the vacuum system give off hydrocarbon vapors, which produce hydrogen and carbon monoxide.

That summer's work was so interesting that I dreaded to return to the comparative monotony of teaching, and gladly accepted Doctor Whitney's offer to continue at work in the laboratory. No definite program of work was laid down. I was given first one assistant and then others to continue experiments on the

sources of gas within vacuum apparatus, and a study of the effects produced by the introducton of various gases into tungsten filament lamps. The truth is that I was merely curious about the mysterious phenomena that occur in these lamps. Doctor Whitney had previously found that gases have a habit of disappearing in lamps, and no one knew where they went to, so I wanted to introduce each different kind of gas that I could lay my hands on into a lamp with a tungsten filament and find out definitely what happened to that gas.

It was the universal opinion among the lamp engineers with whom I came in contact that if only a much better vacuum could be produced in a lamp a better lamp would result. Doctor Whitney, particularly, believed that every effort should be made to improve the vacuum, for all laboratory experience seemed to indicate that this was the hopeful line of attack on the problem of a better lamp. However, I really didn't know how to produce a better vacuum, and instead proposed to study the bad effects of gases by putting gases in the lamp. I hoped that in this way I would become so familiar with these effects of gas that I could extrapolate to zero gas pressure, and thus predict, without really trying it, how good the lamp would be if we could produce a perfect vacuum.

Irving Langmuir

This principle of research I have found extremely useful on many occasions. When it is suspected that some useful result is to be obtained by avoiding certain undesired factors, but it is found that these factors are very difficult to avoid, then it is a good plan to increase deliberately each of these factors in turn so as to exaggerate their bad effects, and thus become so familiar with them that one can determine whether it is really worth while avoiding them. For example, if you have in lamps a vacuum as good as you know how to produce, but suspect that the lamps would be better if you had a vacuum, say, 100 times as good, it may be the best policy, instead of attempting to devise methods of improving this vacuum, to spoil the vacuum deliberately in known ways, and you may then find that no improvement in vacuum is needed or, just how much better the vacuum needs to be.

During these first few years, while I was thus having such a good time satisfying my curiosity and publishing scientific papers on chemical reactions at low pressures, I frequently wondered whether it was fair that I should spend my whole time in an industrial organization on such purely scientific work, for I confess I didn't see what applications could be made of it, nor did I even have any applications in mind. Several times I talked the matter over with Doctor Whitney, saying that I could not tell where this work was going to lead us. He replied that it was not necessary, as far as he was concerned, that it should lead anywhere. He would like to see me continue working along any fundamental lines that would give us more information in regard to the phenomena taking place in incandescent lamps, and that I should feel myself perfectly free to go ahead on any such lines that seemed of interest to me. For nearly three years I worked in this way with several assistants before any real application was made of any of my work. In adopting this broad-minded attitude Doctor Whitney showed himself to be a real pioneer in the new type of modern industrial research.

For my study of the effect of gases, I had to devise new types of vacuum apparatus. I needed particularly to be able to analyze the small quantities of gas that existed in the tungsten lamp. With some of this special apparatus I was able to make a practically complete quantitative analysis of an amount of gas which would occupy about 1 cu. mm. at atmospheric pressure. In this sample of gas we could determine the percentages of oxygen, hydrogen, nitrogen, carbon dioxide, carbon monoxide, and the inert gases.

In regard to the fate of the different gases which I introduced into the lamp bulb, I found that no two gases acted alike. Oxygen attacked the filament and formed tungstic oxide, WO_3. That seemed simple enough, but the kinetics of the reaction presented many features of considerable scientific interest.

In studying the effect of hydrogen very peculiar phenomena were observed. A limited amount of hydrogen disappeared and became adsorbed on the bulb, where it remained in a chemically active form, which was capable of reacting with oxygen at room temperature even long after the tungsten filament had been allowed to cool. This suggested hydrogen atoms and seemed to confirm some conclusions that I had already drawn from observations on the heat losses from tungsten filaments in hydrogen at atmospheric pressure. In making squirted tungsten filaments, and sometimes in cleaning the drawn wire, filaments were heated in this manner in hydrogen. Because tungsten filaments melt at a temperature more than 1500° higher than platinum, it had seemed to me that tungsten furnishes a tool of particular value for the scientific study of phenomena in gases at high temperatures. From my work on lamps I knew approximately the relation between the resistance of tungsten wire and its temperature, and could thus use a tungsten wire as a kind of resistance thermometer. By connecting a voltmeter and an ammeter to the tungsten filament which was being heated in hydrogen, I could determine the temperature from the resistance and also find the heat loss from the filament in watts. I wanted to see if anything abnormal happened when the temperature was raised to the extremes which were only possible with tungsten.

The results greatly interested me, for they showed that the energy loss through the gas, which increased in proportion to the square of the temperature up to about 1800° K., increased at a much higher rate above that, until at the highest temperatures the energy varied in proportion to about the fifth power of the temperature. This result could be explained if the hydrogen at high temperatures were dissociated into atoms. The diffusion of the hydrogen atoms from the filament, and their recombination at a distance from it, would cause an enormous increase in heat conduction. After publishing these preliminary results, I was naturally much interested in getting other information in regard to the properties of these hydrogen atoms. A large number of experiments, extending over several years, were thus made in this study of atomic hydrogen. Nearly all of these experiments would have seemed quite useless, or even foolish, to a man who was making a direct and logical attack on the problem of improving tungsten lamps.

When nitrogen at low pressure was introduced into a bulb containing a tungsten filament at extremely high temperatures, such as 2800° K., the nitrogen disappeared at a rate which was independent of its pressure; in other words, here was a case of a reaction of zeroth order. This suggested that the reaction velocity was limited by the rate at which the tungsten evaporated from the filament. To check this hypothesis the rate of loss of weight of filaments at various temperatures was measured in

good vacuum. This rate varied with the temperature in accordance with known thermodynamic laws, and since the rate per unit area was independent of the size of the filament, it was concluded that the loss of weight was really due to evaporation and not to chemical action of residual gases or to electric currents that passed from the filament to the surrounding space.

A comparison of the rate of disappearance of nitrogen with the loss of weight in the filament showed that one molecule of nitrogen disappeared for every atom of tungsten that evaporated. A brown compound, WN_2, was formed which deposited on the bulb and decomposed when water vapor was introduced, forming ammonia gas.

From time to time the question kept arising—how good would a lamp be if it had a perfect vacuum? And now, from studies of the character I have described, I began to have an answer. Hydrogen, oxygen, nitrogen, carbon monoxide, and in fact every gas that I introduced, with the exception of water vapor, did not produce blackening of the lamp bulb. The serious blackening that occurred with only small amounts of water vapor depended upon a cyclic reaction in which atomic hydrogen played an essential part. The water-vapor molecules coming in contact with the hot filament produce a volatile oxide of tungsten, and the hydrogen is liberated in atomic form. The volatile oxide deposits on the bulb where it is reduced to the metallic state by the atomic hydrogen, while the water vapor produced returns to the filament and causes the action to be repeated indefinitely. Thus, a minute quantity of water vapor may cause a relatively enormous amount of tungsten to be carried to the bulb.

The question then arose whether the traces of water vapor, which might still exist in a well-exhausted lamp, were responsible for the blackening which limited the life or the efficiency of many of these lamps. We made some tests in which well-made lamps were kept completely immersed in liquid air during their life, so that there could be no possibility of water vapor coming in contact with the filament. The rate of blackening, however, was exactly the same as if no liquid air had been used.

Having thus proved that the blackening of a well-made lamp was due solely to evaporation, I could conclude with certainty that the life of the lamp would not be appreciably improved even if we could produce a perfect vacuum.

Early in 1911 William Stanley, one of the pioneers in the electrical industry, felt that our company should do more fundamental work in connection with heating devices. Since I had become interested in the theory of heat losses from filaments in gases, I was glad to work along these lines, so I undertook to direct a small laboratory at Pittsfield, Mass., at which I spent about two days a week. Besides studying the heat losses from plane surfaces at various temperatures, I measured the heat losses from wires of various sizes in air at different temperatures, working at first with platinum wires, and was able to develop a theory of the heat losses which enabled me to calculate the loss from a wire of any size at any temperature in any gas, assuming, however, that the gas did not dissociate at high temperatures.

Having now a definite theoretical basis on which to calculate the normal loss by convection, I was able to prove that the abnormal rate of heat loss previously observed with tungsten filaments at high temperatures in hydrogen was due to actual dissociation; in fact I was thus able to calculate the heat of dissociation and the degree of dissociation at different temperatures.

However, to make sure of these conclusions I wished to make measurements of the heat losses in gases which could not possibly dissociate, and therefore undertook experiments with heated tungsten wires in mercury vapor at atmospheric pressure. A little later I experimented with nitrogen to see if this gas dissociated at high temperatures, but found that it did not do so. In both of these gases the filaments could be maintained at temperatures close to the melting point for a far longer time than if heated in vacuum at the same temperature. Thus the rate of evaporation was greatly decreased by the gas, many of the evaporating tungsten atoms being brought back to the filament after striking the gas molecules.

By this time I was familiar with all the harmful effects which gas can produce in contact with filaments and knew under what conditions these bad effects could be avoided. In particular, I realized the importance of avoiding even almost infinitesimal traces of water vapor. Thus, when I found a marked effect of mercury vapor and nitrogen in reducing the rate of evaporation, it occurred to me that it might be possible to operate a tungsten filament in gas at atmospheric pressure and obtain a long useful life. Of course, it would be necessary to raise the temperature far above that at which the filament could be operated in vacuum in order to compensate for the serious loss in efficiency due to convection by the improved efficiency resulting from the rise in filament temperature. Whether or not the increased rate of evaporation, due to this increase in temperature, would more than offset the decrease in the rate due to the gas was a matter that could only be tested by experiment.

In connection with my studies of the heat losses from filaments of various diameters at incandescent temperatures, I had found that the heat loss increased only very slowly with the diameter, so that the loss per unit area from a small filament was enormously greater than from a large filament. Calculations showed that it was hopeless to get practical lamps with filaments in nitrogen, if these filaments were of very small diameter. For example, a filament 1 mil in diameter, which corresponds to an ordinary 25-watt lamp, if run in nitrogen at atmospheric pressure would consume 4.8 watts per candle at a temperature of 2400° K., which would give 1 watt per candle with a filament in vacuum. This great loss in efficiency is due to the cooling effect of gas. To bring back the efficiency of the gas-filled lamp to that of the vacuum lamp, it would be necessary to raise the temperature from 2400° to 3000° K., which would have caused a 2000-fold increase in the rate of evaporation, and such an increase could certainly not be compensated for by the effect of the gas in retarding the evaporation.

With filaments of much larger diameter, however, the effect of the gas in decreasing the efficiency was not nearly so marked. We therefore constructed lamps having filaments of large diameter in the form of a single loop and filled these lamps with nitrogen at atmospheric pressure. We ran these lamps with a filament temperature so high that, in spite of the gas, the efficiency corresponded to about 0.8 watt per candle, instead of the usual 1 watt per candle at which we tested our vacuum lamps. We were disappointed to find that these lamps blackened much more rapidly than vacuum lamps of similar efficiency so that the total useful life of the lamp was short.

This result, which is what most lamp engineers would have expected, seemed to indicate that the rise in temperature necessary to offset the heat losses by the gas increased the evaporation by more than the amount of the reduction in evaporation due to the gas. If I had not previously become so familiar with the behavior of various gases, this discouraging result might easily have stopped further experimenting in this direction. However, I noticed that the bulb had blackened during the short life of the lamp, whereas from my knowledge of the interaction of tungsten and nitrogen I had expected a deposit of a clear brown color. I felt that the black deposit, therefore, could mean only one thing, water vapor, notwithstanding the fact that to avoid this water vapor we had taken precautions which were greater, I believe, than had ever been used before for the preparation of moisture-free gases and glass surfaces. We were thus led to take still greater precautions and use still larger bulbs, so that the glass surfaces could not become overheated by the convection currents in the gas that rose from the filament. We were then soon able to make lamps having a life of over 1000 hours with an efficiency about 30 to 40 per cent better than could have been obtained with filaments in vacuum.

As I look back upon these experiments I think that we were

very fortunate at that time in not having had at our disposal a supply of argon gas. From theoretical reasons I had concluded that argon should be better than nitrogen, and if I had had argon I should probably have tried it first. If these lamps had blackened because of traces of water vapor, I would naturally have attributed this to the increase in evaporation caused by the high temperature, and would have had no reason for suspecting that water vapor was the cause of the trouble, for, of course, in argon a brown deposit would not be expected in any case.

The lamps that we were able to make in this way, with an improved efficiency, were limited to those which took a current of 5 amperes or more, so that the method was not applicable for 110-volt lamps with less than 500 watts. Some time later, however, it occurred to me that the benefits derived from the large diameter of the filament could be obtained with one of smaller diameter by coiling the filament in the form of a helix, bringing the turns of the helix very close together. In this way, and by the use of improved tungsten filaments that do not sag so readily at high temperatures, and by using argon instead of nitrogen, it has gradually been possible to construct gas-filled lamps which are better than vacuum lamps down to about 40 or 50 watts. These smaller lamps, although not much better in efficiency than the vacuum lamp, have the advantage of giving a much whiter light. In the case of the larger lamps, the use of the gas filling, together with the special construction of the lamp, more than doubles the efficiency.

The invention of the gas-filled lamp is thus nearly a direct result of experiments made for the purpose of studying atomic hydrogen. I had no other object in view when I first heated tungsten filaments in gases at atmospheric pressure. Even at the time that I made these experiments at higher pressures, they would have seemed to me useless if my prime object had been to improve the tungsten lamp.

I hope I have made clear the important role that properly encouraged scientific curiosity can have in industrial research. The illustration that I have given is not at all exceptional. I could have given any one of several others equally well. Many industrial laboratories have followed Doctor Whitney's lead, in devoting a fairly large fraction of their activities to these rather purely scientific researches. Certain men, at least, are not expected to be responsible for practical applications, put are freely allowed to make fundamental scientific investigations. The type of man who does this work best can usually only be attracted to those industrial laboratories that have adopted this policy.

However, I do not believe that this second method of research is growing in popularity solely because it is found to be profitable. I feel rather that most of our leaders in industrial research are eager to adopt this method, in so far as economic factors may permit, because they realize the debt that modern industry owes to the pure science of the past and because the modern conception of service and the growing *esprit de corps* of American industry help make them glad of any opportunity to contribute to scientific knowledge. I know personally that such motives as these have guided Doctor Whitney in the leadership he has taken.

I believe in the near future there will be a much increased demand for men with scientific training who are capable of doing more independent thinking.

Better Education Needed

Our schools and universities devote so much effort in imparting information to students that they almost neglect the far more important function of teaching the student how to get for himself what knowledge of any subject he may need. Even in grammar school children are crammed with more information on arbitrarily selected subjects than even the average well-educated adult can retain. Of course students should be taught the fundamental principles of mathematics, and of various sciences as well as of other subjects, but much of the knowledge of data upon which these principles depend and necessary information should be obtained by the efforts of the student through experimentation and individual reading.

In looking back on my own school and college days, it seems to me that the things of most value were learned spontaneously through interest aroused by a good teacher, while the required work was usually comparatively uninteresting. The university student should have leisure for some independent work and opportunities for continuing his interest in hobbies of various kinds which he should have had long before he entered college. I realize that it is difficult so to arouse the student's interest that he will spend the added leisure in these ways rather than in spending still more on the bleachers, cheering the football team in their practice games, but a well-planned effort is worth while.

The importance of arousing even a young boy's interest in independent work can hardly be overemphasized. My real interest in science was derived from my brother Arthur, who encouraged me to have a workshop at the age of nine, and later a laboratory when I was only twelve.

I can illustrate my father's influence in stimulating independence by the following incident: When I was twelve I climbed one or two Swiss mountains of moderate height with my older brother, Arthur. Soon after Arthur had to go to Heidelberg to arrange for his studies, leaving me with my mother and younger brother at a hotel in the Rhone Valley. I had become so enthusiastic over mountain climbing that I wished to climb everything in sight, but the dangers were such that my mother did not dare let me go alone. When my father arrived for a week-end visit from Paris, he consented to allow me to climb alone any mountain I liked if I would promise to do it in accord with the following three rules: (1) I must stay on a distinct trail; (2) I must use the same trail going and returning; (3) I must make certain of returning at six o'clock by allowing as much time for descending as for ascending. Before these rules went into effect, however, I had to prove that I could and would make such sketches, maps, and notes of the trails used for the ascent that I could always return by the same route. I thus climbed several mountains about 7000 feet high, often requiring several days of repeated effort before I could discover a route that led to the top. Perhaps it is this experience which makes me even today always wish to find my own way rather than be told.

Until I was fourteen I always hated school and did poorly at it. At a small boarding school in the suburbs of Paris, however, being an American and having a friend who was influential with the head of the school, I was freed from much of the absurdly rigorous discipline to which the French boys were subjected. Thus, I could spend time alone in the school laboratory and was encouraged by one of the teachers to learn to use logarithms and solve problems in trigonometry, subjects not required by the curriculum.

I have been fortunate in having many wonderful teachers. Three of them have been recipients of this Perkin Medal. Whitaker and Chandler were my teachers at Columbia and Whitney during the last eighteen years. Prof. R. S. Woodward, at Columbia, in connection with his courses in mechanics, was extremely stimulating and encouraged me to choose and solve my own problems for class work instead of those required in the regular course.

I should like to see spontaneous work of this kind take a much more prominent part in our educational system—at least for students who have more than average ability.

The Value of Hobbies

Very great benefit may be derived from hobbies. Probably each person should have several of them. Recently I met a small boy, only six years old, who had an overpowering, wide-eyed enthusiasm for collecting insects. He weighed each one of them within a milligram, and then, after desiccating them thoroughly over calcium chloride, weighed them again. Many elaborate notes and even correspondence resulted. I am afraid

our universities, with their dormitories and other standardizations, tend to discourage such wholesome individual activites.

After talking of hobbies, I cannot resist the temptation to tell something about my own. Perhaps my most deeply rooted hobby is to understand the mechanism of simple and familiar natural phenomena. I will give only two illustrations, but these, I hope, will show how easy it is to find around us simple phenomena that are not well understood.

Every chemist knows that after he stirs a liquid in a beaker having a precipitate in the bottom, the precipitate collects near the center. Probably few know why this is so. It is not due to the slower velocity of rotation near the center, nor to the slower motion with respect to the glass. This is proved by the fact that if you put the beaker, with the precipitate in suspension in the liquid, upon a rotating table, the precipitate will collect in a ring as far from the center as possible, although the relative angular motion of the beaker and its contents is the same as before. A little study proves that the phenomena are due to unbalanced centrifugal forces. For example, when the liquid is stirred to set it in rotation, centrifugal force produces a greater hydrostatic pressure near the walls of the beaker. But the liquid very close to the bottom surface of the beaker, because of friction, cannot rotate so fast, and therefore the centrifugal force is not so great and does not counteract the radial hydrostatic pressure difference existing in the upper layers. The liquid in contact with the glass bottom is thus forced inwards and carries the precipitate with it.

The phenomena connected with the formation and the disappearance of ice in a large lake, such as Lake George, have interested me for years. One clear night at the end of December, when the water of a large bay was at a uniform temperature of not over 0.2° C. and the air temperature was −22° C., ice, which formed slowly at some places on the shore, melted in a couple of minutes when pushed out a few meters from the shore. There was no wind in the bay, but a slight breeze over the central part of the lake caused a very slow circulation of water in the bay with a velocity of perhaps 1 or 2 cm. per second.

In contrast with this consider the phenomena observed one clear afternoon of the following April. The body of the lake was still covered with ice, which was about 20 cm. thick, but close to the shore there were places where the ice had melted back for a distance of 5 meters or more. Although the air temperature was +3° C. and the water 10 cm. below the surface was at +2.5° C., ice crystals about 50 cm. long formed in these pools in less than half an hour. After considerable analysis I believe I can explain this apparent paradox by the stability in the stratification of the water in April caused by the denser underlying warm water which had been heated by the sun. With this stability which prevented vertical convection the surface water could freeze because of the radiation into the clear sky. But in December the water temperature was so uniform that the differences of density were not sufficient to prevent vertical circulation, and thus the surface could not cool to the freezing point. It appears, then, that a pool of water at +1° C., exposed to cold air with a slight wind, can be made to freeze more rapidly if the water is heated from the bottom. Sometime I want to try this as an experiment.

All hobbies, however, stimulate individual action, and many develop wholesome curiosity. The child should acquire them early, and our educational system should foster them.

BOOK REVIEWS

Final Report of the Committee on Spray Coating. 53 pages. Chemical Section, National Safety Council, Chicago, 1927.

Recognizing the possible importance of the health problems involved in applying paints and other coating materials by means of the spray method, the National Safety Council created a committee to study this problem. The twenty-three members were representatives of federal and state bureaus, universities, national health organizations, insurance companies, organized labor, and manufacturers of materials and equipment used in spray coating.

The field studies were conducted in automobile and automobile body factories, in vitreous enameling plants, and among contracting painters, embracing twenty-nine groups of workers. Eighty-six air tests were made for benzene, twenty-seven for lead, and thirty-six for silica. A total of 364 physical examinations were made as were 349 blood examinations.

The report discloses the fact that workers spraying materials containing benzene, lead, and silica are liable to become poisoned by these materials, and in the case of the last substance are likely in a period of occupation of over three years to develop silicosis or fibrosis of the lungs. Using a full-sized spray booth as an experimental unit the committee found that an exhaust velocity of 200 feet per minute was required to protect the worker. In the absence of such protection the use of a positive pressure respirator is recommended as the only device tested which does not impede respiration and still yields protection. The elimination of benzene and lead and the substitution of a balanced fritted mixture free from soluble lead and free silica is urgently recommended by the committee.

The present study of the problem is the first of any real scope and significance with which the writer is familiar. And to one who is familiar with the technic of field studies in industrial hygiene, the facts presented in this report must bear much weight and appear of real significance.

The last page of the pamphlet contains a summary of a minority report presented by two members of the committee.

LEONARD GREENBURG

Textile Color Mixing. A Manual Intended for the Use of Dyers, Calico Printers, and Color Chemists. BY DAVID PATERSON. 3rd revised edition. 137 pages. D. Van Nostrand Co., Inc., New York, 1927. Price, $4.50.

When a third revised edition of a book appears twenty-seven years after the publishing of the first, one may well sense a feeling of disappointment in finding no substantial changes in the new edition. In this case, with the exception of a paragraph on wave theory of light in the first chapter and the substitution in some instances of modern dyes for pre-war ones, this book repeats word for word its first edition. It may be true that little more progress has taken place in this period in the art and practice of color mixing, yet we look to writers of texts such as this to interpret whatever is new in physics and chemistry in terms of the art or industry.

The first five chapters deal with theory of light and color and serve well to define the various terms and conditions involved. A practical dyer who is interested in an explanation of the phenomena of color mixing should find these chapters worth reading. The student of the theory of color production is likely to be dissatisfied with the lack of details concerning such practical applications as the mechanism and operation of spectroscopes and photometers.

The last three chapters deal with actual color mixing and should be of interest, particularly to a student or beginner, though offering little help for the experienced dyer.

E. M. SHELTON

The Making of a Chemical. A Guide to Works Practice. BY E. I. LEWIS AND GEORGE KING. 280 pages. John Wiley and Sons, Inc., New York, 1926. Price, cloth, $4.00.

If the reader of this book expects to learn of the scientific and technical method of procedure in making a chemical product, he will be disappointed. As the authors indicate in the preface, it is meant for the student who expects to enter industry. The

material given is no different from what a teacher experienced in industry would give a class in courses in chemical engineering. If the teacher has had no such experience, the book will call to his attention some of the things the students ought to know. It might be called a book on orientation for the chemist or chemical engineer who expects to enter the chemical industries. Though not very technical, it should make excellent supplementary reading. The language in some sections is not entirely appropriate to the subject.

The subjects discussed include the educational preparation required for the chemist, the four stages in the development of a chemical process, economics of making and selling a chemical product, materials of construction in a plant, energy and power, and the chemical engineering unit operations. These unit operations, however, are discussed too briefly and in a non-technical way.

This book should be helpful to the chemical engineer already in industry. Much in the book can be learned only through the hard knocks of experience and not by mere reading or laying down of rules.

C. S. MANN

The Chemistry of Water and Sewage Treatment. BY A. M. BUSWELL. A. C. S. Monograph Series No. 38. 362 pages. The Chemical Catalog Company, Inc., 1928. Price, $4.00.

Workers in the field of water and sewage have long awaited a comprehensive treatise on their subject. Particularly in the treatment of sewage progress has been so rapid that it has been difficult to keep informed on the latest methods and theories. The author has done a very satisfactory piece of work in assembling recent data and in interpreting a bibliography of over four thousand references on water and sewage.

The author has commendably kept within his subject and has not tried to cover construction or operation of mechanical devices. He emphasizes the lack of a satisfactory yardstick for measuring purification processes, but leaves the discussion of methods of analysis to previously published books. The reviewer feels that the book would have been of additional value had it called more attention to the fallacies and difficulties encountered in sewage and waste analysis.

The chemistry of water and sewage is so intimately associated with the laws of dilute solutions and colloidal properties that the first three chapters are devoted appropriately to a review of the present knowledge and theories of these subjects, particularly as they apply to water and sewage. In the chapters on water-softening the author did not follow out the ionic conception so thoroughly developed in the first few chapters, but reverted to the classification and treatment of waters on the basis of hypothetical combinations instead of ions and milliequivalents. The latter method would have been a more logical development from the theoretical basis established in the first chapters.

The theories on the mechanisms of water and sewage treatment are ably given. The author favors the biological theories of sewage treatment over the mechanical ones. The discussions, however, are very fair to both sides of the argument.

The subject matter is well presented, meets a crying need in its field, and deserves to be on the book shelves of all interested in water and sewage.

W. D. HATFIELD

Thermionic Phenomena. BY EUGENE BLOCH, translated by J. R. CLARKE. 145 pages. E. P. Dutton & Co., New York, 1927. Price, $2.50.

The contents of this small volume constitute practically an abridgment of the classic treatise by Richardson on the same subject (1921), although a chapter has been added at the end in which there are discussed the results published by Dushman in 1915 on the kenotron, and the work of Buckley, Found, and Dushman on the ionization gage. While there is an excuse, owing to date of publication, for the omission of more recent results in the French edition, there seems to be no reason for the glaring defects in this respect of the present translation. Thus no mention is made of Langmuir's work on thoriated tungsten filaments (1923), nor of the work of Langmuir and Kingdon on thermionic effects observed with caesium on tungsten (1925), while the discussion of oxide coated cathodes is very brief.

Other illustrations could be added of results published in this field prior to 1926, none of which are even mentioned. On the whole, the reader will be very much disappointed if he expects to find in this volume an up-to-date discussion of the subject. It is at least six years behind the times.

SAUL DUSHMAN

Fuel for Motor Transport. Fourth Memorandum. Power Alcohol from Grasses, Straws, and Waste Vegetable Materials. FUEL RESEARCH BOARD, DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH. 26 pages. His Majesty's Stationery Office, London, 1927. Price, 9 d. net.

The fourth memorandum on Fuel for Motor Transport, issued by the Fuel Research Board of Great Britain, points out the possibility of producing power alcohol from grasses, straws, and waste vegetable materials. Results of a number of experiments are discussed and the details of a process given. Apparently, no insurmountable technical difficulties are involved, the principal consideration being the economic one of a sufficient supply of raw materials at low cost for collection and storage.

Organic Syntheses. An Annual Publication of Satisfactory Methods for the Preparation of Organic Chemicals. Vol. VII. FRANK C. WHITMORE, Editor-in-chief. 105 pages. John Wiley and Sons, Inc., New York; Chapman and Hall, Ltd., London, 1927. Price, $1.50.

This valuable contribution to chemical literature presents detailed directions for preparing thirty organic chemicals. The list covers a wide range, including some compounds of mercury and arsenic, several heterocyclic compounds and a few of the commoner reagents. Every necessary step in each synthetic process is described with precision and references to earlier work are included. Each preparation has been carefully checked. Every time a volume in this series appears the research chemist becomes less dependent upon the commercial supply of reagents. The book contains one page of additions and corrections for preceding volumes.

C. W. PORTER

Die Chemie der Braunkohle. BY E. ERDMANN AND M. DOLCH. 2nd edition. $7^3/_4$ by 11 inches. 598 pages. 191 illustrations. Wilhelm Knapp, Halle (Saale), 1927.

This edition of Erdmann's comprehensive work on the chemistry of brown coal has been revised and enlarged by Doctor Dolch with the collaboration of other leading specialists. Erdmann and Dolch in the first 288 pages cover the scientific part of the subject. In the remaining 310 pages processes, equipment, and operating methods used in the brown-coal industry are discussed by A. Thau; the working up of brown coal tar, by J. Metzger; the gasification of brown coal, by H. R. Trenkler; and the technology of bitumen extracting, refining, and utilization, by H. Bube and R. Heinze.

All the chapters bear evidence of thorough search of the literature and careful editing. The technical standing of the collaborators insures authoritative information. The entire volume is replete with original references. Although brown coals are not found in America, much of the subject matter of this book can be read with profit by American fuel technologists interested in the processing of coal in general.

A. C. FIELDNER

Hütte. Taschenbuch für den praktischen Chemiker. Edited by FRANZ PETERS. xvi + 898 pages. Many illustrations. Wilhelm Ernst & Sohn, Berlin, 1927. Price, linen, 28 marks; leather, 31 marks.

This is a handbook designed for the chemical executive, chemical engineer, and industrial chemist. It is not to be confused with standard handbooks of chemistry. While it contains sections devoted to chemical and physical data, these are incidental to the sections concerning, for example, the unit operations of chemical industry, such as distillation, filtration, etc. In addition there are sections given over to such general topics as world economics, prices of raw materials, industrial hazards, factory construction, etc. The book is replete with descriptions and illustrations of industrial equipment that pertain to the chemical industries. There is an excellent survey of chemical operations and reactions in the inorganic and organic fields. The book is a nine hundred page encyclopedia of industrial chemical practice together with necessary data of the underlying sciences for convenient reference. There is an excellent index.

The reviewer knows no other book where so much useful information concerning the chemical industries in general is concentrated as it is in this volume of the Hütte series. The chemical engineer may use it as the mechanical engineer uses Kent.

B. B. FREUD

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

Leather Production and Trade of Canada. J. SCHNITZER. *Trade Information Bulletin* 528. 11 pp. Paper, 10 cents.

Marketing of Crude Rubber (with Trade Statistics). E. G. HOLT. *Trade Promotion Series* 55. 257 pp. Paper, 45 cents.

Trade Association Activities (Supersedes Trade Association Activities, Elimination of Waste Series, 1923). I. S. PAULL, J. W. MILLARD, AND J. S. TAYLOR. *Domestic Commerce Series* 20. 381 pp. Cloth, 75 cents.

Bureau of Mines

Accident Severity Rates for Certain Mines and Quarries. W. W. ADAMS. *Reports of Investigations* 2848. 14 pp.

Analyses of Crude Oils from the West Texas District. A. J. KRAEMER, PETER GRANDONE, AND C. S. LUCE. *Reports of Investigations* 2849. 18 pp.

Analyses of Indiana Coals. *Technical Paper* 417. 50 pp. Paper, 10 cents.

Coal in 1925. F. G. TRYON AND L. MANN. *Mineral Resources of the United States, 1925.* Part II, pp. 393–533. Paper, 25 cents.

Coal-Mine Fatalities in November, 1927. W. W. ADAMS. *Reports of Investigations* 2844. 6 pp.

Coke and By-Products in 1925. F. G. TRYON AND H. L. BENNIT. *Mineral Resources of the United States, 1925.* Part II, pp. 535–615. Paper, 15 cents.

Coke-Oven Accidents in the United States during the Calendar Year 1926. W. W. ADAMS. *Technical Paper* 437. 40 pp. Paper, 10 cents.

Consumption of Reagents Used in Flotation, 1926. THOMAS VARLEY. *Reports of Investigations* 2852. 4 pp.

Descriptive List of Motion Picture Films of the U. S. Bureau of Mines. M. F. LEOPOLD AND R. A. WOOD. 20 pp.

Fifty-Nine Coal-Mine Fires. How They Were Fought and What They Teach. G. S. RICE, J. W. PAUL, AND M. W. VON BERNEWITZ. *Bulletin* 229. 156 pp. Paper, 40 cents.

Gases from Blasting in Tunnels and Metal-Mine Drifts. E. D. GARDNER, S. P. HOWELL, AND G. W. JONES. *Bulletin* 287. 96 pp. Paper, 20 cents.

Geophysical Methods of Prospecting. A Brief and Elementary Account of the Principles Involved. A. S. EVE AND D. A. KEYS. *Technical Paper* 420. 26 pp. Paper, 10 cents.

Hydraulic Classification. Its Theory, Mechanical Development, and Application to Ore Dressing with a Chapter on Methods of Determining the Densities of Liquids and Ore Pulps. A. W. FAHRENWALD. *Technical Paper* 403. 51 pp. Paper, 15 cents.

Petroleum, Petroleum Products, and Natural-Gas Gasoline, December, 1927. *Monthly Petroleum Statement* 32. 10 pp.

Petroleum, Petroleum Products, and Natural-Gas Gasoline, 1927 (Preliminary). *Annual Petroleum Statement* 33. 12 pp.

Petroleum Refinery Statistics 1926. G. R. HOPKINS. *Bulletin* 289. 92 pp. Paper, 20 cents.

Potash Mining in Germany and France. G. S. RICE AND J. A. DAVIS. *Bulletin* 274. 92 pp. Paper, 25 cents.

Prevention of Accidents with Explosives in the Tri-State Zinc and Lead Ore Producing District. S. P. HOWELL. *Circular* 6056. 6 pp.

Properties of California Crude Oils. III—Additional Analyses. A. J. KRAEMER. *Reports of Investigations* 2846. 1 p.

Rare Metals: Cobalt, Molybdenum, Nickel, Tantalum, Titanium, Tungsten, Radium, Uranium, and Vanadium in 1926. F. L. HESS. *Mineral Resources of the United States, 1926.* Part I, pp. 249–74. Paper, 5 cents.

Silver, Copper, Lead, and Zinc in the Central States in 1926. Mine Report. J. P. DUNLOP AND H. M. MEYER. *Mineral Resources of the United States, 1926.* Part I, pp. 181–215. Paper, 10 cents.

Stocks of Petroleum Products Held by Exporters. G. R. HOPKINS. *Reports of Investigations* 2850. 11 pp.

The Determination of Carbon Monoxide in Mines with the "Iodine Pentoxide" Detector. G. S. MCCAA AND J. A. DAVIS. *Circular* 6057. 5 pp.

The Function of Steam in the Limekiln. E. E. BERGER. *Technical Paper* 415. 43 pp. Paper, 10 cents.

The Resistance of Coal-Mine Entries to the Flow of Air. Part IV—The Resistance Caused by Right-Angle Bends. H. P. GREENWALD AND G. E. MCELROY. *Reports of Investigations* 2853. 6 pp.

Bureau of Standards

Directory of Commercial Testing and College Research Laboratories. *Miscellaneous Publications* 90. 46 pp. Paper, 15 cents.

Physical Properties of the Principal Commercial Limestones Used for Building Construction in the United States. D. W. KESSLER AND W. H. SLIGH. *Technologic Paper* 349. 94 pp. Paper, 30 cents.

Congress

Muscle Shoals. Legal Rights of the United States and the State of Alabama in the Muscle Shoals Project. Memorandum Opinion for the Attorney General Relative to the Legal Rights of the United States in the Muscle Shoals Project with Specific Reference to the Wilson Dam and Power Plant at Sheffield, Ala., and the Claims of the State of Alabama in Relation Thereto. *Senate Document* 31. 44 pp.

Department of Agriculture

Dehulling Barley Seed with Sulfuric Acid to Induce Infection with Covered Smut. F. N. BRIGGS. *Journal of Agricultural Research*, 35 (November 15, 1927), 907–14.

Relation of Temperature to Growth of *Penicillium italicum* and *P. digitatum* and to Citrus Fruit Decay Produced by These Fungi. H. S. FAWCETT AND W. R. BARGER. *Journal of Agricultural Research*, 35 (November 15, 1927), 933–7.

Relation of Temperature to Rate and Type of Fermentation and to Quality of Commercial Sauerkraut. H. B. PARMELE, E. B. FRED, W. H. PETERSON, J. E. MCCONKIE, AND W. E. VAUGHN. *Journal of Agricultural Research*, 35 (December 1, 1927), 1021–38.

The Growth of *Bacillus radicicola* on Artificial Media Containing Various Plant Extracts. F. E. ALLISON. *Journal of Agricultural Research*, 35 (November 15, 1927), pp. 915–24.

The Occurrence of Acetaldehyde in Bartlett Pears and Its Relation to Pear Scald and Breakdown. C. P. HARLEY AND D. F. FISHER. *Journal of Agricultural Research*, 35 (December 1, 1927), 983–93.

Geological Survey

A Manganese Deposit of Pleistocene Age in Bannock County, Idaho. D. F. HEWETT. *Bulletin* 795-H. 8 pp.

A Section of the Kaibab Limestone in Kaibab Gulch, Utah. L. F. NOBLE. *Professional Paper* 150-C. 20 pp.

Geography, Geology, and Mineral Resources of Part of Southeastern Idaho. G. R. MANSFIELD. *Professional Paper* 152. 453 pp. Paper, $2.40.

Geology and Coal Resources of the Salina Canyon District, Sevier County, Utah. E. M. SPIEKER AND A. A. BAKER. *Bulletin* 796-C. Paper, 15 cents.

Geology and Oil and Gas Possibilities of the Bell Springs District, Carbon County, Wyoming. C. E. DOBBIN, H. W. HOOTS, AND C. H. DANE. *Bulletin* 796-D. 201 pp.

Geology and Oil and Gas Prospects of Northeastern Colorado. K. F. MATHER, JAMES GILLULY, AND R. G. LUSK. *Bulletin* 796-B. 124 pp. Paper, 20 cents.

Large Springs in the United States. O. E. MEINZER. *Water-Supply Paper* 557. 94 pp. Paper, 30 cents.

Mineral Resources of Alaska. Report on Progress of Investigations in 1925. F. H. MOFFIT AND OTHERS. *Bulletin* 792. 122 pp. Price, 25 cents.

Phosphate Rock in the Three Forks-Yellowstone Park Region, Montana. D. D. CONDIT, E. H. FINCH, AND J. T. PARDEE. *Bulletin* 795-G. 63 pp.

National Advisory Committee for Aeronautics

Effects of Fuel and Cylinder Gas Densities on Characteristics of Fuel Sprays for Oil Engines. W. F. JOACHIM AND E. G. BEARDSLEY. *Report* 281. 9 pp. Paper, 10 cents.

N. A. C. A. Photographic Apparatus for Studying Fuel Sprays from Oil Engine Injection Valves and Test Results from Several Researches. E. G. BEARDSLEY. *Report* 274. 14 pp. Paper, 10 cents.

Public Health Service

Lead Poisoning from the Use of Snuff. *Public Health Reports*, 43 (January 20, 1928), 121–2.

The Oxygen Demand of Polluted Waters. I—Bibliographical. A Critical Review. II—Experimental. The Rate of Deoxygenation. E. J. THERIAULT. *Public Health Bulletin* 173. 185 pp. Paper, 25 cents.

Tariff Commission

Eleventh Annual Report of the United States Tariff Commission, 1927. 176 pp. Paper, 20 cents.

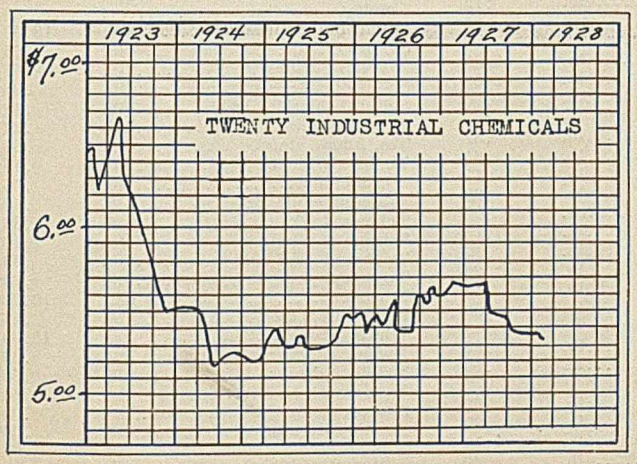
Magnesite: Report of the United States Tariff Commission to the President of the United States. Paper, 5 cents.

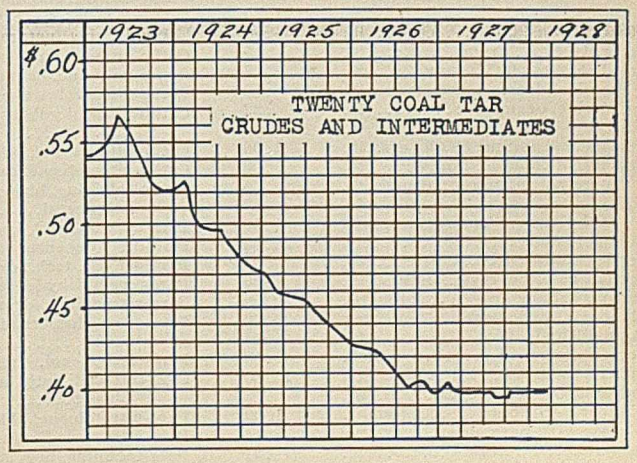
Phenol: Report of the United States Tariff Commission to the President of the United States. With Appendix Proclamation by the President. 12 pp. Paper, 5 cents.

MARKET REPORT—FEBRUARY, 1928

FIRST-HAND PRICES FOR CHEMICALS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET ON FEBRUARY 15

Acetanilide, tech., bbls.	lb.	.24
Acetic anhydride, 92–95%, cbys.	lb.	.29
Acetone, C. P., drums, wks.	lb.	.13
Acetophenetidine, bbls.	lb.	1.40
Acid, acetic, 28%, c/l. bbls.	100 lbs.	3.38
56%, c/l. bbls.	100 lbs.	6.34
Glacial, c/l. bbls.	100 lbs.	11.92
Acetylsalicylic, bbls.	lb.	.85
Anthranilic, 99–100%, drums	lb.	.98
Benzoic, tech., bbls.	lb.	.57
Boric, bbls.	lb.	.08½
Butyric, 60%, pure, 5-lb. bot.	lb.	.55
Chloroacetic, mono-, bbls., wks.	lb.	.25
Di-, cbys.	lb.	1.00
Tri-, bbls.	lb.	2.50
Chlorosulfonic, drums, wks.	lb.	.15
Chromic, pure, 98%, drums	lb.	.25
Cinnamic, 5-lb. cans	lb.	3.25
Citric, U. S. P., kegs, bbls.	lb.	.44
Cresylic, pale, drums	gal.	.72
Formic, 85%, cbys., N. Y.	lb.	.11
Gallic, U. S. P., bbls.	lb.	.74
Glycerophosphoric, 25%, 1-lb. bot.	lb.	1.40
H, bbls., wks.	lb.	.57
Hydriodic, 10%, U. S. P., 5-lb. bot.	lb.	.67
Hydrobromic, 48%, cbys., wks.	lb.	.45
Hydrochloric, 20°, tanks, wks.	100 lbs.	1.10
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.	.04¾
66%, light, bbls., wks.	lb.	.26
Mixed, tanks, wks.	N unit	.07¾
	S unit	.01
Molybdic, 85%, kegs	lb.	1.25
Naphthionic, tech., bbls.	lb.	.55
Nitric, C. P., cbys.	lb.	.12
Nitric, 38°, c/l. cbys., wks.	100 lbs.	5.00
Oxalic, bbls., wks.	lb.	.11
Phosphate, bulk	ton	9.00
Phosphoric, 50%, cbys.	lb.	.08
Picramic, bbls.	lb.	.50
Picric, bbls., c/l.	lb.	.40
Pyrogallic, tech., bbls.	lb.	.86
Salicylic, tech., bbls.	lb.	.27
Stearic, d. p., bbls., c/l.	lb.	.11¼
Sulfanilic, 250-lb. bbls.	lb.	.15
Sulfuric, 66°, c/l. cbys., wks.	100 lbs.	1.60
66°, tanks, wks.	ton	15.00
60°, tanks, wks.	ton	10.50
Oleum, 20%, tanks, wks.	ton	18.00
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.	1.00
Valeric, C. P., 10-lb. bot.	lb.	2.50
Alcohol, U. S. P., 190 proof, bbls.	gal.	3.70
Amyl, 10%, Imp. drums	gal.	1.40
Butyl, drums, c/l., wks.	lb.	.19½
Cologne spirit, bbls.	gal.	3.90
Denatured, No. 5, comp. denat., c/l. drs.	gal.	.50
No. 1, comp. denat., drs.	gal.	.52
Isoamyl, drums	gal.	2.50
Isobutyl, ref., drums	lb.	...
Isopropyl, ref., drums	gal.	1.00
Propyl, ref., drums	lb.	1.00
Wood, *see* Methanol		
Alpha-naphthol, bbls.	lb.	.65
Alpha-naphthylamine, bbls.	lb.	.35
Alum, ammonia, lump, bbls., wks.	100 lbs.	3.25
Chrome, casks, wks.	100 lbs.	5.25
Potash, lump, bbls., wks.	100 lbs.	3.10
Soda, bbls., wks.	100 lbs.	3.75
Aluminum, metal, N. Y.	lb.	.26
Aluminum chloride, anhyd., drums	lb.	.35
Aluminum stearate, 100-lb. bbl.	lb.	.23
Aluminum sulfate, comm'l, bags, wks.	100 lbs.	1.40
Iron-free, bags, wks.	100 lbs.	1.75
Aminoazobenzene, 110-lb. kegs	lb.	1.15
Ammonia, anhydrous, cyl., wks.	lb.	.13½
Ammonia water, 26°, drums, wks.	lb.	.03
Ammonium acetate, kegs	lb.	.34
Bifluoride, bbls.	lb.	.21
Bromide, 50-lb. boxes	lb.	.48
Carbonate, tech., casks	lb.	.08¾
Chloride, gray, bbls.	100 lbs.	5.40
Lump, casks	lb.	.11
Iodide, 25-lb. jars	lb.	5.20
Nitrate, tech., cryst., bbls.	lb.	.21
Oxalate, kegs	lb.	.35
Persulfate, cases	lb.	.27½
Phosphate, dibasic, tech., bbls.	lb.	.18
Sulfate, bulk, wks.	100 lbs.	2.45
Thiocyanate, tech., kegs	lb.	.40
Amyl acetate, tech., drums	gal.	1.90
Aniline oil, drums	lb.	.15¼
Anthracene, 80–85%, casks, wks.	lb.	.60
Anthraquinone, subl., bbls.	lb.	.90
Antimony, metal	lb.	.09¼
Antimony chloride, anhyd., drums	lb.	.17
Oxide, bbls.	lb.	.16¼
Salt, dom., bbls.	lb.	.18
Sulfide, crimson, bbls.	lb.	.25
Golden, bbls.	lb.	.16
Vermilion, bbls.	lb.	.38
Tartrolactate, bbls.	lb.	.45
Argols, red powder, bbls.	lb.	.08
Arsenic, metal, kegs	lb.	.45
Red, kegs, cases	lb.	.10½
White, c/l. kegs	lb.	.03¾
Asbestine, bulk, c/l.	ton	14.75
Barium carbonate, bbls., bags, wks.	ton	47.00
Chloride, bags, wks.	ton	55.50
Dioxide, bbls., wks.	lb.	.13
Hydroxide, bbls.	lb.	.04⅜
Nitrate, casks	lb.	.07½
Barium sulfocyanate, 400-lb. bbls.	lb.	.27
Barytes, floated, 350-lb. bbls., wks.	ton	23.00
Benzaldehyde, tech., drums	lb.	.65
F. F. C., cbys.	lb.	1.40
U. S. P., cbys.	lb.	1.15
Benzene, pure, tanks, mills	gal.	.21
Benzidine base, bbls.	lb.	.70
Benzoyl chloride, carboys	lb.	1.00
Benzyl acetate, cbys.	lb.	1.30
Alcohol, 5-liter bot.	lb.	1.40
Chloride, tech., drums	lb.	.25
Beta-naphthol, bbls.	lb.	.24
Beta-naphthylamine, bbls.	lb.	.63
Bismuth, metal, cases	lb.	2.20
Bismuth, nitrate, 25-lb. jars	lb.	1.95
Oxychloride, boxes	lb.	3.35
Subnitrate, U. S. P., 25-lb. jars	lb.	2.30
Blanc fixe, dry, bbls.	ton	80.00
Bleaching powder, drums, wks.	100 lbs.	2.00
Bone ash, kegs	lb.	.06
Bone black, bbls.	lb.	.08¼
Borax, powd., bbls.	lb.	.04
Bordeaux mixture, bbl.	lb.	.11
British gum, com., c/l.	100 lbs.	4.37
Bromine, bot.	lb.	.45
Bromobenzene, drums	lb.	.50





Bromoform, 5-lb. bot.	lb.	1.65
Butyl acetate, 100-gal. drums	gal.	1.55
Cadmium bromide, 50-lb. jars	lb.	1.20
Cadmium, metal, boxes	lb.	.70
Cadmium sulfide, cs.	lb.	1.35
Caffeine, U. S. P., 5-lb. cans	lb.	2.90
Calcium acetate, bags	100 lbs.	3.50
Arsenate, bbls.	lb.	.07½
Carbide, drums	lb.	.05
Chloride, drums, wks.	ton	20.00
Cyanide, 100-lb. drums	lb.	.30
Lactate, tech., bbls.	lb.	.35
Nitrate, bbls.	ton	52.00
Phosphate, monobas., bbls.	lb.	.07
Tribas., bbls.	lb.	.11
Calcium carbonate, tech., bgs.	100 lbs.	1.00
U. S. P., precip., 175-lb. bbl.	lb.	.06½
Camphor, Amer., bbls.	lb.	.62
Jap., cases	lb.	.60
Camphor, monobrom, cs.	lb.	1.85
Caramel, bbls.	gal.	.63
Carbazole, bbls.	lb.	.15
Carbon, activated, drums	lb.	.05
Carbon bisulfide, drums	lb.	.05½
Carbon black, cases	lb.	.12
Carbon dioxide, liq., cyl.	lb.	.06
Carbon tetrachloride, drums	lb.	.07
Casein, stand. gr., bbls.	lb.	.17
Cellulose acetate, kegs	lb.	1.40
Cerium oxalate, kegs	lb.	.32
Charcoal, willow, powd., bbls.	lb.	.06
China clay, imp., bags	100 lbs.	15.00
Chloral hydrate, drums	lb.	.60
Chloramine U. S. P., 5-lb. bot.	lb.	1.75
Chlorine, liq., c/l., cyl.	lb.	.04
Chlorobenzene, mono-, drums	lb.	.07
Chloroform, tech., drums	lb.	.20
Chromium acetate, 20° sol., bbls.	lb.	.05½
Coal tar, tanks, bbls., wks.	gal.	.07
Cobalt, metal, kegs	lb.	2.50
Cobalt oxide, bbls.	lb.	2.10
Cold-liver oil, bbls.	bbl.	41.00
Collodion, drums	lb.	.23
Copperas, c/l., bulk	ton	13.00
Copper, metal, elec.	100 lbs.	12.90
Copper carbonate, bbls.	lb.	.16¼
Chloride, bbls.	lb.	.28
Cyanide, drums	lb.	.48
Oxide, red, bbls.	lb.	.16½
Sulfate, c/l., bbls.	100 lbs.	5.05
Cotton, soluble, bbls.	lb.	.40
Cream tartar, bbls.	lb.	.26¾
Cyanamide, bulk, N. Y.	Ammon. unit	1.67½
Diaminophenol, kegs	lb.	3.80
Dianisidine, kegs	lb.	2.85
Dibutylphthalate, drums, wks.	lb.	.29½
Diethylaniline, drums	lb.	.55
Diethylene glycol, l. c. l. lots, drums	lb.	.20
Carload lots, drums	lb.	.15
Diethylphthalate, drums	lb.	.24
Diethylsulfate, tech., drums	lb.	.20
Dimethylaniline, drums	lb.	.30
Dimethylsulfate, drums	lb.	.45
Dinitrobenzene, drums	lb.	.15½
Dinitrochlorobenzene, bbls.	lb.	.15
Dinitronaphthalene, bbls.	lb.	.32
Dinitrophenol, bbls.	lb.	.31
Diphenylamine, bbls.	lb.	.45
Diphenylguanidine, bbls.	lb.	.68
Epsom salt, tech., bbls., c/l., N. Y.	100 lbs.	1.75
Ether, nitrous, bot.	lb.	.90
Ether, U. S. P., drums	lb.	.15
Ethyl acetate, 85%, drums	gal.	.75
Bromide, drums	lb.	.70
Chloride, drums	lb.	.22
Methyl ketone, drums	lb.	.30
Ethylbenzyl aniline, 300-lb. drs.	lb.	1.05
Ethylene dichloride, tanks	lb.	.06
Chlorohydrin, anhyd., drums	lb.	.75
Glycol, c/l., wks.	lb.	.30
Ethyl ether, drums, cars	gal.	1.79
Feldspar, bulk	ton	20.00
Ferric chloride, tech., bbls.	lb.	.07½
Ferrous chloride, cryst., bbls.	lb.	.05
Ferrous sulfide, bbls.	100 lbs.	2.50
Fluorspar, 95%, bags	ton	25.00
Formaldehyde, bbls.	lb.	.08¾
Formaniline, drums	lb.	.38
Fuller's earth, bags, c/l., mines	ton	15.00
Furfural, 500-lb. drs., c/l.	lb.	.17½
Glauber's salt, bbls.	100 lbs.	1.00
Glucose, 70°, bags, dry	100 lbs.	3.14
Glycerol, C. P., drums	lb.	.21
G salt, bbls.	lb.	.50
Hexamethylenetetramine, tech., drums	lb.	.62
Hydrogen peroxide, 25 vol., bbls.	lb.	.06½
Hydroquinone, kegs	lb.	1.25
Indigo, 20%, paste, bbls.	lb.	.14
Iodine, crude, 200-lb. kgs.	lb.	4.20
Iodine, resubl., jars	lb.	4.65
Iodoform, bot.	lb.	6.00
Iridium, metal	oz.	110.00
Kieselguhr, bags	ton	60.00
Lead, metal	100 lbs.	6.25
Lead acetate, bbls., white	lb.	.13
Arsenate, bbls.	lb.	.13½
Oxide, litharge, bbls.	lb.	.08¾
Red, bbls.	lb.	.09¾
Peroxide, drums	lb.	.25
White, basic carb., bbls.	lb.	.09
Sulfate, bbls.	lb.	.08¼
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.	1.45
Lithopone, bbls.	lb.	.06½
Magnesite, crude	ton	36.00
Calcined, 500-lb. bbls., wks.	ton	48.00
Magnesium, metal sticks, wks.	lb.	.85
Magnesium carbonate, bags	lb.	.06
Chloride, drums	ton	37.00
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.	1.58
Mercury, flasks, 75 lbs.	flask	122.00
Meta-nitroaniline, bbls.	lb.	.72
Meta-phenylenediamine, bbls.	lb.	.90
Meta-toluylenediamine, bbls.	lb.	.72
Methanol, pure, tanks	gal.	.48
Denaturing grade, tanks	gal.	.45
Methyl acetone, drums	gal.	.80
Salicylate, cases	lb.	.42
Methyl chloride, cylinders	lb.	.55
Michler's ketone, bbls.	lb.	3.00
Monoethylaniline, drums	lb.	1.05
Naphtha, solvent, tanks	gal.	.35
Naphthalene, flake, bbls.	lb.	.05
Nickel, metal	lb.	.35
Nickel salt, single, bbls.	lb.	.10¼
Double, bbls.	lb.	.09
Niter cake, bulk	ton	4.50
Nitrobenzene, drums	lb.	.10¼
Oil, castor, No. 1	lb.	.14
China wood, bbls.	lb.	.16½
Coconut, Ceylon, tanks	lb.	.08⅞
Cod, N. F., tanks	gal.	.62
Corn, crude, tanks, mills	lb.	.10
Cottonseed, crude, tanks	lb.	.08
Lard, edible, bbls.	lb.	.15¾
Linseed, bbls.	lb.	.10
Menhaden, crude, tanks	gal.	nom.
Neat's-foot, pure, bbls.	lb.	.15¾
Oleo, No. 1, bbls.	lb.	.16¼
Olive oil, denat., bbls.	gal.	1.20
Foots, bbls.	lb.	.09¾
Palm, Lagos, casks	lb.	.08
Peanut, crude, tanks	lb.	.12
Perilla, bbls.	lb.	.13
Rapeseed, bbls., English	gal.	.88
Red, bbls.	lb.	.09¾
Soy bean, crude, bbls.	lb.	.12
Sperm, 38°, bbls.	gal.	.84
Whale, bbls., natural, winter	gal.	.76
Ortho-aminophenol, kegs	lb.	2.20
Ortho-anisidine, drums	lb.	2.35
Ortho-dichlorobenzene, drums	lb.	.06
Ortho-nitrochlorobenzene, drums	lb.	.32
Ortho-nitrophenol, bbls.	lb.	.85
Ortho-nitrotoluene, drums	lb.	.17
Ortho-toluidine, bbls.	lb.	.29
Palladium, metal	oz.	80.00
Para-aminophenol, kegs	lb.	1.15
Para-dichlorobenzene	lb.	.17
Paraldehyde, tech., drums	lb.	.26
Para-formaldehyde, cases	lb.	.45
Para-nitroaniline, drums	lb.	.48
Para-nitrochlorobenzene, drums	lb.	.32
Para-nitrophenol, bbls.	lb.	.50
Para-nitrosodimethylaniline, bbls.	lb.	.92
Para-nitrotoluene, bbls.	lb.	.30
Para-phenylenediamine, bbls.	lb.	1.15
Para-toluidine, bbls.	lb.	.40
Paris Green, 500-lb. kegs	lb.	.19
Phenol, drums	lb.	.17
Phenolphthalein, drums	lb.	1.10
Phenylethyl alcohol, 1-lb. bot.	lb.	7.00
Phosphorus, red, cases	lb.	.60
Phosphorus trichloride, cyl.	lb.	.45
Phthalic anhydride, bbls.	lb.	.18
Platinum, metal	oz.	95.00
Potash, caustic, drums	lb.	.07⅛
Potassium acetate, kegs	lb.	.29
Bicarbonate, casks	lb.	.09
Bichromate, casks	lb.	.08¼
Binoxalate, bbls.	lb.	.16
Bromate, cs.	lb.	.35
Carbonate, 80–85%, calc., casks	lb.	.05⅝
Chlorate, kegs	lb.	.08½
Chloride	ton	34.55
Cyanide, cases	lb.	.55
Meta-bisulfite, bbls.	lb.	.11½
Permanganate, drums	lb.	.15¼
Prussiate, red, casks	lb.	.37½
Yellow, casks	lb.	.18
Titanium oxalate, bbls.	lb.	.25
Pyridine, drums	gal.	1.50
Quinine bisulfate, 100 oz.	oz.	.40
Sulfate, 100-oz. cans	oz.	.40
Resorcinol, tech., kegs	lb.	1.30
Rochelle salt, bbls., U. S. P.	lb.	.23
R salt, bbls.	lb.	.45
Saccharin, cans	lb.	1.75
Salt cake, bulk	ton	19.00
Saltpeter, gran., bbls.	lb.	.06⅛
Silica, ref., bags	ton	22.00
Silver nitrate, 16-oz. bot.	oz.	.41⅞
Soda ash, 58%, light, bags, contract, wks.	100 lbs.	1.40
Soda, caustic, 76%, solid, drums, contract, wks.	100 lbs.	3.00
Sodium acetate, bbls.	lb.	.04½
Benzoate, bbls.	lb.	.50
Bicarbonate, bbls.	100 lbs.	2.41
Bichromate, casks	lb.	.06¼
Bisulfite, bbls.	lb.	.04
Bromide, bbls.	lb.	.42
Carbonate, sal soda, bbls.,	100 lbs.	1.30
Chlorate, kegs	lb.	.06½
Chloride, bags	ton	12.00
Cyanide, cases	lb.	.20
Fluoride, bbls.	lb.	.08¾
Metallic, drums, 12¼-lb. bricks,	lb.	.27
Naphthionate, bbls.	lb.	.55
Nitrate, crude, bags, N. Y.	100 lbs.	2.35
Nitrite, bbls.	lb.	.08
Perborate, bbls.	lb.	.21
Peroxide, cases	lb.	.27
Phosphate, trisodium	lb.	.04
Picramate, kegs	lb.	.69
Prussiate, bbls.	lb.	.12
Silicate, drums, tanks, 40°,	100 lbs.	1.20
Silicofluoride, bbls.	lb.	.04½
Stannate, drums	lb.	.48½
Sulfate, anhyd., bbls.	lb.	.02¼
Sulfide, cryst., bbls.	lb.	.02½
Solid, 60%	lb.	.03½
Sulfocyanide, bbls.	lb.	.40
Thiosulfate, reg., crys., bbls.	lb.	.02½
Tungstate, kegs	lb.	.80
Strontium carbonate, bbls.	lb.	.07¼
Nitrate, bbls.	lb.	.08¾
Strychnine alkaloid, 100 oz., powd.	oz.	.46
Sulfate, powder	oz.	.38
Sulfur, bulk, mines, wks.	ton	18.00
Sulfur chloride, red, drums	lb.	.05
Yellow, drums	lb.	.03½
Sulfur dioxide, commercial, cyl.	lb.	.08
Sulfuryl chloride, drums	lb.	.10
Thiocarbanilid, bbls.	lb.	.22
Tin, Amer., stand	lb.	.58
Tin bichloride, 50% sol., bbls.	lb.	.16¼
Oxide, bbls.	lb.	.75
Titanium oxide, bbls., wks.	lb.	.40
Toluene, tanks	gal.	.35
Tribromophenol, cases	lb.	1.10
Triphenylguanidine, drums	lb.	.69
Triphenyl phosphate, bbls.	lb.	.70
Tungsten	WO_3 unit	10.50
Urea, pure, cases	lb.	.18
Whiting, bags	ton	18.00
Xylene, 5°, drums, mills	gal.	.32
Xylidine, drums	lb.	.38
Zinc, metal, N. Y.	100 lbs.	6.40
Zinc ammonium chloride, bbls.	lb.	.05¾
Chloride, granulated, drums	lb.	.06¼
Oxide, Amer., bbls.	lb.	.07⅜
Stearate, bbls.	lb.	.19
Zinc dust, bbls., kegs, c/l.	lb.	.09