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EDITORIALS

Attention, Recognition, and Support

A BROCHURE has been sent by the General Federation of Women's Clubs, the Woman's Department of the National Civic Federation, the Girl Scouts, the American Association of University Women, and the Daughters of the American Revolution "to American Women, as members of the responsible American Public," with the plea

That women assess anew the value of the intimate and unending service of chemistry to home, community, and country.

That they weigh afresh the obligation resting upon them to bring this country abreast of the world's foremost nations in that branch of knowledge which literally underlies the physical and economic life of America; and

That to meet this national obligation women do their obvious parts in their accustomed walks of life.

As chemists who have been striving to persuade the non-technical public to evaluate the importance of chemistry to individual and national life, we have a real interest in this step. It is in line with the efforts of our SOCIETY through the News Service, popular addresses, and other channels, to win general sympathetic understanding for the constructive, productive, and creative work of chemistry.

Some of our foremost chemists, absorbed in their pursuit of a new truth, fail to see any need to interpret their problems and results for the public. They forget the importance of public sympathy and appreciation, without which there would be no encouragement for music, poetry, or art, just as there will be no adequate support for scientific research unless a considerable portion of our population comes to know something of it.

To quote from the brochure:

In an empire or kingdom whose reigning heads are not responsible to the people, either for their policies or their administrative acts, the cause of research can be left safely to the empowered and enlightened few. But in a democracy research can achieve healthy growth only when its roots strike deep into a widespread and informed public sympathy.

We are encouraged by the increasing amount of valuable space accorded chemistry in our daily press. During 1922, without the news which springs from any international conference or meeting, there was a gain of nearly fifteen per cent. We owe a debt of gratitude to the press for this timely support and must not fail to coöperate with those editors who try to interest their readers in scientific work. In a recent editorial in the *New York Times* it was pointed out that men engaged in scientific research are the frontiersmen of to-day, and the fact that they are so considered, their findings being placed among the most important news items of the day, is indeed an encouraging sign. "But," says the editorial, "the scientists should take the great public into their confidence. If the scientist has not the ability to speak to the people, then he should have in his city laboratory or his field tent with him an interpreter, the reporter, one who can 'merge scientific facts into new human relations.'"

Second only in importance to the accomplishment of a piece of research is the task of informing others that it has been done. The account for fellow-scientists comes first, but the public must also be taken into consideration. If this is done thoroughly, generally, and continually, recognition is the reward and the result is cumulative. The step from appreciation to support is a relatively short one.

With the mailing of the brochure the work is just begun. Consideration of the questions raised will bring a demand for authentic information which chemists must be ready to supply. Be prepared to recommend books and reading courses. If called upon, accept service to explain principles, reactions, and problems. Lay stress upon the trend of research and its influence upon the problems just around the corner. Overlook no opportunity to speak before groups of women upon the topic of immediate interest to them. All this will probably make inroads upon your time and entail some extra studying, but the effort will repay you directly and be a contribution to the advancement of your science.

The women of America, without turning aside from any of their accustomed work, can do as much as, if indeed not more than, any other group to create an atmosphere in which research will thrive. Chemists must see to it that the interest of American women is maintained.

An Important Decision

IN THE United States District Court, Southern District of New York, Judge Augustus N. Hand has made a decision in the suit brought by Hugo Junkers *vs.* the Chemical Foundation, Inc., in which it was sought to enjoin the defendant from infringement of letters patent covering certain inventions relative to airplanes.

This ruling is of great importance, particularly because Judge Hand emphasizes the fact that "while the Alien Property Custodian is a common law trustee, he holds the property, not in the interest of the former owner, but in the public interest." The decision cites sections of the Trading-with-the-Enemy Act, the treaties of peace, and the Treaty of Versailles, and the judge based his opinion on some of the same points which have been cited as proving the perfectly sound position of the Chemical Foundation as defendant in the suit which has been brought by the Department of Justice to recover patents, trade marks, and copyrights, and which is to be further argued in April.

The decision states that in the seizure of these patents the Treaty with Prussia of 1799 is not violated, as it has no bearing upon the situation. The clauses in the treaty relating to the property of Germans "are directed to German merchants residing in this country—a class to which the complainant avowedly does not belong." The decision concludes:

After seizure by the Alien Property Custodian the enemy alien no longer "owned or controlled" the patent, and consequently did not come within Sec. 10-g of the Trading-with-the-Enemy Act. It is to be noted that without that provision patents which had not been seized would have had no protection because a suit by an enemy alien, except for the privilege given under Sec. 10-g, would not have been allowed to proceed in our courts. After seizure, however, the original owner had no title, legal or equitable, which he could assert. The present suit, having been instituted by an enemy alien after lawful seizure of his patent by the Alien Property Custodian, is without legal foundation.

The motion to dismiss the suit was granted. This decision is not only of direct importance to the case pending against the Chemical Foundation, but should make entirely clear in the minds of the people the fact that the Chemical Foundation is acting, not as a trustee for individuals, commercial groups, nor alien patentees, but solely as a trustee for the American people.

The Syracuse Section

THE Syracuse Section is to be congratulated upon one of the pieces of work recently completed. This is a collection of the titles of papers and names of authors representing all contributions to chemical literature made by members of the Syracuse Section during the past twenty years. The list may not be complete, but it gives some indication of the productivity of the members of the section. It is arranged alphabetically by subjects, under some of which are many entries. The breadth of interest is surprising. The number of subjects indexed is sixty and the total number of titles is one hundred twenty-one.

We have previously commented upon the desirability of writing chemical history, both in local sections and in the chemical departments of our universities and colleges. The Syracuse Section has made a good beginning. It would be interesting to learn how other sections compare on a pro rata basis in their contributions to the advancement of chemistry.

Wanted—An American Federation of Chemical Industries

WE HAVE always believed in the principle of deciding upon a few definite objectives and then working consistently and persistently to attain them. Once an objective has been chosen, it is surprising how many small things can be made to contribute to its attainment.

The most wonderful demonstration of forgetting differences in the successful accomplishment of a task was that get-together movement called "winning the war." Americans seem to work together best when there is an emergency and when there is a definite objective. An emergency still confronts the chemical industry. It is not firmly established. It is not sufficiently integrated and cohesive. Any observer will note that as a whole it proceeds apparently without a well-defined purpose, and that the various organizations, not to mention their component parts, too often use the word "we" editorially and not in the true coöperative sense. "Coöperation" when correctly spelled requires only the two letters "w" and "e."

Suspicion and selfishness cloud the goal toward which all should work. There is much independent effort but little coördination. There is but little agreement as to ways and means, much duplication of effort, and apparently no apportionment of the work on a well-thought-out plan.

If the chemical industry is the key industry we claim it to be, and basic to success in peace and safety in war, then we must insist on that broadmindedness which makes an individual or a corporation a little less selfish and a little more willing to work over the rough places for the sake of the ultimate reward. Each member of a successful team of stars plays with reference to his fellows; otherwise they could easily be defeated by any well-trained team of determined though mediocre men. The experience through which our industry has been passing should serve as training to produce the team work that insures success.

Several worthy organizations, representing special groups of interests in the industry, are already at work. There may be some duplication of membership, but there is little duplication of effort. Their paths seem too divergent for that.

The next step is the formation of an American federation of chemical industries in which all interests should be adequately represented, and from which should issue plans to be followed uniformly by all participants. In our school readers there was the story of the man who called his several sons together, gave them a bundle of sticks, and bade them break it. All failed, but when the bundle was separated, the individual sticks could be snapped with ease. The component parts of the chemical industry must be bound together with a unity of purpose and a will to work for it. Inspired with a comprehensive vision of what real research means, we shall have the strength to resist all efforts to destroy this industry which has cost so much in the building.

The Importance of a Name

PERHAPS one of the most important contributions of the AMERICAN CHEMICAL SOCIETY to the nomenclature has been the word "methanol," coined, we believe, by one of our committees to which the late Dr. Baskerville devoted much of his thought and effort. The term has been accepted by many of the large manufacturers, by the Forest Products Laboratory, the Tariff Commission, and scientists generally.

The National Wood Chemical Association has just adopted this term, and the following paragraph is quoted from its announcement:

Our Association has given the matter due consideration and at a recent meeting of the Board of Governors adopted a resolution recommending that the term "wood alcohol" be discontinued and the term "crude methanol" or "refined methanol" used hereafter as the case might be. Railroad companies will be requested to make such changes in their classifications and tariffs as they may consider necessary to apply the same rates on shipments of "methanol" as are now published on shipments of wood alcohol, and your coöperation in effecting this change will do much towards accomplishing the desired result.

There is much work to be done in the revision of the nomenclature of any science, and a great part of it has to do with simplification and exactitude. It is, therefore, highly gratifying when we are able to contribute a word, the importance of which can actually be measured in terms of the saving of human life.

New Relationships

IN SOME quarters there is impatience because of what is thought to be unnecessary delay in the formulation of rules and regulations to govern importations under the new tariff act, and in the assessment of duties. The problem is a very complex one which cannot be solved with quite the rapidity that has been possible in previous instances after the passage of tariff acts. Heretofore, tariff has been considered a matter between the Government and the importers. Other interests were scarcely recognized and rarely consulted. For the first time in the history of tariff matters, not only is serious consideration being given to the interests of other groups, but their assistance and counsel are being sought. We refer to such committees as have been appointed to aid the United States customs-appraising officers in New York in formulating suitable rules and regulations for the assessment of duty on imported dyes under the provisions of the Tariff Act of 1922. These committees, on which are represented the importers, American manufacturers, consumers, and those importers who also manufacture in America, are preparing lists of noncompetitive dyes, and it requires no imagination to foresee the potential importance of their service.

We believe this new policy is commendable and, if followed out to its logical conclusion, should guarantee justice to the interests of the various groups concerned, including the ultimate consumer.

Research in Refractories

THE Refractories Manufacturers' Association has undertaken to obtain from the industry exact information with regard to furnace conditions which the material must encounter in actual service.

Research in refractories as an activity of this association has been in progress for some time, but has been largely confined to the laboratory. It now becomes important to obtain the greatest possible amount of data from the industries where rapidly changing conditions have made it necessary for refractories to meet a correspondingly extensive change in service requirements. While bricks of various characteristics have been developed, there has not been the coördination between all factors that can be obtained when the data from research are translated into works practice, and a study of furnace conditions is made with sufficient breadth, not only to understand the causes of many troublesome failures, but from a knowledge of conditions to predict service and avoid expense, disappointment, and dissatisfaction.

The questionnaire that is being distributed deserves thoughtful response. If coöperation is widely obtained, every consumer of refractory brick will undoubtedly derive benefit from the progress reports for the various industries, which are to be issued at intervals during the two years required for the survey.

Earning Power of Research

IT IS refreshing to find in a daily paper a statement by the vice president of a great motor-vehicles corporation that "Undoubtedly the improvement of quality in automobiles has been due to the development and work of laboratories more than to any other single factor. Laboratories have been an influence, not only in determining qualities of materials, but they have been potent in guiding the design of cars as well. Every idea bearing on the service rendered by the automobile to its owner has first been subjected to the severest kind of tests in the laboratories and on the roads. In no industry have laboratories played a more practical and vital part than in the automobile industry. And in but few industries indeed has their influence been anywhere near so great."

This corporation employs one hundred twenty-five skilled men in its various laboratories, including chemical laboratories, and considers it a practical investment. It feels, and properly so, that it might be difficult to uphold a reputation built through many years of service to the public without that safeguard to quality in which the laboratory plays a vital part every day in the year.

At one of the early chemical expositions, the American Electrochemical Society displayed the chassis of an automobile and indicated by placards and ribbons the parts for which electrochemistry was responsible. A little thought will suggest the multitudinous ways in which chemical research plays a part in the modern motor vehicle. The chemist needs no better example than the automobile to illustrate the practical worth of research.

The duplication of proprietary compounds affords another striking example of what the chemist can do for industry. A liquid metal polish containing iron oxide owed part of its popularity to the fact that this iron remained in suspension in the liquid. Analysis showed calcium to be present, but the analyst interpreted it as an impurity in the iron oxide. Then a more experienced chemist suggested that the lime might have been added to form a lime soap with the oils present, and that it was this lime soap which tended to keep the iron

in suspension. The problem was solved, but rather than pay a reasonable fee the client preferred to have this chemist manufacture the polish for him. In the end the chemist realized forty times the fee.

It pays to consult experienced chemists.

Ethics

BY VOTE of the Council, the AMERICAN CHEMICAL SOCIETY some years ago decided not to formulate a code of ethics. We have no quarrel with that decision, but it has been our experience that many groups of men find it advantageous to lay down a code of ethics for the salutary effect on some members of the organization and also on the public.

The latest of the great technical societies to adopt such a code is the American Society of Mechanical Engineers, with a membership of approximately twenty thousand. It is believed that this code will be of great assistance to those employing or having business relations with engineers. There is much in the code adopted which applies to other professions and it is quoted here for the benefit of chemists:

1—The engineer will carry on his professional work in a spirit of fairness to employees and contractors, fidelity to clients and employers, loyalty to his country, and devotion to high ideals of courtesy and personal honor.

2—He will refrain from associating himself with or allowing the use of his name by an enterprise of questionable character.

3—He will advertise only in a dignified manner, being careful to avoid misleading statements.

4—He will regard as confidential any information obtained by him as to the business affairs and technical methods or processes of a client or employer.

5—He will inform a client or employer of any business connections, interest, or affiliations which might influence his judgment or impair the disinterested quality of his services.

6—He will refrain from using any improper or questionable methods of soliciting professional work, and will decline to pay or to accept commissions for securing such work.

7—He will accept compensation, financial or otherwise, for a particular service, from one source only, except with the full knowledge and consent of all interested parties.

8—He will not use unfair means to win professional advancement or to injure the chances of another engineer to secure and hold employment.

9—He will coöperate in upbuilding the engineering profession by exchanging general information and experience with his fellow-engineers and students of engineering and also by contributing to work of engineering societies, schools of applied science, and the technical press.

10—He will interest himself in the public welfare in behalf of which he will be ready to apply his special knowledge, skill, and training for the use and benefit of mankind.

Technical Representatives

WE BELIEVE there are many, many cases involving expert representation where the interests of all concerned would be better served by the chemist than any other spokesman.

In several industrial establishments the services of the chemist have been called upon in adjusting questions involving raw materials and finished products, and not infrequently the chief chemist of a plant is the man always sent where these questions arise. When the tariff occupied the center of the stage, it was the chemists and men with technical training who were able to answer the questions and who created the best impressions upon Congress. A favorable attitude toward the helium program has been assured because a chemist has made clear with the aid of experiments conducted in the committee rooms just what it is all about and its real importance to our defense program. With knowledge came enthusiasm and open-mindedness.

The Water-Gas Reactions[1,2]

By R. T. Haslam, F. L. Hitchcock, and E. W. Rudow

Massachusetts Institute of Technology, Cambridge, Mass.

*By means of a variation in steam pressure a study of the formation of water gas through a range of temperature from 650° to 1200° C., with a threefold change in steam pressure and using two kinds of carbon, leads us to the conclusion that the essential reactions are:**

$$C + H_2O = CO + H_2 \qquad (A)$$
$$C + 2H_2O = CO_2 + 2H_2 \qquad (B)$$
$$C + CO = 2CO \qquad (D)$$
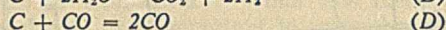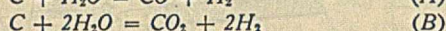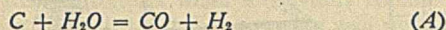
These reactions, taking place at the surface of the carbon, are all monomolecular and a possible explanation of the mechanism by which CO_2 is formed monomolecularly is given.

The rate of formation of CO_2 at temperatures below 900° C. is found to be

$$(CO_2) = 0.5[(H_2O) - (H_2O)^2] \qquad (9)$$

and at temperatures above 900° C.,

$$(CO_2) = 0.47[(H_2O) - (H_2O)^{1.85}] \qquad (10)$$

Considering the rate of Reaction B as unity, we find that at temperatures below 900° C. Reaction A is practically nonexistent and the velocity constant of Reaction D is 2.0, and at temperatures above 900° C. the velocity constant of Reaction A is 1.0 and that of D is 2.18.

The influence of undecomposed steam in the $CO:CO_2$ ratio is shown to be the controlling factor rather than the temperatures at which the reactions take place.

An increase in pressure under which a water-gas generator is operated may be used to obtain the same effect as an increase in the time of contact, in the depth of fuel bed, or an increase in temperature. Thus, a threefold increase in pressure will produce almost a threefold increase of water gas without a change in composition of fixed gases.

WATER GAS is considered as formed by means of some or all of the following reactions:

$$C + H_2O = CO + H_2 \qquad (A)$$
$$C + 2H_2O = CO_2 + 2H_2 \qquad (B)$$
$$CO + H_2O = CO_2 + H_2 \qquad (C)$$
$$C + CO_2 = 2CO \qquad (D)$$

Previous Investigations

Clement, Adams, and Haskins[3] conclude that Reactions A and B both take place, although A is the dominant one accompanied to some extent by Reaction B, and the effective direction of Reactions C and D is to the right.

H. S. Taylor[4] states that the steam is decomposed by Reaction A, the CO_2 being formed by the establishment of the water-gas equilibrium through Reaction C going to the right. He further points out how the ash in the coke catalyzes Reaction C, causing an increase in the CO_2 content.

J. Gwosdz[5] concludes that even at low temperatures (600° C.) carbon dioxide is not formed by Reaction B but that the CO_2 comes from Reaction C speeded up catalytically by ash in the carbon. He arrives at this conclusion from the fact that with arc-lamp carbon containing 0.1 per cent ash the $CO:CO_2$ ratio is about 11:1, whereas with charcoal containing 1.4 per cent ash the $CO:CO_2$ ratio averages about 1:5. If the 55-fold change here noted is due only to the catalyst, it seems peculiar that such a result would be accomplished when the amount of catalyst changed from only 0.1 per cent to 1.4 per cent. The results would be more significant had the lampblack been ash-free. This anomaly is further borne out by another set of Gwosdz's own experiments in which he used gas coke containing 8.5 per cent ash, where under comparab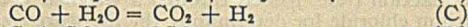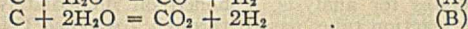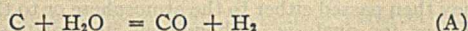le conditions of temperature and undecomposed steam he found a $CO:CO_2$ ratio averaging 1:2, or one-half the amount of CO_2 present in the water gas from charcoal containing 1.4 per cent ash. One might explain Gwosdz's results on the basis of some particular component of the ash catalyzing Reaction B or C, and that the charcoal contained more of this catalyst than did the lampblack or coke.

Kohn,[6] from stoichiometrical calculations of Von Harries'[7] data, reached the conclusion that Reaction A does not occur at all, that the steam is decomposed by Reaction B, the resultant

CO_2 being decomposed below 900° C. by Reaction C going to the *left* while above 900° C. the CO_2 is decomposed by Reaction D.

Throughout the literature the general statement is made that the $CO:CO_2$ ratio increases with temperature, indicating that temperature is the controlling factor in the production of CO_2.

The explanations of nearly all these investigators in a qualitative way account satisfactorily for the formation of water gas, as far as the end composition of the gases is concerned. The exact mechanism of the reactions, the influence of catalysts, and the relative rates of the reactions, particularly when these reactions act in conjunction with one another, are, however, unknown.

Method of Attack

An examination of the reactions shows that water enters into Reactions A, B, and C, but not into D, while Reaction B calls either for the simultaneous or subsequent interaction of two water molecules. Therefore, changing the pressure of the water vapor should throw light on the mechanism of water-gas reactions, and a review of the literature failed to show any experiments wherein the pressure of the water vapor was varied while the time of contact, the temperature, the kind of carbon, and the amount of carbon surface were kept constant. Therefore, it was decided to study the influence of steam pressure on the formation of water gas throughout the range of 650° to 1200° C.

Apparatus

The apparatus used, in its simplest form, consisted of a heated reaction tube of porcelain filled with coke, through which a stream of superheated steam was passed. On leaving the reaction tube the excess water vapor was condensed and the dry gases measured in a flowmeter. Gas samples were taken immediately after leaving the reaction tube.

Plate 1 shows the apparatus in detail. Steam was tapped from a main through a spiral copper-tube superheater and then to the reaction tube. By cracking the lower valve the water was bled out, also allowing regulation of the steam pressure. The superheater was constructed of $1/4$-in. copper tubing, 10 ft. in length, coiled and surrounded by sheet asbestos with baffles forcing the flame from the gas burner to play vigorously on all parts of the tube.

The electric furnace consisted of a 12-in. (diameter) cylindrical shell of asbestos sheeting with asbestos slate disks for the ends,

[1] Presented before the Division of Gas and Fuel Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

[2] Contribution No. 30 from the Department of Chemical Engineering, Massachusetts Institute of Technology.

[3] *Bur. Mines, Bull.* 7.

[4] "Fuel Production and Utilization," p. 149.

[5] *Z. angew. Chem.*, **31** (1918), I, 137.

[6] This Journal, **14** (1922), 69.

[7] *J. Gasbel.*, **1894**, 82.

1. STEAM MAIN
2. COPPER COIL SUPERHEATER
3. ELECTRIC FURNACE
4. REACTION TUBE
5. THERMOCOUPLE
6. COLD JUNCTION
7. MILLI-VOLTMETER
8. RHEOSTAT
9. MANOMETER
10. CONDENSER
11. SEPARATOR
12. DRYING TUBE
13. FLOW METER
14. VACUUM TAP
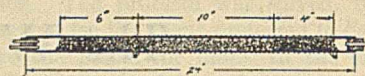15. WEIGHING TUBE
16. SAMPLE BOTTLE
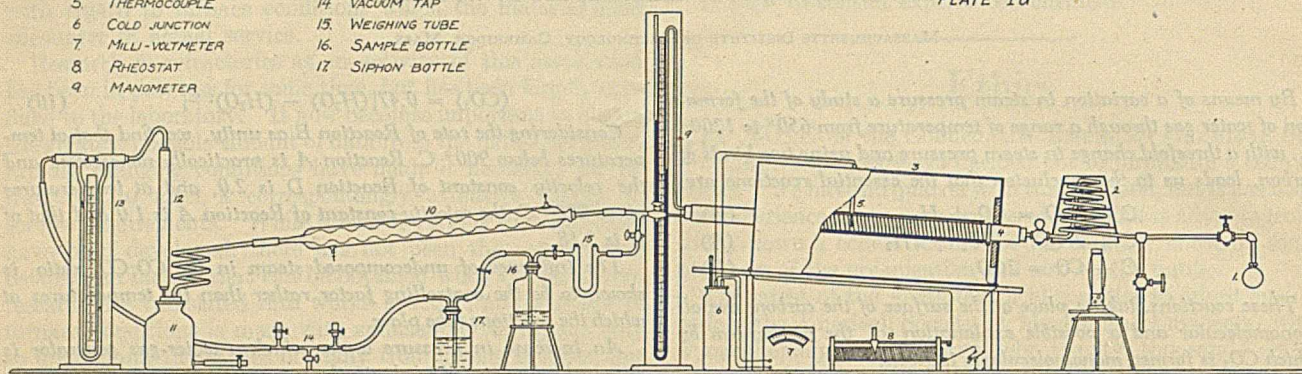17. SIPHON BOTTLE

PLATE 1a

PLATE 1

further protected by asbestos board 1 in. thick. For heat-insulation purposes the cylinder was completely filled with Sil-O-Cel.

The reaction tube was a $^3/_4$ x 24-in. porcelain tube wound with No. 14 Nichrome A wire, 5 turns to the inch. The current for heating this was adjusted by means of a rheostat. Only the central portion of the tube was filled with the reacting coke or carbon, both ends being filled with crushed porcelain which served on the entrance end of a superheater for the steam and in the other to reduce the size of the passageway. This latter factor increased the velocity of the gases through the region of variable temperature, giving greater assurance of a frozen equilibrium.

Temperature measurements were made by means of a chromel-alumel thermocouple and millivoltmeter. The thermocouple was inserted in a well in the kieselguhr and laid against the outside of the reaction tube.

A 2-hole rubber stopper at the end of the reaction tube permitted the insertion of a tube leading to a manometer for the measurement of pressure and vacuum, and also one for the passage of the gaseous products. Through a valve used to regulate the pressure on the inside of the reaction tube, the gases passed to a condenser where the excess steam was condensed, the condensate flowing through a coil to a separating bottle. The remaining fixed gases passed up through a tube containing calcium chloride to remove the moisture and thence through a calibrated flowmeter where the flow of dry gases was measured. They then passed either to the atmosphere or to the vacuum tap.

Gases for analysis, siphoned off immediately after leaving the reaction tube, passed through a weighed U-tube containing calcium chloride for determining the moisture content, and then into a sample bottle, from which samples were analyzed by the Hempel apparatus for CO_2, CO, H_2, and CH_4. When running under vacuum the siphon bottle was connected to the vacuum tap so that the flow of brine was regulated by the siphon the same as when running under pressure. It is to be noted that during a vacuum run all parts of the apparatus were under vacuum, while in a pressure run only the reaction tube was under pressure.

TABLE I

Run (1)	Temp. °C. (2)	Pressure Mm. Abs. (3)	Per cent H_2O in Exit Gas (4)	Velocity through Tube Cc./Sec. (5)	Analysis of Fixed Gases Per cent by Vol.				Analysis of Wet Gases Per cent by Vol.				
					CO_2 (6)	CO (7)	H_2 (8)	CH_4 (9)	H_2O (10)	CO_2 (11)	CO (12)	H_2 (13)	$CO + 2CO_2$ (14)
SERIES I													
1a	900	363	75.8	325	14.8	27.2	57.3	0.8	75.8	3.6	6.6	14.0	13.8
1b	900	1123	84.3	317	17.6	22.5	58.2	0.8	84.3	2.8	3.6	9.3	9.2
2a	1000	363	60.2	334	13.6	28.0	55.7	0.8	60.2	5.4	11.5	22.9	22.2
2b	1000	1123	68.4	326	16.6	24.5	57.2	0.8	68.4	5.3	7.9	18.4	18.5
3a	1100	365	24.7	320	8.6	37.5	52.8	1.0	24.7	6.5	28.6	40.2	41.7
3b	1100	1125	27.8	328	10.7	33.5	54.0	1.2	27.8	7.9	24.6	39.7	40.4
4a	1200	365	5.9	318	1.2	47.3	50.1	0.8	5.9	1.1	45.3	47.7	47.5
4b	1200	1125	7.2	322	2.2	47.5	49.3	1.0	7.2	2.0	44.5	46.3	48.5
SERIES II													
1a	900	368	51.2	163	17.2	23.4	58.2	0.8	52.1	8.3	11.3	28.3	27.9
1b	900	1128	55.5	167	19.0	20.7	58.6	0.8	55.5	8.6	9.3	26.6	26.5
1c	900	368	54.3	158	17.4	23.2	57.7	0.8	54.3	8.1	10.8	26.8	27.0
2a	1000	368	39.4	155	15.3	26.8	56.5	0.8	39.4	9.4	16.5	34.7	35.1
2b	1000	1128	42.1	167	15.7	24.8	57.0	0.8	42.1	9.3	14.7	34.9	33.3
2c	1000	368	39.0	162	15.5	26.6	56.6	0.8	39.0	9.6	16.4	35.0	35.6
3a	1100	358	19.2	165	7.3	38.7	52.6	0.8	19.2	5.97	31.7	43.0	43.6
3b	1100	1118	25.3	160	9.2	35.3	54.4	1.0	25.3	6.95	26.6	41.1	40.5
3c	1100	358	21.7	160	7.4	37.7	52.3	1.0	21.7	5.95	30.3	42.1	42.2
4a	1200	358	2.8	163	0.9	47.4	50.0	1.0	2.8	0.87	46.8	49.5	48.5
4b	1200	1118	4.1	167	1.6	46.9	49.4	0.8	4.1	1.43	46.0	48.4	48.86
4c	1200	358	3.4	167	1.1	47.5	49.5	1.2	3.4	1.06	46.7	48.8	44.8
SERIES III													
1a	650	366	82.5	162	25.4	11.9	61.6	0.8	82.5	4.5	2.1	10.8	11.1
1b	650	1126	86.1	167	27.6	7.9	62.8	0.8	86.1	3.9	1.1	8.9	8.9
2a	750	366	70.5	167	22.0	17.2	59.5	0.8	70.5	6.6	5.1	17.8	18.3
2b	750	1126	75.4	158	22.5	15.8	59.9	0.8	75.4	5.6	4.0	15.0	15.2
3a	850	366	56.1	162	18.7	21.4	58.6	0.8	56.1	8.3	9.5	26.1	26.1
3b	850	1126	59.5	163	20.5	19.0	59.0	0.8	59.5	8.4	7.8	24.3	24.5
SERIES IV													
1a	900	355	40.7	160	14.4	28.1	56.2	0.8	47.7	8.7	16.9	33.7	34.3
1b	900	1115	44.9	164	16.2	25.3	56.8	0.8	44.9	9.0	14.2	31.8	32.2
1c	900	355	39.1	168	14.4	28.2	56.7	0.8	39.1	8.8	17.3	34.8	34.9
2a	1000	355	31.1	161	10.6	34.0	54.5	0.8	31.1	7.3	23.7	37.9	38.3
2b	1000	1115	36.4	159	12.9	30.5	55.4	0.8	36.4	8.3	19.6	35.7	36.2
3a	1100	357	15.2	160	5.3	41.6	51.5	1.0	15.2	4.0	35.9	44.3	45.1
3b	1100	1117	19.2	164	7.1	38.4	43.1	1.2	19.2	5.9	31.8	44.1	43.6
4a	1200	357	2.0	160	0.7	48.7	49.6	0.8	2.0	0.69	48.2	49.1	49.6
4b	1200	1117	2.9	160	1.3	47.5	50.0	1.0	2.9	1.26	6.7	49.2	49.2

All joints were sealed with gasket cement. The burning out of the rubber stopper at the hot end of the reaction tube was eliminated by cooling this end by means of a lamp wick dipped into a dish of cooling water.

METHOD

The coke and carbon used in the reaction tube were ground and screened between 5- and 8-mm. screens to insure, as far as possible, the same amount of surface area and voids through the tube during each run. The length of the fuel bed in every case was 10 in., the rest of the tube being filled with crushed porcelain as shown in Plate 1. To further insure a constant time of contact when a constant volume of steam was passing through the tube, the coke was replaced after each change in temperature. While this meant a considerable loss of time, it is important to remember that the gas composition, and especially the percentage of fixed gases, vary considerably with the change in time of contact as shown by the experiments of Clement and Adams.[3] Throughout Series II each high-pressure run was preceded and followed by a low-pressure run to check the fact that the area of contact surface had remained substantially unchanged (Table I).

Measurement of the volume of dry gases and the percentage of water vapor, determined by weighing the U-tube after the passage of a liter of gas, gave the quantity of steam entering the fuel bed. By this means, with suitable temperature factors introduced, the time of contact was kept as nearly constant as possible. Naturally, this assumed that the volume of the gas underwent no change during the reaction. With small amounts of steam being decomposed this assumption was nearly correct, the error becoming larger with increased steam decomposition.

In a way, Series I was a preliminary series to determine a velocity which would give a suitable range of moisture content in the product gases between the temperatures 900° and 1200° C., inclusive. A velocity through the tube of 320 cc. per sec. (corresponding to a time of contact equal to approximately 0.113 sec.) was used.

On calculating some of the results, it was decided to increase the time of contact, and Series II was made at a velocity of 160 cc. per sec. (time of contact approximately 0.226 sec.) in the same temperature range. Series III was made at the same velocity but a lower temperature range—that is, 650°, 750°, and 850° C.

Series IV was made under identical conditions as Series II, except that the coke, which contained 15.4 per cent ash, was replaced by crushed electric-arc-light carbon containing over 80 per cent lampblack and approximately 20 per cent coal-tar pitch coke, the ash content being 1.12 per cent. The carbon was crushed to the same size as the coke particles so as to give the same superficial surface exposed to the steam. By this means it was possible to determine whether the ash content or the form of carbon had any material effect on the reactions.

The analytical accuracy of the results may be tested easily since twice the percentage of CO_2 plus the percentage of CO should equal the percentage of H_2, no matter what reactions take place. Columns 13 and 14 show this comparison.

The results are shown graphically in Plates 2, 3, and 4. Plate 2 shows for a given time of contact the change in composition of the dry gases with temperature. Plate 3 shows the same change in the gases on a wet basis and Plate 4 illustrates the difference in the behavior of coke and the lampblack carbon.

PRESENTATION OF DATA

Although every effort was made to maintain the time of contact throughout a given series of runs, it is quite possible to make serious errors in this respect. Therefore, instead of studying the *actual* rate at which the constituents of the gas change with time, it is advantageous to compare their *relative* rates. In Plate 5, therefore, we have plotted the fractions of H_2, CO, and CO_2 against the fraction of undecomposed water, for by this means two advantages have been gained—first, a reduction in the number of variables, and, second, the elimination of any experimental error in the determi-

Plate 2
Fixed Gas Analyses
Series 2 and 3

High Pressure approx. 1126 mm
Low Pressure approx. 366 mm

Hydrogen

Carbon Monoxide

Carbon Dioxide

% by Volume

Temp. °C

Plate 3

Wet Gas Analyses

Series 2 and 5

High Pressure approx. 1126 mm

Low Pressure approx. 366 mm
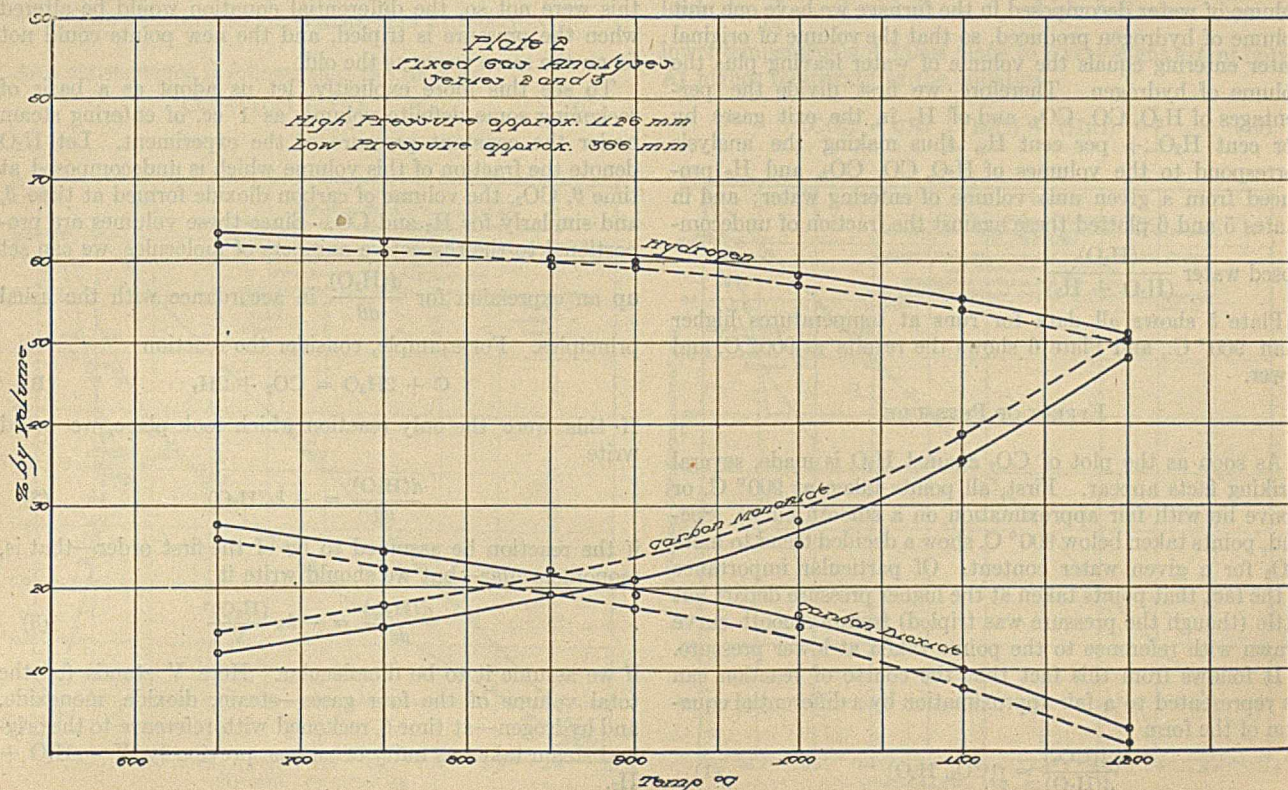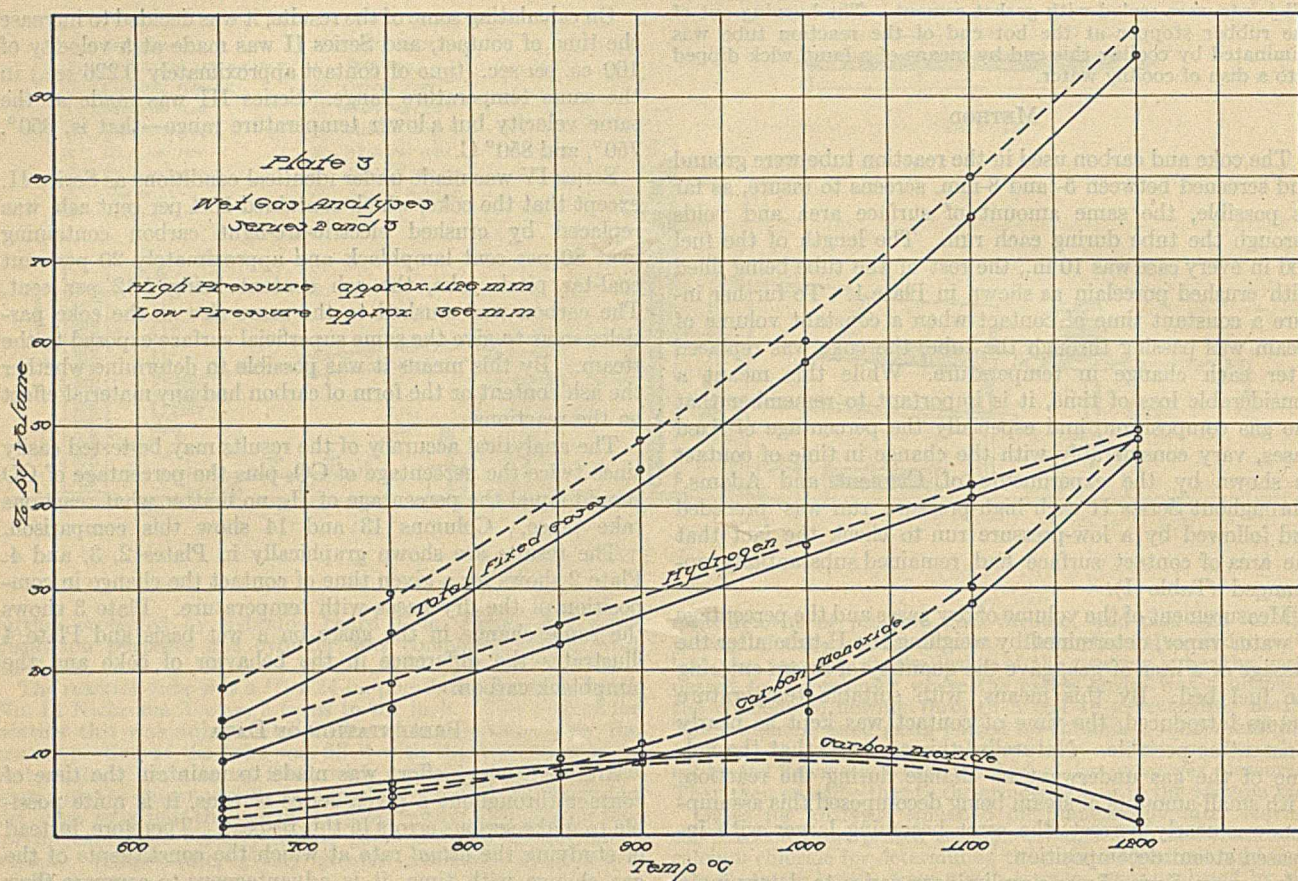
nation of time. In addition, the analyses of the wet water gas are not on any comparable basis—that is to say, 100 cc. of wet water gas from various runs do not correspond to the same amount of water entering the reaction furnace. From stoichiometrical relationships we see that for every unit volume of water decomposed in the furnace we have one unit volume of hydrogen produced, so that the volume of original water entering equals the volume of water leaving plus the volume of hydrogen. Therefore, we first divide the percentages of H_2O, CO, CO_2, and of H_2 in the exit gases by per cent H_2O + per cent H_2, thus making the analysis correspond to the volumes of H_2O, CO, CO_2, and H_2 produced from a given unit volume of entering water; and in Plates 5 and 6 plotted these against the fraction of undecomposed water $\dfrac{(H_2O)}{(H_2O + H_2)}$.

Plate 5 shows all data for runs at temperatures higher than 900° C., and Plate 6 shows the results at 900° C. and lower.

Effect of Pressure

As soon as the plot of CO_2 against H_2O is made, several striking facts appear. First, all points taken at 900° C. or above lie with fair approximation on a smooth curve. Second, points taken below 900° C. show a decided trend to more CO_2 for a given water content. Of particular importance is the fact that points taken at the higher pressure depart but little (though the pressure was tripled) from a smooth curve drawn with reference to the points taken at lower pressure.

It follows from this fact that the course of reaction can be represented to a fair approximation by a differential equation of the form

$$\frac{d(CO_2)}{d(H_2O)} = f(CO_2, H_2O) \qquad (1)$$

where the function f is a homogeneous function of the amounts of dioxide and water present at time θ, and this function must be zero degree—that is, it must be a function which is entirely unaltered when the amounts of H_2O and of CO_2 are both multiplied by a common factor (in this case, 3). For if this were not so, the differential equation would be altered when the pressure is tripled, and the new points could not lie on the same curve as the old.

To see this more explicitly, let us adopt as a basis of reckoning some definite volume, as 1 cc. of entering steam under the constant pressure of the experiment. Let H_2O denote the fraction of this volume which is undecomposed at time θ, CO_2, the volume of carbon dioxide formed at time θ, and similarly for H_2 and CO. Since these volumes are proportional to the respective numbers of molecules, we can set up an expression for $\dfrac{d(H_2O)}{d\theta}$ in accordance with the usual principles. For example, consider the reaction

$$C + 2H_2O = CO_2 + 2H_2 \qquad (B)$$
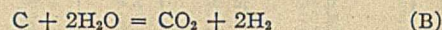
If this were the only reaction which took place, we could write

$$\frac{d(H_2O)}{d\theta} = - k_b(H_2O) \qquad (2)$$

if the reaction be assumed to be of the first order—that is, monomolecular—but we should write it

$$\frac{d(H_2O)}{d\theta} = - k_b \frac{(H_2O)^2}{V} \qquad (3)$$

if we assume it to be dimolecular. Here V stands for the total volume of the four gases—steam, dioxide, monoxide, and hydrogen—at time θ, reckoned with reference to the original steam taken as unity or as seen previously, V = H_2O + H_2.

In the formation of water gas it is evident that other reactions also take place, so we shall have other terms in the expression for $\dfrac{d(H_2O)}{d\theta}$; but the most general hypothesis in regard to the nature of the reaction is

Plate 4
Difference in Analyses when using carbon and coke
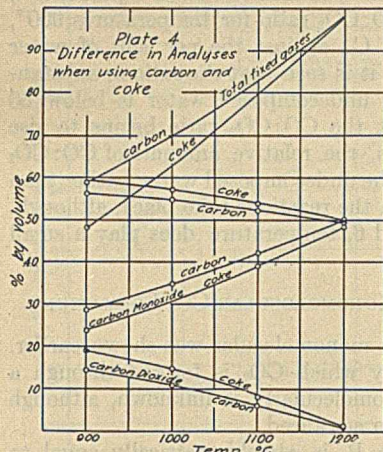
$$\frac{d(H_2O)}{d\theta} = V \text{ times a}$$

polynomial expressed in the partial pressures, and similarly we must have

$$\frac{d(CO_2)}{d\theta} = V \text{ times}$$

another polynomial expressed in the partial pressures, and by division

$$\frac{d(CO_2)}{d(H_2O)} = \text{the quotient of two polynomials in the partial}$$

pressures, since V cancels. Now, since the CO_2 vs. H_2O curve is not altered when the pressures are tripled, it follows that these two functions must be homogeneous of the same degree, hence their quotient is of zero degree, as mentioned above.

There does not seem to be any reasonable set of assumptions by which the functions expressing the rate of formation of CO_2 and the rate of decomposition of the H_2O can be regarded as both of the second or higher degree, still keeping them homogeneous. Therefore, we have proceeded on the simplest and only obvious assumption—namely, that to a fair degree of approximation, these functions are both homogeneous of the first degree.

THE MECHANISM OF WATER-GAS FORMATION

As a consequence it follows that the reaction

$$CO + H_2O = CO_2 + H_2 \tag{C}$$
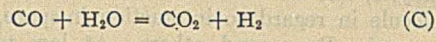
only takes place *in space* to a nearly negligible extent. It also follows that Reaction B is monomolecular. Our deductions are then that the two reactions

$$C + H_2O = CO + H_2 \tag{A}$$
$$C + 2H_2O = CO_2 + 2H_2 \tag{B}$$
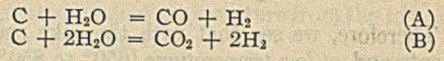
first take place, that the reaction

$$C + CO_2 = 2CO \tag{D}$$

is consecutive upon the others, and that *all* three are monomolecular.

RELATIVE RATES OF REACTIONS

In accordance with these hypotheses we may write

$$\frac{d(H_2O)}{d\theta} = (-k_a - k_b)(H_2O) \tag{4}$$

where the constant k_a, k_b, and k_d are the respective velocity constants of A, B, and D, and

$$\frac{d(CO_2)}{d\theta} = \frac{k_b}{2}(H_2O) - k_d(CO_2) \tag{5}$$

whence by division

$$\frac{d(CO_2)}{d(H_2O)} = \frac{\dfrac{k_b}{2}(H_2O) - k_d(CO_2)}{(-k_a - k_b)(H_2O)} \tag{6}$$

This equation is linear in CO_2. If we write for convenience

$$\beta = \frac{2k_a}{k_b} \text{ and } \alpha = 2 + \frac{2k_a}{k_b} \tag{7}$$

the integral of the differential equation, with the initial conditions that $CO_2 = 0$ when $H_2O = 1$, is easily found to be

$$(CO_2) = \frac{1}{\beta - \alpha}\left[(H_2O) - (H_2O)^{\beta/\alpha}\right] \tag{8}$$

By trial it is found that the equation

$$(CO_2) = \frac{1}{2}\left[(H_2O) - (H_2O)^2\right] \tag{9}$$

also fits the lower temperatures very closely indeed. This leads to $\dfrac{k_d}{k_b} = 2$ and $k_a = 0$, which indicates that at lower temperatures A takes place to a very slight extent only. At higher temperatures the equation

$$(CO_2) = 0.47\left[(H_2O) - (H_2O)^{1.85}\right] \tag{10}$$
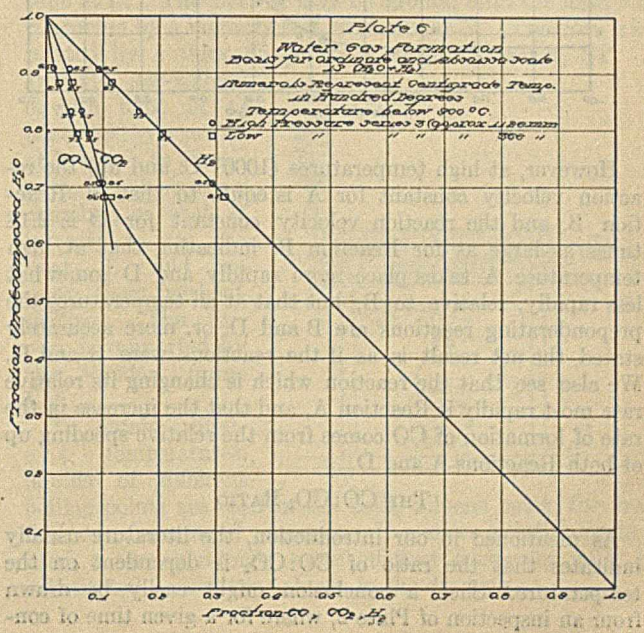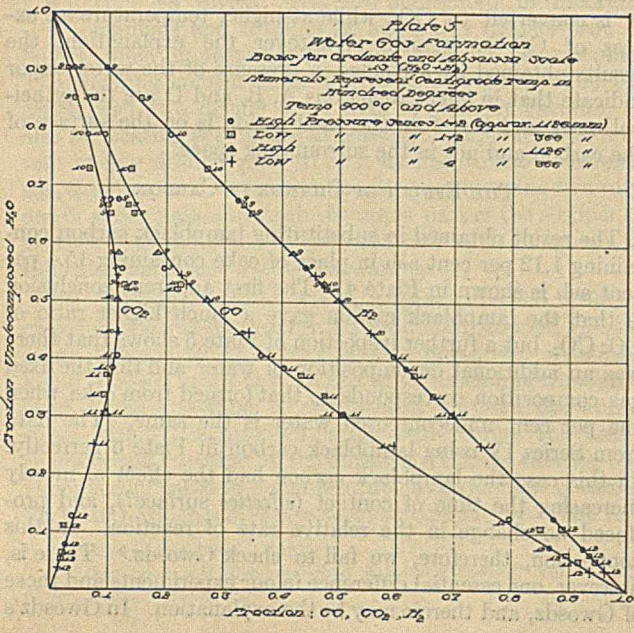
fits with fair accuracy. This leads to

$$\frac{k_d}{k_b} = 2.18 \text{ and } \frac{k_a}{k_b} = 1.0$$

Therefore, we see that with the coke used in our experiments and *at low temperatures* (650° to 850° C.), Reaction A does not take place, and that the reaction velocity constant of D is twice as large as the reaction velocity constant of B.

Plate 7
Ratio $\frac{CO}{CO_2}$ vs Undecomposed H_2O
Temp 900°C and above
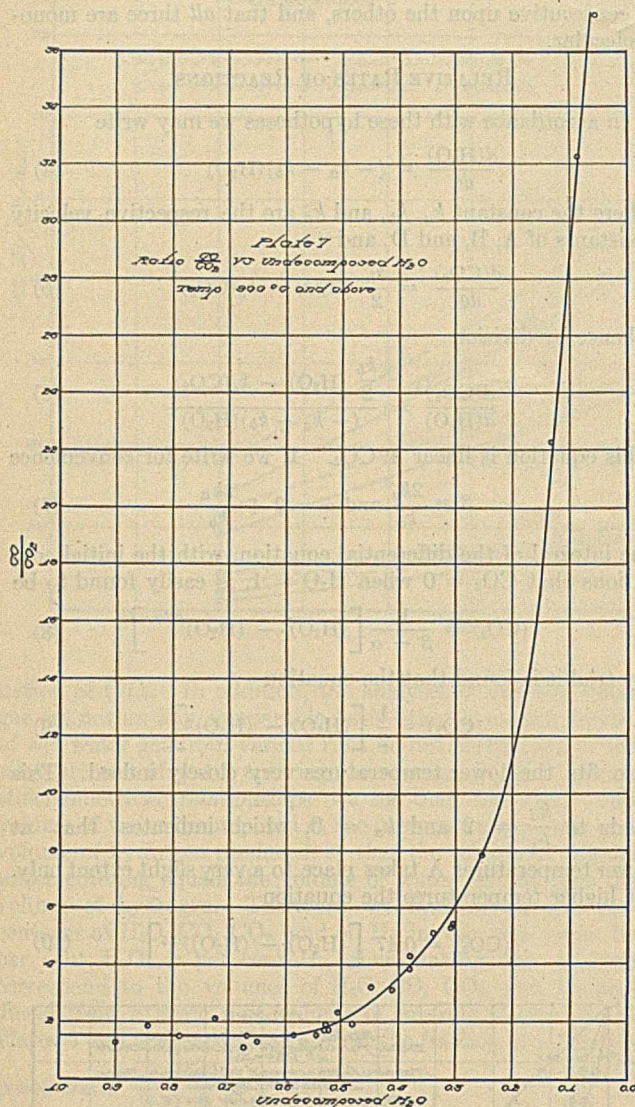
However, at high temperatures (1000° C. and up) the reaction velocity constant for A is equal to that of Reaction B, and the reaction velocity constant for D is 2.18 times as large as for Reaction B, indicating that at high temperature A takes place more rapidly and D somewhat less rapidly, relative to B, but that at all temperatures the preponderating reactions are B and D, or, more accurately stated, the net result is as if the reactions were B and D. We also see that the reaction which is changing its relative rate most rapidly is Reaction A, and that the increase in the rate of formation of CO comes from the relative speeding up of both Reactions A and D.

THE CO:CO₂ RATIO

As mentioned in our introduction, the literature usually indicates that the ratio of $CO:CO_2$ is dependent on the temperature. Such a conclusion might easily be drawn from an inspection of Plate 2, where for a given time of con-

tact the $CO:CO_2$ ratio increases greatly with temperature. However, from Plate 5 we see that the amounts of CO and CO_2 are influenced almost wholly by the percentage of water undecomposed, which in turn is dependent, not only on temperature, but time of contact, surface of carbon exposed, etc., as well. Plotting the $CO:CO_2$ ratio for temperatures 900°, 1000°, 1100°, and 1200° C., against the per cent of water undecomposed (Plate 7), it is seen that the ratio is substantially constant until the undecomposed water is below 60 per cent, at which point the $CO:CO_2$ ratio begins to rise rapidly. In other words, the relative amounts of $CO:CO_2$ seem to be a function of the undecomposed water, rather than the temperature at which the reactions take place, although, as shown in Plates 5 and 6, temperature does play a small part.

MECHANISM OF THE MONOMOLECULAR CO₂ FORMATION

That the Reaction B is monomolecular was shown earlier. The exact mechanism by which CO_2 is formed through a reaction which acts monomolecularly is unknown, although several theories have been advanced.

For example, Reaction B is stoichiometrically equal to Reaction A followed by C.

$$C + H_2O = CO + H_2 \qquad (A)$$
$$CO + H_2O = CO_2 + H_2 \qquad (C)$$
$$\text{Adding} \quad C + 2H_2O = CO_2 + 2H_2 \qquad (B)$$
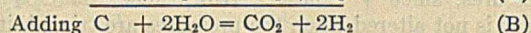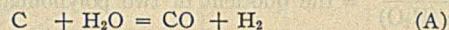
However, we have shown that Reaction C cannot take place in the usual sense—that is, as a reaction in space between the two molecules, CO and H_2O. It is possible, however, that Reaction A may take place first and the CO produced be adsorbed by the carbon. If H_2O reacts rapidly with adsorbed CO, and if Reactions A and C under these circumstances have approximately the same reaction velocities, then the resultant of these two reactions will be the same as if Reaction B were taking place monomolecularly. It should be realized that *Reaction C taking place on the surface of the carbon is vastly different from the same reaction taking place in space.* The possibility for the markedly different behavior between H_2O and CO on a carbon surface and in space is easily visualized, not only when we consider the frequency of adsorption catalysis, but also when we realize the stability of the CO molecule in regard to interaction in space, as indicated by Langmuir, Bone, and others. At low temperatures and with coke as used in these experiments, all the CO formed by A is converted to CO_2, while at higher temperature an excess of CO is formed. Whatever the explanation, the results obtained by a change in pressure of the water vapor indicate that in effect Reactions A, B, and D are the principal ones, and therefore the total action is on the surface of the carbon and not in the surrounding space.

THE EFFECT OF CHANGE IN CARBON

The result obtained in substituting lampblack carbon containing 1.12 per cent ash in place of coke containing 15.4 per cent ash is shown in Plate 4. The first apparent conclusion is that the lampblack carbon gave a much higher ratio of $CO:CO_2$, but a further inspection of Plate 5 shows that there was an additional decomposition of water and that the fixed gas composition corresponds to that formed from coke when the per cent undecomposed water is the same. The data from Series IV using lampblack carbon fit Plate 6 perfectly. In this case the lampblack carbon had the effect of merely increasing the time of contact (*effective* surface?), and produced no change in the relative rate of reaction. In this connection, therefore, we fail to check Gwosdz.[5] There is, however, one essential difference in our experiments and those of Gwosdz, and therein may be the explanation. In Gwosdz's

experiments he worked in the region of 90 per cent or less undecomposed water, whereas our lampblack-carbon runs were at 50 per cent or less undecomposed water.
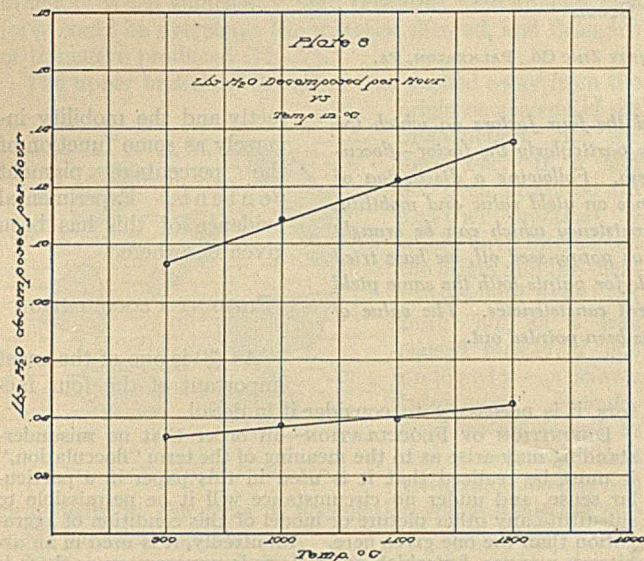
UPPER CURVE, 1128-MM. PRESSURE
LOWER CURVE, 363-MM. PRESSURE

PRACTICAL ASPECT

Aside from the light thrown on the mechanism of water-gas formation, there are also practical results from the investigation. Inspection of Plate 5 shows that a threefold increase in pressure produced almost a threefold decompo-sition of water, and that the composition of the resultant gas corresponds to that formed at equivalent water decomposition at a low pressure. This increased rate of decomposition of water is also shown in Plate 8 where the pounds of water decomposed is plotted against temperature from the low- and high-pressure runs of Series II.

Increase in pressure, therefore, affords an excellent means for increasing the capacity of a given sized water-gas generator. For example, if a generator is operating at atmospheric pressure, its capacity can be increased almost fourfold by operating at 70 lbs. per sq. in. gage, and the composition of resultant gas will remain as formerly. In other words, increased pressure gives approximately the same effect as an increased time of contact. Again, it is almost impossible to increase the thickness of a water-gas generator fuel bed owing to the increase in CO during the air blow. Increase in the pressure will permit the decrease in the thickness of a fuel bed if increased capacity is not desired, thus resulting in a lower CO content in the blow gases. An increase in the pressure may be used to prolong the duration of a steam blow, or may be used to operate at a reduced temperature of the fuel bed where such is desirable. Still again, one of the difficulties in the use of bituminous coal as a water-gas generator fuel lies in the smaller amount of surface when the coke is produced in the generator as compared with the surface of the usual coke as charged. Increased pressure may be used to compensate this decrease in surfaces, thus removing one of the obstacles to the wider use of bituminous coals in water-gas production. Many other advantages of increased pressure no doubt suggest themselves.

Incidentally the results of this work permit a more quantitative study of producer gas, as will be shown in another paper.

A Constant-Temperature Oven[1]

By Colin M. Mackall, G. E. Miller, and E. Emmet Reid

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THE OVEN here described is built on the same principle as several that are illustrated in laboratory manuals and catalogs of apparatus dealers[2] but embodies some improvements which add to its usefulness. The drawing represents a longitudinal section. The oven serves well as a drying oven, with or without vacuum, and also for heating substances at constant temperature in a current of any desired gas. If it is desired to use a current of gas, the stopper C is replaced by a stopper carrying two tubes, one of which passes through the upper part of the stopper and extends over the boats to the back end of the chamber and the other ends just inside the stopper.

The heating chamber AB is a glass tube 3.5 × 50 cm. closed at one end and carrying a ground-in stopper, C, at the other, through which it may be evacuated, etc. A suitable liquid is boiled in the flask H, the vapor ascending through the head J and the tube K and passing through the annular space within the fused-on jacket surrounding the heating chamber and escaping by the downward sloping tube E. The vapor is condensed in P and returned into the flask H through the trap G, which serves also as an expansion coil. The vapor which condenses in the heating jacket drains into the return tube at F. The flask H may be ground onto the head J or connected by a mercury seal, as shown at N. The oven is insulated by a thick 85 per cent magnesia jacket, ST. A small, low-voltage electric light at Q controlled by a switch at R serves to illuminate the heating chamber, so that it is easy to see the boats U, and remove them without spilling. The furnace is supported by the wooden frame LM.

To obtain different temperatures, liquids of different boiling points are used in the flask, toluene being the most desirable for general purposes. If a more volatile liquid is used, a correspondingly more efficient condenser must be substituted for the type shown in the drawing.
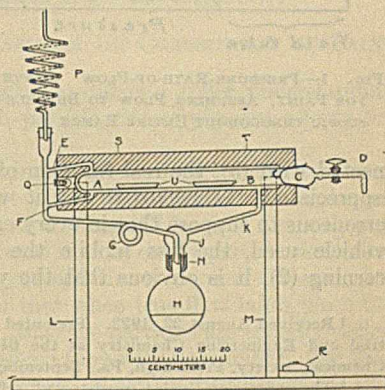
Factors Governing Paint Consistency[1]

By Henry Green

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In this paper we have described the four factors on which the consistency of paint depends, more particularly the factor—flocculation in the pigment-vehicle system. Following a discussion of the force of flocculation, its influence on yield value and mobility, and the great change in paint consistency which can be brought about by a heavy bodied oil, such as poppy-seed oil, we have tried to show whether or not it is possible for paints with the same yield value and mobility to have different consistencies. The value of such a study to paint technology has been pointed out.

THE FOUR FACTORS GOVERNING PAINT CONSISTENCY[2]

IT HAS been shown that paint is not a truly viscous liquid, but instead, a slightly plastic material;[3] further, it has been demonstrated that if its flow through a capillary tube could be maintained *completely telescopic* throughout the lowest pressures, then its pressure-rate-of-flow curve would be linear and intersect the pressure axis at the right of the origin[4] (Fig. 1). From these facts it follows that for a given paint there is a definite shearing stress below which telescopic flow cannot take place. This stress has been called the *yield value*. The slope of the curve, Fig. 1, is a function of the *mobility* of the paint; it may be considered as the reciprocal of *viscosity*, though it is not strictly correct to apply this term to plastic materials.[5]

All resistances to paint flow, regardless of their inception or manner of functioning, will be recorded either in the yield value or mobility, or jointly in both. On the basis of this, a tentative definition of paint consistency will be made: *The consistency of paint is that property imparted to it by virtue of its yield value and mobility.*

Before analyzing this definition, in order to ascertain if it is possible to have two paints of the same yield value and mobility and still recognize them as having different consistencies, it will be necessary to study the governing factors on which yield value and mobility depend. These factors are (1) the viscosity of the vehicle, (2) the pigment-vehicle ratio, (3) the force of flocculation in the pigment-vehicle system, (4) particle size of the pigment.

That the consistency of paint depends on (1) and (2) is self-evident and has always been so regarded. The importance of (3), however, has been overlooked; and, as (4) is closely connected with (3), the real function of (4) has not been fully appreciated. In regard to (1), it will be shown that it is erroneous to suppose that in every case the more viscous the vehicle used, the less mobile the paint produced. Concerning (2), it is obvious that the yield value will vary directly and the mobility inversely as some function of the percentage pigment content. Experimental evidence of this has been given elsewhere.[4]
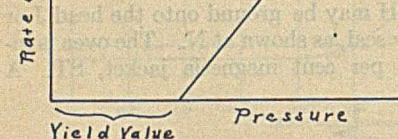
FIG. 1—PRESSURE-RATE-OF-FLOW CURVE FOR PAINT, ASSUMING FLOW TO BE TELESCOPIC THROUGHOUT ENTIRE RANGE

PIGMENT FLOCCULATION

As (3) is one of the most important of the four factors, it is necessary to consider it in detail.

DEFINITION OF FLOCCULATION—In order that no misunderstanding may arise as to the meaning of the term "flocculation," it must be realized that it is used in this paper in a particular sense, and under no circumstance will it be permissible to substitute any other picture or model of this condition of aggregation than the one given here. Admittedly, it is used in an arbitrary manner, for which an apology is unnecessary as there is no choice left in the matter to one who wishes to be perfectly definite in regard to this important phenomenon.

Flocculation is a condition of aggregation; it is that condition or state of affairs which has arisen when the dispersed phase ceases to be *uniformly* dispersed and exists in groups or clusters, the individual units (particles) of which are closely held together apparently by the residual surface tension existing in the interface between the dispersed and continuous phases.
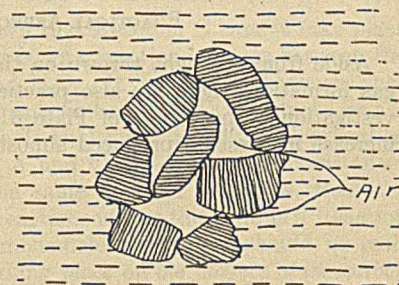
FIG. 2—UNDISPERSED LUMP

When the word "flocculation" is used it implies three things: (1) a previous state having existed in which the discontinuous phase was dispersed in a continuous phase; (2) the units of the discontinuous phase brought into contact with each other (owing to convection currents, mechanically produced motion, etc.) forming groups (flocculates); and (3) adherence (apparently due to surface tension) of the touching units.

Fig. 2 shows an undispersed lump of pigment immersed in a liquid vehicle. The vehicle is in contact only with the exterior of the lump; the interior contains air spaces. By mechanical means this lump is broken up and completely dispersed (Fig. 3). In this illustration the air spaces have been eliminated and the vehicle is presumably in complete contact with the surface of each particle. Assuming that gravity has no effect and there still remains a sufficient amount of surface energy in the pigment vehicle interface, then, if these particles are brought in contact with each other, they will loosely adhere (presumably owing to the surface energy), forming a flocculate (Fig. 4). The intervening spaces between the pigment particles are now filled with the vehicle. Furthermore, even between the apparent points of particle contact there probably exists a film of vehicle. There is no penetration of the vehicle into the intermolecular spaces of the particle. The particles do not get so closely together that they cohere forming larger ones. Flocculates in no way behave as large individual particles.

The author has shown that under low pressures paint flow through a capillary is not telescopic, and, hence, the actual curve produced in practice is such as that shown in Fig. 5. By studying under the microscope the flow of paint through capillaries, it was possible to see that when low pressures were applied, corresponding to Branch *a*, internal telescopic shearing did not take place and the material (owing to slippage) moved in a solid mass (Fig. 6). This cessation

of telescopic shearing was caused by the fact that the pigment was flocculated—a natural condition in paints—and that the force of flocculation was sufficient to hold the mass intact.[6] When sufficiently high pressures were applied, this force could be overcome, the material sheared, and Branch *b* of the curve produced (Fig. 7).

The upper branch of the curve was pushed away from the origin on account of the introduction of the lower one. If *a* had not been produced (in a c t u a l practice), *b* would have intersected the origin and the yield value would have been zero; but as *a* was caused mostly, if not e n t i r e l y—as shown below—by flocculation, we are forced to the conclusion that yield value itself is due principally to the *force* of flocculation which holds the pigment particles together.
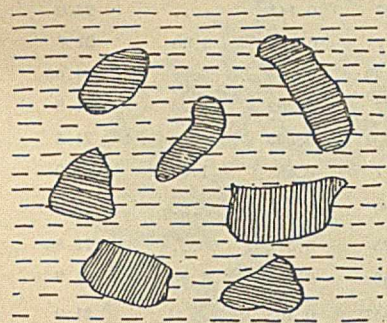
FIG. 3 —PARTICLES DISPERSED

If Sulman's theory[7] is accepted as the explanation of flocculation, this force resides in the solid-liquid interface, and is due to incompleteness of wetting. The less the degree of wetting the greater the force of flocculation and consequently the greater the yield value.

In order to fully appreciate the importance of flocculation to paint consistency it is necessary to perform the following experiment:

Make up a semipaste of zinc oxide with either kerosene or Nujol (two poorly wetting oils). It will be noticed in the process of mixing vehicle and pigment, that an abnormal quantity of the liquid can be added without producing a mixture with a tendency to flow out under its own weight. This paste will be decidedly plastic and possesses a yield value. When the consistency is correct for the experiment, the mass should be sufficiently plastic to retain its form, as shown in Fig. 8. Now add a drop or two of *bodied* (heat-thickened or air-blown) poppy-seed oil and rub in well with a spatula. The effect is striking; the paste loses its yield value and becomes extremely fluid (Fig. 9). It no longer bears the slightest resemblance to its former consistency; in fact, the entire range in consistency from one extreme to the other seems to have been passed through by the mere addition of but a few drops of heavy-boiled oil.[8]

This phenomenon is not a case of the fluidity of the added poppy-seed oil being so great as to cause a thinning of the mixture, for, in the first place, only a relatively small amount is added, and, secondly, the fluidity of this oil *is actually less* than the mobility of the mixture of zinc oxide and kerosene or Nujol. In other words, if it were to produce any effect at all, on the basis of this reasoning, it should be one of thickening rather than thinning of the paste. How, then, are we to arrive at a satisfactory explanation? With the knowledge that

FIG. 4—FLOCCULATE

flocculation is the principal cause of yield value in paint, and that the degree of flocculation is a function of wetting of pigment with vehicle, it is not difficult to suppose that the poppy-seed oil has diminished the surface energy in the solid-liquid interface and thereby produced deflocculation.

The flocculated pigment is the "structure" which holds the mass together, giving it a plastic nature; when this structure is destroyed plasticity tends to vanish.

It is not necessary to remain content with this statement as a pure theory, for it is easily verified as a fact. Fig. 10 is a photomicrograph, under low power, of the zinc oxide and kerosene in its original state—that is, as a plastic material; Fig. 11 is the same after the addition of the poppy-seed oil; the first is flocculated and the second, deflocculated. Experimental data, taken with a Bingham and Green plastometer, on the mixtures of various pigments and oils before and after deflocculation, are given in Table I. It was necessary to make these mixtures fairly stiff in order to prevent the separation of pigment and vehicle during the running of the test, and hence they are not ideal for illustrating the fact that yield value can, under proper conditions, be reduced to a nearly negligible quantity by deflocculation. The best example is the Nujol-lithopone mixture where the yield value drops from 3.77 to 0.054, the smaller quantity being scarcely measurable. In the case of the white leads with Nujol, and zinc oxide with linseed oil, wetting is fairly high to begin with; consequently, the effect of the poppy-seed oil is lessened. The residual yield values in these cases can be attributed either to imperfect deflocculation or frictional[9] resistance between the particles from close packing.

FIG. 5—ACTUAL FORM OF PRESSURE-RATE-OF-FLOW CURVE PRODUCED IN PRACTICE

The importance of flocculation to the phenomenon of "oil absorption" should be apparent from a study of photographs (Figs. 8 and 9). Both mixtures possess practically the same pigment-vehicle ratio, but the pigment in Fig. 8 could be made to absorb many times its present volume of oil before it would assume the fluid appearance shown in Fig. 9. The flocculated mass acts like a sponge. The specific surface of the pigment—usually granted to be of major importance in oil absorption—is the same in both cases, and therefore cannot be regarded as the deciding factor.

EFFECT OF SIZE OF PARTICLE ON CONSISTENCY OF PAINT

It should now be possible to obtain a fuller understanding of the manner in which particle size of pigment affects the consistency of paint.

Let us consider two zinc oxide paints ground in the same vehicle and in the same proportions; further, let it be assumed that the degree of wetting is identical for both pigments. The only difference is to be one of particle size. Let the first one be a coarse-grained zinc oxide, and the second, a fine one. Bear in mind that when true flow takes place the flocculates are sheared; that the particles are thereby pulled away from the ones to which they were flocculated; and that a resistance to "pulling away" is set up, because of the surface energy residing in the interface. It is then clear that the more extensive the pigment surface per unit area of shearing surface, the greater will be the amount of surface energy created, and consequently the higher the yield value produced.

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[6] The reason for the *gradual* discontinuance of telescopic flow under decreasing pressures is given by E. Buckingham, *Proc. Am. Soc. Testing Material*, **21** (1921), 1154.

[7] "A Contribution to the Study of Flotation," *Bull. Inst. Mining Metal.*, **182** (1919).

[8] This experiment was first shown to the author by F. P. Ingalls.
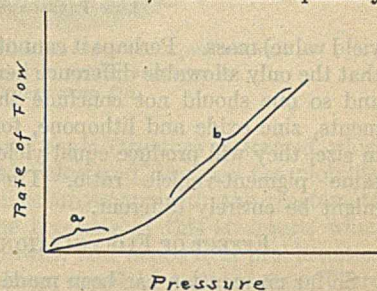
[9] E. C. Bingham, *Bur. Standards, Sci. Paper* **278**.

As the finer oxide has the larger surface per given volume, it follows that it will give the higher yield value.

It is unnecessary to check this fact with measurements taken on the plastometer, for it becomes at once self-evident, when two such pigments are mixed with similar amounts of vehicle, that the finer grained one produces the stiffer (higher
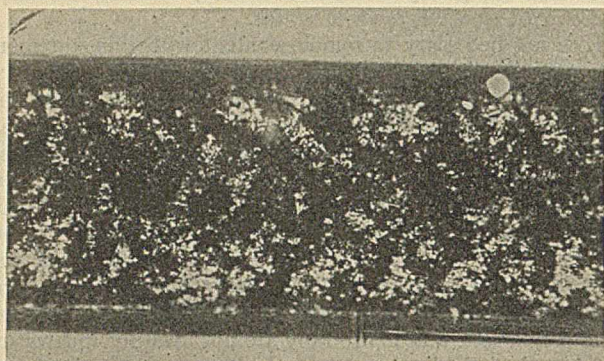

Fig. 6—Photomicrograph of Paint in Capillary Tube. The Pigment Particles Are Flocculated and the Flocculates Interlocked, thus Holding the Mass Intact under Low Pressures

yield value) mass. Perhaps it cannot be emphasized too often that the only allowable difference here is that of particle size; and so one should not conclude that if two different pigments, zinc oxide and lithopone, for example, are identical in size, they will produce equal yield values if ground to the same pigment-vehicle ratio. Their degrees of wetting might be entirely different.

Effect of Flocculation on Mobility

So far no mention has been made of the effect of flocculation on mobility. It is comparatively easy to visualize a structure imparting a yield value—a definite stress below which the structure refuses to shear—to a paint, but its effect on mobility is less easily grasped. It is not difficult, however, to visualize this if we start reasoning at the correct place—with a viscous liquid. Qualified by suitable units of measurement, viscosity may be considered as the force required to maintain a stated relative uniform velocity between two shearing surfaces. It is necessary to apply a constant force because a constant resistance is offered. Any sudden alteration in the system causing an increase in resistance will demand a corresponding increase in the force applied, in order that the required velocity may not be impaired. The introduction of solid particles will do this; if these particles flocculate, forming a structure, a still greater resistance is developed, and this must be met with a still greater applied force if
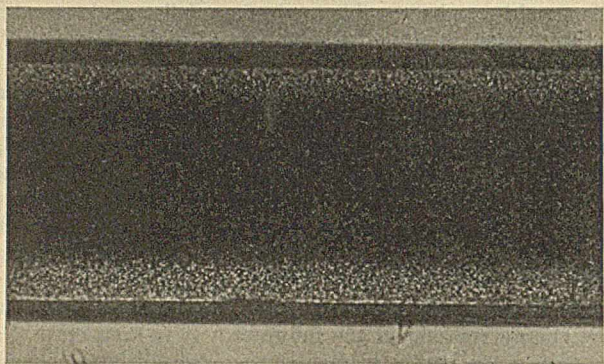
Fig. 7—Photomicrograph of Paint in Capillary Tube under Pressure Sufficiently High to Shear the Flocculates. Complete Telescopic Flow Has Ensued

the original (and required) velocity is to be maintained intact. Hence, flocculation should cause an increase in viscosity, or—more correctly speaking with regard to paints—a decrease in mobility.

Table I—Effect of Deflocculation on Yield Value and Mobility

	Yield Value	Mobility	Density	Temperature °C.
Nujol, B. C. W. L. +	1.86	0.110	2.59	22.0
Poppy-seed Oil	1.17	0.141	...	22.0
Nujol, S. W. L. +	1.17	0.188	2.00	21.7
Poppy-seed Oil	0.199	0.245	...	21.65
Nujol, Lithopone +	3.77	0.202	1.23	21.8
Poppy-seed Oil	0.054	0.529	...	21.8
Nujol, ZnO +	3.17	0.188	1.35	22.9
Poppy-seed Oil	0.90	0.302	...	22.9
+ Poppy-seed Oil	0.25	0.342	...	22.85
Raw Linseed Oil, ZnO +	1.56	0.403	1.83	21.9
Poppy-seed Oil	0.857	0.465	...	21.9
KAPXX, Acid No. 6, ZnO +	3.17	0.238	2.02	22.0
Poppy-seed Oil	2.57	0.261	...	22.0
Poppy-seed Oil { Fluidity (Mobility) 0.0792 Viscosity 0.00126 Temperature, °C. 21.9				

In order to secure experimental evidence that this line of reasoning has led to a correct conclusion, it is necessary to work with a system in which it is possible to alter the state of flocculation without appreciably changing its composition.
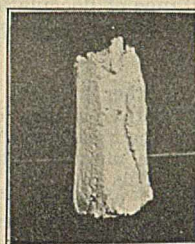
Fig. 8   Fig. 9

Fig. 8—Plastic Mixture of Zinc Oxide and Kerosene. Particles Flocculated
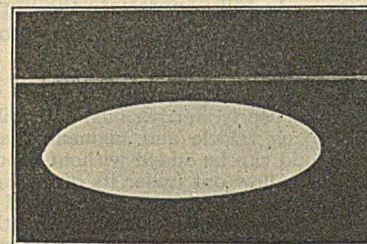
Fig. 9—After the Addition of a Small Amount of Poppy-seed Oil. Particles Deflocculated

This is accomplished most successfully by working with mixtures of either lithopone or zinc oxide and Nujol, where the effects of deflocculation can be exaggerated. The method, of course, is by working backwards—i. e., starting with a flocculated mixture, measuring its mobility, deflocculating with poppy-seed oil, measuring again and noting the difference, if any. Table I records the data of this series of experiments. It will be observed that in each case deflocculation causes an *increase in mobility;* this is tantamount to a decrease of mobility on flocculation.

Value to Paint Technology

We are now in a position to realize the value that the study of flocculation is to paint technology. It has been shown that flocculation materially influences both mobility and yield value, and that these in turn define paint consistency. This fact alone is of great importance, but perhaps even greater is the radical change that can be produced in consistency by the application of literally homeopathic doses of a heavy-bodied oil. Poppy-seed oil is by no means the only oil that is capable of introducing this change, for, in fact, nearly any properly bodied vegetable oil possesses this property to some extent. For this reason we cannot always assume that, of two paints, the one containing the more viscous vehicle will necessarily be the less mobile, because

very viscous oils are often good deflocculators, and it would be conceivable that such a paint might even be more mobile than one formed from a less viscous but strongly flocculating oil.

It might be worth while mentioning, at this point, that the thinning of paints, either shortly after application and

anomalies sometimes occurring in paint, as gelatinization and stringiness? It is certainly proper and permissible to speak of gelatinous and stringy consistencies. The phenomenon of gelatinization may manifest itself in two ways— either the vehicle gelatinizes or the pigment particles become covered with soap, firmly binding them together into
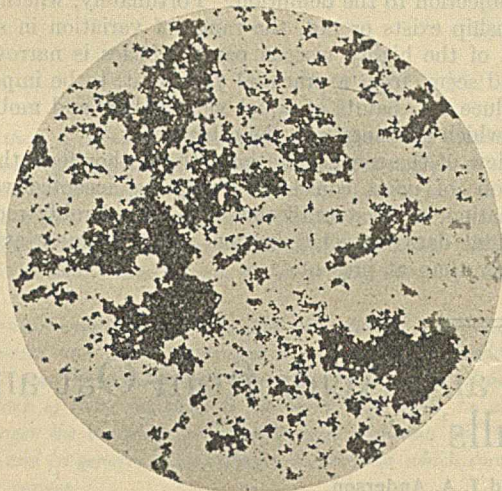
Fig. 10—Photomicrograph of the Plastic Mixture Shown in Fig. 8. Particles Flocculated into Dense Masses
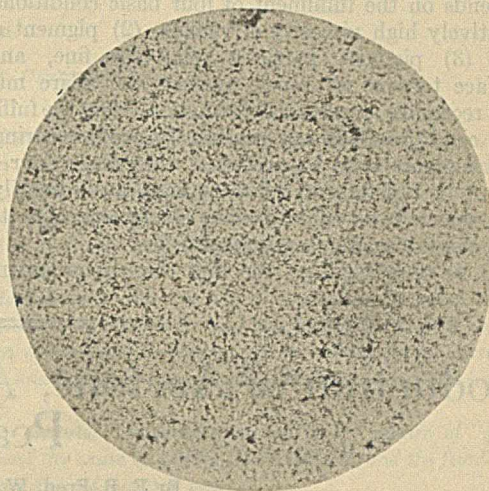
Fig. 11—Photomicrograph Showing Completeness of Deflocculation after Addition of Poppy-seed Oil

before drying, or while still in the container, is probably due to an increase in wetting power of the vehicle arising from the absorption of oxygen, most likely from the surface of the pigment itself. Increased wetting causes deflocculation, which in turn destroys the yield value of the paint, enabling it to flow easily under its own weight.

Fig. 12 shows the effect on the plastic flow curve of simple deflocculation—a decrease in yield value plus an increase in mobility. Fig. 13 shows the result from oxidation. If oxidation is slight it should produce practically the same effect as illustrated in Fig. 12, for oxidation increases wetting; on the other hand, if the absorption of oxygen continues until the vehicle becomes *extremely* viscous, then the mobility of the paint will fall. Paradoxically, such a paint has thinned and thickened at the same time. In the case of soap formation, we have simply the addition of new particles, either colloidal or crystalloidal, and perhaps the removal of a certain percentage of the finest of the pigment particles. The net result is likely to be an increase in the total number of particles, which produces the same effect as increasing the pigment-vehicle ratio—i. e., a raising of the yield value and a lowering in mobility.

The object of this paper has been to discuss the four *cardinal* factors controlling paint consistency. Naturally there are others, such as temperature, for instance, but this may be called a minor one, for no investigator is liable to judge consistency at any temperature that varies radically from normal room temperature; hence, the range is small and the effect of secondary importance. Soap formation has a pronounced influence on paint consistency, but this, in most cases, can be considered as a subdivision of factor (2) or (4).

Problems of Gelatinization and Stringiness

It is now necessary to consider the question raised in the opening paragraphs. Is it possible to have two paints possessing identical yield values and mobilities, and at the same time recognize them as having different consistencies? As pointed out, all resistances to flow are recorded in the yield value and mobility; but do these quantities express such

an elastic mass. In both cases structure is formed which would increase the yield value and decrease the mobility. An attempt to secure measurements with the plastometer would only result in the breaking of this structure, which was a matter of slow growth, and hence it is problematical whether or not the readings would be true values. Therefore, it will be a difficult matter to decide, from experimental evidence, if gelatinization is defined by and incorporated in the figures given by yield value and mobility. It might be well to point out that flocculates themselves are always dispersed during their passage through the capillary tube, but it is not actually the existence of the flocculates that influences yield value and mobility, but the *force* of flocculation, and this remains intact as long as the wetting properties of pigment and vehicle are unaltered.

If it should become possible to

Fig. 12—The Effect of Deflocculation on Yield Value and Mobility, Shown Graphically

simulate gelatinization by a proper combination of the four governing factors, then certain yield values and mobilities would result that would henceforth be indicative of this type of consistency. Furthermore, if these yield values and mobilities should happen to match those of a truly gelatinized paint, then the tentative definition of paint consistency would be immune from attack as far as gelatinization is concerned.

Fig. 13—The Effect of Oxidation and So a Formation on the Plasticity of Paints

At first glance these suppositions seem far removed from the realm of possibility, but deeper reflection will instill caution against arriving at a hasty and doubtful conclusion; it will develop the realization of the existence of undiscovered and latent possibilities, and emphasize the extreme difficulty of

visualizing the mechanism of a model possessing the properties of a gelatinous paint. At present no one has produced any evidence indicating that the idea of simulating gelatinization is untenable, and so the question remains an open one from this aspect.

In regard to stringiness of paints, the author believes that this depends on the fulfilment of four basic conditions: (1) comparatively high viscosity of vehicle, (2) pigment defloc-culated, (3) pigment particles relatively fine, and (4) low surface tension of vehicle against air. Care must be taken to recognize an essential distinction—that the fulfilment of these conditions will not necessarily produce stringiness, but if stringiness is to be produced, then these four condi-tions must be maintained. For instance, an ordinarily high pigment-vehicle ratio could destroy stringiness, even though the four conditions were entirely satisfied.
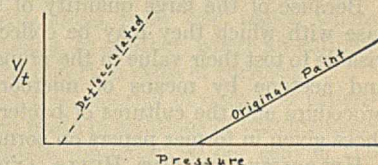
It will be observed that the first three requirements di-rectly govern yield value and mobility, and, if it were not for the fourth, stringiness might be indicated in the meas-urements of paint consistency. If, however, a fundamental relationship exists between surface tension of vehicle against air and vehicle against pigment, then the fourth condition would be a function of flocculation and could not be raised as an objection to the definition. Fortunately, whether this relationship exists or not, the range of variation in surface tension of the highly viscous paint vehicles is narrow, and it would seem, from a practical viewpoint, to be impossible to produce two paints of equal yield values and mobilities, one of which is stringy and the other not.

In view of these considerations, the author feels that the definition of paint consistency may be accepted without qualification, at least until there are considerably more ex-perimental data on gelatinization and stringiness available for study than at present.

Production of Acetone, Alcohol, and Acids from Oat and Peanut Hulls[1]

By E. B. Fred, W. H. Peterson, and J. A. Anderson

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IN PREVIOUS papers[2] the authors have pointed out that acetone, alcohol, and acids may be produced from the fermentation of hydrolyzed corncob sirup. Since these products are formed by the action of certain bacteria on pentose sugars, it is highly probable that similar results will be obtained from any substance which on hydrolysis yields pentose sugars.

In the manufacture of oatmeal and of peanut butter and oil, an enormous quantity of oat hulls and peanut hulls are ob-tained as by-products. These by-products are used as filler for stock feed, burned as fuel, or discarded as waste products.

Because of the large quantity of these materials and the ease with which they may be collected, it was deemed ad-visable to test their value in the preparation of acids, alcohol, and acetone by means of microörganisms. The general procedure and the cultures of bacteria used are the same as those given in former papers on corncobs.

HYDROLYSIS OF OAT HULLS AND PEANUT HULLS—The crude sirup was prepared by hydrolyzing the hulls with 2 per cent sulfuric acid for 2 hrs. at 15 lbs. pressure. After hy-drolysis the acid was neutralized with milk of lime and the sugars removed by pressing and washing the insoluble residue. In this way the oat hulls gave an average yield of 26.5 per cent of reducing sugars as glucose, and the peanut hulls 7.6 per cent of sugars. The concentrated sirup from the hulls was diluted and its fermentability tested. Complete de-tails of the media and methods of analyses are given in pre-vious papers, and need not be repeated here.

FERMENTATION WITH BACILLUS ACETOETHYLICUM—Here the strong sugar solution was diluted with water, a small amount of peptone and sodium phosphate added, and the medium inoculated. A vigorous fermentation ensued, with the evolution of considerable quantities of carbon dioxide and hydrogen, which reached its maximum about the third or fourth day. At this time a layer of foam 2 or 3 in. thick covered the surface of the liquid. The rate of gas production decreased from this time until at the end of 10 days, when it had practically ceased. Analyses of the fermented liquors for sugar, acetone, alcohol, and volatile acids, are given in Table I.

TABLE I—YIELD OF PRODUCTS WITH BACILLUS ACETOETHYLICUM

	Age of Culture Days	Reducing Sugars as Glucose G.	Acetone G.	Alcohol as Ethyl G.	Volatile Acid as Acetic G.	Total Products G.
Oat hulls	0	3.41	....	....	....	....
	10	0.37	0.385	0.822	0.137	1.344
	0	3.22	....	....	....	....
	7	0.44	0.470	0.876	0.169	1.515
Peanut hulls	0	2.43	....	....	....	....
	5	0.691	0.289	0.585	0.370	1.244
	8	0.462	0.314	0.546	0.426	1.286

Calculated for 100 Cc. of culture

An examination of the data shows that the reducing sugars obtained from both materials are almost completely fer-mented. The relation of the various products to one another and to the sugar consumed is approximately the same as that previously reported for the pure sugars and for corncob sirup.

Because of the larger percentage of reducing sugars ob-tained from oat hulls, the yield of products per hundred pounds of dry material is greater than from peanut hulls. On the basis of 100 lbs. of oat hulls, about 3.9 lbs. of acetone, 7.2 lbs. of ethyl alcohol, and 1.4 lbs. of volatile acid were ob-tained.

FERMENTATION WITH LACTOBACILLUS PENTOACETICUS— The crude xylose sirup was diluted with yeast water until the medium contained about 2 per cent of sugar calculated as glucose. The fermentation was slow and considerable quantities of sugar remained unfermented even after 30 days. The results of the analyses are given in Table II.

TABLE II—YIELD OF PRODUCTS WITH LACTOBACILLUS PENTOACETICUS

	Culture No.	Acid as Acetic G.	Acid from Fer-mentation G.	Total Non-volatile Acid as Lactic G.	Nonvola-tile Acid from Fer-mentation G.	Total Acetic and Lac-tic Acids by Fer-mentation G.
Oat hulls	118-8	0.632	0.423	0.833	0.608	1.031
Peanut hulls	118-8	0.736	0.421	1.115	0.781	1.202
Peanut hulls	124-2	0.439	0.124	1.432	1.098	1.222

[1] Received August 12, 1922.
[2] THIS JOURNAL, 13 (1921), 211, 757.

The Mechanism of the Corrosion of Iron and Steel in Natural Waters and the Calculation of Specific Rates of Corrosion[1,2]

By Robert E. Wilson

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More than a dozen variables have been shown, by experiments under a variety of conditions, to have an important effect on the rate of corrosion of iron and steel. This makes comparisons and correlation difficult, but an analysis of the fundamental reactions involved, together with some recently obtained data, brings out a number of important considerations which greatly simplify corrosion studies.

The fundamental reactions in the corrosion of iron and steel are discussed and it is shown that the entire field of underwater corrosion may be divided into three distinct ranges depending upon which of these reactions is the controlling one. In each of these ranges the variables which determine corrosion are few in number, and in general quite different from those which control in the other ranges.

In alkaline solutions with a pP above 11 or 11.5, Reaction 1 is the slowest of the series and therefore determines the rate of corrosion in this range. As a result, corrosion is always comparatively slow, and the hydrogen-ion concentration and the temperature are the two most important variables. In the range from a pH of about 11 to one of about 4, which includes practically all natural waters, Reaction 2 is slower than Reaction 1, but faster than the parallel Reaction 3, and hence it determines the rate of corrosion. It further appears that the slowest factor in this reaction is the

rate of diffusion of dissolved oxygen through the stationary film of water on the iron surface, and hence oxygen concentration and velocity of flow are the two most important variables, temperature also being important, though less so than in the other ranges, while the effect of hydrogen-ion concentration and the nature of the metal are negligible.

In acid solutions, below a pH of around 4, Reaction 3 becomes more rapid than Reaction 2, and determines the rate of corrosion. Hydrogen overvoltage, the nature of impurities in the metal, temperature, and hydrogen-ion concentration become the most important variables.

Certain popular misconceptions as to the nature of "galvanic action" and the cause of pitting are discussed, and the fundamental mechanism thereof pointed out.

"Ferroxyl indicator" tests are shown to be unreliable, owing to the depolarizing action of the ferricyanide, and the dangers of using accelerated corrosion tests as a basis for practical conclusions is emphasized.

For corrosion in natural waters it is suggested that the specific rate of corrosion be defined as the loss in weight in milligrams per square centimeter per year per cc. oxygen in 1 liter. Conversion factors are given to convert the foregoing figures into other units.

A NYONE who undertakes a survey of the voluminous literature on the corrosion of iron and steel is certain to be discouraged, if not overwhelmed, by the number of variables which have been shown to affect the rate of corrosion of iron in aqueous solutions. Among these may be mentioned the solution pressure of the metallic iron, the hydrogen-ion concentration of the water, the hydrogen overvoltage of the metal and of the impurities contained therein, or of other metals in electrical contact, the oxygen, ferrous- and ferric-ion contents of the solution, the catalysis of the reaction between hydrogen and oxygen by various agencies, the temperature, the velocity of convection or flow, the salt content of the water, the presence of oxidizing or passivating agents, the character of the rust films, etc., etc.

If all these factors were in reality as important as they frequently appear from isolated sets of experiments, it would be practically impossible to correlate corrosion data obtained with different natural waters on different samples of steel. Fortunately, however, while each of these factors is undoubtedly important under some particular set of conditions, there are wide ranges of conditions within which comparatively few have any large effect on the rate of corrosion, that of the others being either negligible or zero. The failure, however, to distinguish between these ranges within which different factors are controlling, is one of the fundamental reasons why erroneous conclusions have so frequently been drawn in measuring the relative rates of corrosion of

different kinds of iron or steel, or in attempting to determine the relative importance of different variables. Similarly, attempts to accelerate corrosion tests are very likely to lead to erroneous conclusions, because this acceleration is usually obtained by changing conditions from one region where one set of factors is controlling, to another where an entirely different set determines the observed rates of corrosion.

In spite of the fact that the majority of corrosion experiments appear to have been made in solutions of varying acidity or high salt concentration, probably 90 per cent of the iron destroyed by immersion in any liquid is corroded by contact with natural waters, whose salt content and acidity or alkalinity is quite low. Fortunately, as the following analysis shows, in this highly important range the factors which have a marked effect on the rate of corrosion are very few in number, and most of those enumerated above are of no appreciable importance. Although this might have been deduced from facts long known, it has apparently never been pointed out, nor properly taken advantage of.

FUNDAMENTAL REACTIONS IN CORROSION

Regardless of the school of corrosion theory to which we may give our personal allegiance, there can be no real doubt but that the fundamental reaction in the corrosion of iron is essentially, as first pointed out by Whitney,[3]

$$Fe + 2H^+ \longrightarrow Fe^{++} + 2H \qquad (1)$$
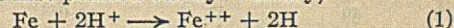
As first stated by Walker,[4] the resulting hydrogen takes the form of a polarizing film which must be disposed of in some way before the reaction can long continue. This elimi-

[3] *J. Am. Chem. Soc.*, **25** (1903), 394.

[4] *Proc. Am. Electrochem. Soc.*, **14** (1908), 175.

nation of hydrogen may be brought about by either of the two following reactions:

$$2H + \frac{1}{2}O_2 \longrightarrow H_2O \qquad (2)$$
$$2H \longrightarrow H_2 \text{ (gas)} \qquad (3)$$
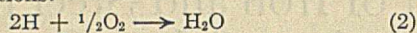
As between these reactions, investigations in this laboratory and in that of the National Tube Company have indicated beyond serious question that the amount of hydrogen evolved as such by the corrosion of steel in natural waters below 200° F. is practically inappreciable compared with the oxygen consumed—except in the case of waters which are substantially oxygen-free, where the rate of corrosion is almost negligible.[5] It is evident, then, that under these conditions, the amount of hydrogen removed by the third reaction is practically negligible, and that the rate of Reactions 1 and 2 in series almost always determines the rate of corrosion in natural waters.

In neutral or alkaline solutions there is still another reaction—the oxidation of $Fe(OH)_2$ to $Fe(OH)_3$—which should be mentioned, but it practically never exerts an important influence on the rate of corrosion, though it does affect the character of the deposit formed.

DIFFERENCES IN THE FACTORS WHICH CONTROL CORROSION AT DIFFERENT HYDROGEN-ION CONCENTRATIONS

Disregarding the electrochemical or any other theory of corrosion, and considering only the ordinary laws governing reaction rates it is obvious that in such a case where two reactions take place in series, whichever is inherently slower will determine the rate of both—except for a narrow intermediate range where the rates are nearly equal and a variation in either will affect the results. It is an experimentally observed fact, as shown by Walker[6] and others, that the rate of corrosion is directly proportional to the oxygen content of natural waters. It is therefore evident that the second reaction is controlling, and it must logically be concluded that the first reaction keeps enough hydrogen on the surface of the metal to care for the available oxygen, *regardless of the hydrogen-ion concentration*, within the ordinary limits in natural waters.

While this conclusion that the hydrogen-ion concentration should not appreciably affect the results in this range is surprising, it has been verified by recent experimental work. For example, the National Tube Company made experiments on the addition of varying amounts of caustic soda to Pittsburgh water, and found that increasing the calculated alkalinity from 0 to 100 p. p. m. did not appreciably affect the rate of corrosion in hot-water pipes. Similarly, experiments in this laboratory showed that treating a water originally slightly acid to phenolphthalein with enough alkali to give a titration corresponding to 30 p. p. m. NaOH did not affect the rate of corrosion at 70° F.

Unfortunately, no determinations were made of the pH of the waters used in these experiments, and the presence of carbonates, etc., as buffer salts, makes the exact figure quite uncertain. To demonstrate this point the following table shows the amount of 0.01 N carbonate-free caustic soda which was required to give a given pH to various samples of water:

PARTS PER MILLION OF NaOH REQUIRED TO GIVE SPECIFIED pH TO VARIOUS SAMPLES OF WATER

pH	Cambridge Tap Water P. p. M.	Distilled Water P. p. M.	Redistilled Water P. p. M.	Theoretical for Pure Water P. p. M. of NaOH
7.0	Trace	Trace	0.0	0.00
8.0	3	2	<0.8	0.04
8.6	7	4	1.6	0.16
10.0	40	17	13.0	4.00

[5] This condition accounts for the appearance of small amounts of H_2 in closed-system hot-water radiators, where the oxygen is inappreciable and the rate of corrosion extremely low. In the case of steam heating systems the concentration of CO_2 in the condensed liquid tends to accelerate this action, owing to the higher hydrogen-ion content.

[6] Walker, Cederholm, and Bent, *J. Am. Chem. Soc.*, **29** (1907), 1251.

The Cambridge tap and ordinary distilled water (from an automatic, electrically heated still) were handled without any precautions, and the redistilled water was prepared by discarding the first 25 per cent coming over and collecting the rest in a previously steamed bottle protected against the air by a soda-lime tube. However, no alkali was added to the water before distillation, as would be necessary in order to remove all CO_2. The aim was not to obtain results of high accuracy or to check up any theory, but to indicate the range of deviation in pH from the value indicated by titration, likely to be encountered in working with different kinds of water. The enormous discrepancy around the neutral point for water containing even such a small amount of dissolved salts as Cambridge (hardness 29, total solids 76 p. p. m.) is evident from this table as is also the need for very special precautions in working with distilled water. In future work on corrosion, this laboratory—and, it is is hoped, other laboratories—will determine the precise pH of all the natural waters and other solutions used, rather than relying on titration data.

In the light of these data and the titration figures presented above, it appears that the pH of water must in general be greater than 10 or 10.5 before alkali begins to exert an appreciable retarding effect on the rate of corrosion.

Eventually, of course, as the alkalinity is further increased the concentration of hydrogen ions must drop low enough to retard corrosion, as shown by the well-known protective action exerted by a few drops of caustic soda in a beaker of water containing pieces of iron. The exact limit of alkalinity at which Reaction 1 is retarded sufficiently to become the controlling factor depends somewhat on other conditions (temperature, rate of circulation, etc.) and has not been accurately located, but it is apparently somewhere in the neighborhood of a pH of 10 or 11, which is much higher than any ordinary natural water. The limit appears to be somewhat lower at the lower temperatures, as might be expected from the decreased ionization of water.

The factors which determine the rate of corrosion in natural waters and weakly acid or alkaline solutions may be made more clear by referring to Fig. 1, which indicates *qualitatively* the effect of hydrogen-ion concentration and of oxygen concentration over a fairly wide range, the velocity and temperature of the water being kept constant.

The dotted line to the left shows roughly the *potential* rate of corrosion according to Reaction 1, if the polarizing film of hydrogen could be removed by Reaction 2 as fast as it was formed. This curve is very low at a pH of 12, but is rising very rapidly around a pH of 10.

Below a pH of around 11 the rate of Reaction 1 becomes so slow as to be largely controlling, the oxygen concentration having comparatively little effect *provided* it is large enough to oxidize the small amount of hydrogen produced by Reaction 1. At lower alkalinities, however, corresponding to those in natural waters, the potential rate of Reaction 1 becomes so high that the rate of corrosion is limited only by the oxygen content, as indicated by the three horizontal lines for different oxygen concentrations.

As we pass through the neutral point and on to the acid side, a point is eventually reached where the tendency to produce hydrogen is so great that some is evolved as gas, regardless of the presence or absence of oxgyen, as indicated by the dotted curve on the right in Fig. 1. If oxygen were present, the rate of corrosion would probably approximate the sum of the two effects, though each reaction would affect the other to some extent. Once hydrogen evolution became at all rapid, however, as in moderately strong acids, the effect of the presence of oxygen would be negligible, and the hydrogen overvoltage would become the most important single factor in determining the rate of corrosion.

The whole field of corrosion in solutions varying in pH from 0 to 14 may therefore be divided into three main regions, in each of which the controlling factors are quite different. There are also two narrow intermediate regions where one condition gradually merges into the next. The comparative effect of the various factors, such as oxygen concentration, velocity, temperature, hydrogen, overvoltage, etc., in each region, is discussed in detail in the following sections.

It is probably not out of place to emphasize again, as has recently been done by Speller,[7] the fallacy of making tests in one region, and applying them in another, as has so frequently been attempted in the past.
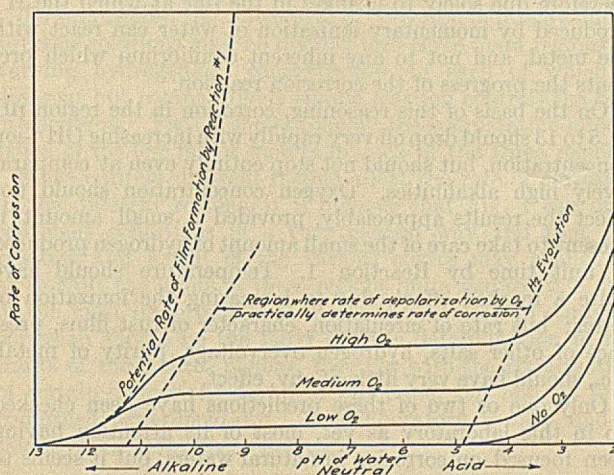

FIG. 1

Factors Determining Corrosion in Natural Waters

As indicated previously, the flat central portion of the curves fortunately appears to cover most of the ordinary range of corrosion in natural waters, although the precise limits of this region are undoubtedly affected by a variety of conditions. It is comparatively simple to determine whether or not a given case lies in this region—if it is feared that the water may be so acid as to pass the right-hand limit, a determination of hydrogen evolved as gas or dissolved in the water would settle the question, whereas, if the question arises as to whether the alkaline limit has been passed, it is merely necessary to determine whether or not a slight decrease in alkalinity affects the results appreciably.

Since it has been demonstrated that Reaction 2 determines the rate of corrosion in most natural waters, the question next arises as to whether the slowest phase in this reaction is the rate at which oxygen *diffuses in* to the metal surface, or the rate at which it *reacts* with the nascent hydrogen after reaching this surface. Either explanation could account for the rate being proportional to the dissolved oxygen content, but it should be readily possible to determine which is correct by noting the effect of stirring or the velocity of flow on the rate of corrosion—if the rate of reaction is the determining thing, velocity should have little effect; whereas if diffusion determines the rate, velocity should have a pronounced effect. The following paper by Speller and Kendall shows clearly that velocity has a very large effect, and it therefore indicates that the determining factor in the rate of corrosion is the rate of diffusion of oxygen through a stationary film of water adjacent to the surface of the metal. This is further borne out by the fact that if the rate of corrosion is calculated on the assumption that the

oxygen must diffuse through a stationary film about 0.3 mm. thick (the average of results calculated for the thickness of diffusion films at electrodes[8]), using approximate values from the literature for the diffusion coefficient of dissolved oxygen, the calculated rates of diffusion check well with the rates of corrosion observed by Speller and Kendall at moderate velocities and temperatures.

The data of Speller and Kendall also confirm this conclusion in another way. Their results indicate that the rate of corrosion in pipes is very low and increases but slowly at low velocities, where straight-line flow is known to prevail and then rises sharply in the critical region, and continues to increase, though less rapidly, as the velocity increases through the turbulent flow region. This behavior is very similar to that observed by McAdams and Frost[9] for the coefficients of heat transfer from pipes to liquids, which similarly depend on the thickness of the stationary film on the pipe surface, through which heat must be conducted.

This point being established, it is a simple matter to predict what factors should have a large effect on the rate of corrosion in natural waters, and what factors should be negligible under ordinary conditions.

Since the rate of diffusion of oxygen through a stationary film is the determining factor in this wide intermediate range of hydrogen-ion concentrations, the variables which should have the largest effect on the rate of corrosion in this range are the oxygen content of the water and the velocity of flow past the steel surface. This checks precisely with the observations of Walker and Speller, respectively. The thickness and impermeability of rust films or other coatings would probably have a marked retarding effect. It is also conceivable that colloidal ferric hydroxide might have some catalytic action, as recently suggested by Friend.[10] Friend believes that colloidal particles of ferric hydroxide diffuse in and oxidize the iron and then diffuse out and take up oxygen from the water. The direct reaction between colloidal particles and the metal appears improbable in view of the overwhelming evidence that the latter is covered with the polarizing film of hydrogen, but Friend's results could just as readily be explained on the more reasonable assumption that colloidal ferric hydroxide is able to oxidize the nascent hydrogen film, and if it is present in large amounts, as in beaker tests where the water is not being continuously renewed, the oxygen transported in this manner might be of the same order of magnitude as that which diffuses in the ordinary way. In most pipe systems, however, the concentration of colloidal ferric hydroxide is quite low and it seems improbable that its catalytic effect can be of more than very slight importance. The possibility of catalysis by accumulated $Fe(OH)_3$, and the impossibility of controlling or reproducing the convection currents which largely determine the rate of diffusion of oxygen, unite to throw doubt on the validity of the ordinary "beaker" corrosion tests as far as they are applied to corrosion by natural waters. The work of Speller in measuring the rate of corrosion when water flows through standard pipe coils marks a great advance in obtaining reliable data applicable to actual operating conditions.

On the other hand, small variations in the acidity or alkalinity of the water, or moderate concentrations of neutral salts should have no direct effect unless they were themselves depolarizing agents for H_2, or affected the catalytic

[7] Discussion of Bancroft's paper, *Proc. Am. Soc. Testing Materials*, **22** (1922), 237.

[8] Wilson and Youtz, "The Importance of Diffusion in Organic Electrochemistry." To appear in a future issue of THIS JOURNAL.

[9] THIS JOURNAL, **14** (1922), 1101.

[10] *Trans. Am. Electrochem. Soc.*, **40** (1921), 63. This laboratory has not been able to check the surprising results of Friend which indicated a drop in corrosion at high velocities in natural waters, or a rise uniform with velocity in acids. These results will form the basis of later papers by other members of the laboratory staff.

properties of the Fe(OH)₃ formed by the reaction. Very high concentrations of salt should tend to decrease corrosion by decreasing the solubility and increasing the viscosity of the solution, the latter factor tending not only to increase the thickness of the stationary film, but also to decrease the specific rate of diffusion of oxygen.

The most important conclusion to be drawn, however, is that, since the limiting factor under these conditions is the rate of diffusion of oxygen to the metal, the composition or heat treatment of the iron or steel, or the presence of impurities, should not appreciably affect the results. While this may seem surprising, it is in entire accord with the best data on the subject—as, for example, the A. S. T. M., under-water corrosion tests on various kinds of sheet iron and steel (final report has not yet been made), the careful tests of Richardson[11] on pure iron *vs.* steel, and the final tacit compromise in the prolonged wrought iron *vs.* steel controversy. The contrary impression has resulted partly from the results of accelerated tests in acid solutions, where composition does affect the results. Some rather erratic results with different kinds of iron or steel in natural waters are almost certainly caused by insufficient control of the important, but frequently unappreciated, variable, the rate of circulation of the water.

It is, of course, possible by alloying iron with relatively large proportions of other elements—for example, silicon—to so far reduce its solution pressure that Reaction 1 is controlling even in natural waters and composition becomes of primary importance. This is not true, however, of the ordinary variations in composition of iron and steel used commercially.

Temperature should have a considerable effect, though not as large as though a rate of reaction were the controlling factor—rates of reaction generally double for an 8- or 10-degree rise in temperature, while rates of diffusion generally require around 25° C. The observed temperature coefficient of corrosion in natural waters approximates the latter figure more closely than the former.

Factors Affecting Corrosion in Moderately Alkaline Solutions

In solutions of greater alkalinity than correspond to a pH of about 11, increasing alkalinity markedly reduces the rate of corrosion, and the oxygen content has a progressively less effect until, at a pH above 12, the rate of the first reaction becomes the determining factor. The precise mechanism of the very slow rates of corrosion in warm or hot solutions of pH 12 or 13 is somewhat obscure—it might at first appear that the rate of diffusion of hydrogen ions would be the determining factor, since so few are present, but this case is, in reality, quite different from the diffusion of a separately dissolved constituent such as oxygen, because hydrogen ions are continually being formed at all points in the solution by the momentary ionization of water, but in the presence of so many OH⁻ ions their average "life," or period of separate existence as such, is very small. Whether or not they react with the metal depends on the relative rates and free-energy decreases of the two possible reactions into which they may enter.

It is frequently, but erroneously, assumed in discussing corrosion in alkaline solutions that as the hydrogen-ion concentration drops off, the free-energy decrease accompanying the fundamental reaction of corrosion drops off very rapidly, and eventually reaches zero, so that corrosion must stop altogether. Actually, however, if the solution pressure of the metal and the equilibrium pressure of hydrogen gas remain constant, the free-energy change accompanying

$$corrosion = -\Delta F = C + k \log \frac{(H^+)^2}{(Fe^{++})}.$$

In acid solutions, where H⁺ is independent of Fe⁺⁺, $-\Delta F$ obviously increases as the log (H⁺)², but the converse is not true in alkaline solutions, for as soon as a point is reached where Fe(OH)₂ begins to precipitate out, any increase in OH⁻ ions will decrease the concentration of Fe⁺⁺ just as rapidly as it decreases (H⁺)², and the *free-energy decrease* accompanying corrosion with the formation of Fe(OH)₂ must, therefore, theoretically *remain constant*, regardless of the concentration of OH⁻, H⁺, or Fe⁺⁺, at least as far as moderately dilute solutions are concerned. Any observed decrease in the *rate* of corrosion with increased alkalinity is therefore due solely to changes in the *rate* at which the H⁺ produced by momentary ionization of water can react with the metal, and not to any inherent equilibrium which prevents the progress of the corrosion reaction.

On the basis of this reasoning, corrosion in the region pH 11.5 to 13 should drop off very rapidly with increasing OH⁻-ion concentration, but should not stop entirely even at comparatively high alkalinities. Oxygen concentration should not affect the results appreciably, provided a small amount is present to take care of the small amount of hydrogen produced in unit time by Reaction 1. Temperature should have quite a marked effect, due to increasing the ionization of water; but rate of circulation, character of rust films, presence of other salts, hydrogen overvoltage, purity of metal, etc., should have very little, if any, effect.

Only one or two of these predictions have been checked up in this laboratory as yet, most of its attention having been focused on corrosion in natural waters, but it seems to accord well with what few data have been published on corrosion under these conditions.

One effect of making water more alkaline, particularly in piping systems, etc., may be to increase the scale formation and thus indirectly lower the rate of corrosion, especially if the alkalinity is maintained for some little time.

Corrosion in very concentrated caustic solutions at high temperatures is quite a separate problem, where even the fundamental reactions involved may be quite different.

Factors Affecting Corrosion in Moderately Acid Solutions

When iron is immersed in acid solution of a pH higher than about 4.5, appreciable amounts of hydrogen begin to appear, first merely as dissolved gas; but by the time a pH of 4 is reached, bubbles are usually evolved. If the iron is in contact with other metals or impurities of low hydrogen overvoltage, this evolution may begin at considerably lower acidities. As soon as the evolution becomes appreciable, and at all high concentrations of acid, the rate of Reaction 3 becomes the controlling factor. This should be somewhat affected by the hydrogen-ion concentration, since this determines the "equilibrium pressure" of the polarizing film. The most important single factor, however, is the hydrogen overvoltage of the metal and impurities present. Marked differences between samples of varying purity show up in this range, and these differences are responsible for many of the broad statements that certain forms of iron are more resistant to corrosion than are others.

Certain other factors are important indirectly on account of their effect on hydrogen overvoltage—as, for example, temperature. A recent interesting paper of McInnes[12] shows that at low values of gas evolution the overvoltage is determined by the amount of work which must be done against surface tension in forming the gas bubbles, and that it should accordingly increase in a vacuum and decrease under pressure.

[11] *Trans. Am. Inst. Chem. Eng.*, **13** (1920), Part I, 64.

[12] McInnes and Contieri, *J. Am. Chem. Soc.*, **41** (1919), 2013.

This leads to the surprising conclusion that vacuum should retard and pressure accelerate corrosion, and McInnes has checked this. Also, according to this theory, anything tending to decrease the average bubble size should also increase overvoltage, and this checks with recent observations in this laboratory (to be published shortly) that moderate rate of stirring tends to *retard* corrosion in acid solutions. Overvoltage is also apparently raised markedly by certain readily adsorbed materials such as arsenic[13] and formaldehyde,[14] and their presence in solution correspondingly retards corrosion in acids.

The oxygen concentration, salt content, solution pressure of metal, etc., should have comparatively little effect on the rate of corrosion in acids.

To summarize, the whole field of corrosion of iron by dilute aqueous solutions may be divided into three main regions of varying hydrogen-ion concentration, in each of which a different but comparatively simple reaction controls the rate of corrosion. Fig. 2 shows roughly the comparative importance of the five major factors in each of the three regions.

Since entirely different factors affect the rate of corrosion in the different regions, it is obvious that Fig. 1 can only represent conditions in a very general way and that the position and height of the various curves may change so as to shift the limits of these regions quite markedly. One of the most important lines of experimentation in studying corrosion should be the fairly definite determination of the limits of these three regions, together with the confirmation of certain deductions drawn in this paper but not yet fully confirmed experimentally. This laboratory is now undertaking work along these lines.

THE EFFECT OF DISSIMILAR METALS ON THE RATE OF CORROSION: PITTING

The new line of reasoning is also of great value in clarifying the mechanism of the action of dissimilar metals in contact. The tendency in the past has frequently been to explain any apparent anomaly in corrosion tests by the glib use of terms such as "galvanic action," "electrolysis," etc.
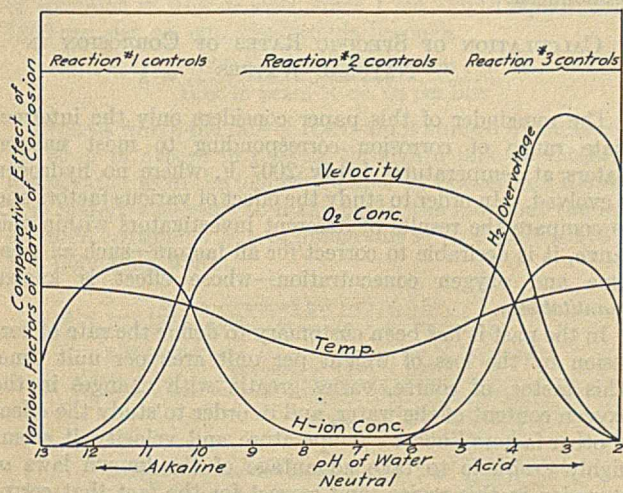
FIG. 2

The underlying mechanism involved in the retardation or acceleration of corrosion by different metals in contact with iron has, however, been clearly discussed by Walker.[15] Any metal, such as iron, which is above hydrogen in the electromotive series and which does not quickly form an impermeable protective film of oxide, will tend to "plate out" a

film of nascent hydrogen on any other less positive metal or electrical conductor in contact with it and the solution. This, of course, involves a flow of current through the metal from the place where hydrogen plates out to the place where the metal dissolves, and in the opposite direction through the solution.

The concentration of hydrogen in this film would eventually become uniform over the entire area in electrical contact if there were no tendency for its removal, but if it is gradually removed by oxidation or otherwise, the electrical resistance of the circuit limits the rate of building up the film at appreciable distances away from the point where metal is passing into solution. The concentration of hydrogen will therefore gradually drop off at greater and greater distances. The area kept saturated with hydrogen will be determined by three factors: (a) the driving force, or e. m. f., developed by the solution of the metal in the particular solution, (b) the conductivity of the circuit (particularly that of the solution), and (c) the rate at which hydrogen is removed. The effective distance is generally a matter of fractions of an inch in fairly pure, natural waters, but may extend to a foot or more in highly conducting solutions.

If iron is in contact with some more electropositive metal the mechanism is precisely similar, but in this case the hydrogen is furnished by the solution of the more electropositive element, and the solution of the iron is prevented, as demanded by their position in the electromotive series. The area over which this protective action is effective is determined by the same factors as those discussed above and is similar in magnitude.

Again, the more electropositive metal, which corrodes rapidly and protects the adjacent iron, may comprise small areas of the iron itself, which, owing to strain difference in crystal form, or other cause, may have a slightly higher solution pressure than the main body of the metal. This results in selective corrosion or "pitting," and makes the surrounding metal appear very resistant; but if the more electropositive areas are removed or covered up, the remainder will corrode just as rapidly, per unit area exposed, as the original sample.

The factors determining the rate of corrosion of the most electropositive element in any given combination are precisely the same as for a single metal—the rate at which the polarizing film of hydrogen is removed by Reactions 2 or 3 is still the limiting condition. In the case of most electronegative elements in contact with iron, the overvoltage is high enough to prevent the escape of appreciable amounts of hydrogen when in contact with natural waters, and in this case the limiting factor must again be the rate of diffusion of oxygen to the surface. In other words, the amount of corrosion will be determined by the *total area saturated with hydrogen*, but the loss in weight will all be concentrated on the iron portion of the surface, so that the rate of corrosion of the iron itself will be accelerated to an extent depending on the area of inert surface which it is able to keep saturated. Preliminary experiments in this laboratory indicate that the corrosion of iron in contact with copper in natural waters is accelerated to very nearly the extent predicted from the relative areas of the two metals. In view of this, relatively small areas of impurities or segregated materials could have but little effect. On the other hand, where an iron pipe is almost completely covered by an inert conductor, such as mill scale or lead, the small unprotected areas should corrode with great rapidity, causing the deep pits characteristic of such conditions.

There are, however, one or two notes in the literature which indicate more than normal acceleration by contact with a small piece of other metal. Thus, Walker,[15] in order

13 Friend, "The Corrosion of Iron and Steel," 1911, 211.

14 Griffin, THIS JOURNAL, 12 (1920), 1159.

15 *Mech. Eng.*, 23 (1909), 677.

to account for the marked accelerating action of a comparatively small area of platinum in contact with iron observed in some tests with "ferroxyl indicators,"[16] postulates an increased reaction rate between the oxygen and hydrogen at the platinum surface. This would be a convenient assumption since it would account for any observed amount of acceleration, but it does not appear to be tenable in view of the reasoning in a previous section which indicated that the rate of reaction, even at an iron surface, was much more than that required to take care of all the oxygen which could diffuse into the surface. Furthermore, this rate of diffusion could not be affected by the nature of the metal surface.

As a possible explanation of Walker's observations, it was considered that the ferricyanide might have been acting as a depolarizer by oxidizing the hydrogen, especially at the platinum surface. On repeating the experiments, it was found that no appreciable acceleration could be observed qualitatively in the absence of ferricyanide, and that when ferricyanide was present, ferrocyanide was rapidly produced around both the platinum and iron surfaces, as shown by the color found in these regions when dilute $FeCl_3$ was poured on top of the jelly. Tests in the absence of oxygen also indicate that under these conditions, some hydrogen is evolved as such (dissolved) from the platinum surface, probably because of the increase in the potential of the corrosion reaction due to the maintenance of a low concentration of Fe^{++} plus the low overvoltage of platinum. The behavior and rate of corrosion in the two tests were quite different, and from the foregoing facts it must be concluded that the ferroxyl test, while very interesting, is not in any sense a reliable indication of what really happens in ordinary corrosion.

In considering the rate of corrosion of electropositive elements, such as zinc, in contact with iron, the tendency to form hydrogen is so great, even in natural waters, that the overvoltage of one of the metals is likely to be exceeded and hydrogen evolved, even the natural-water range giving a greater rate of corrosion than that corresponding to the rate of diffusion of oxygen. Sodium is an excellent example of such a case, while zinc is probably just on the border line, and owes its preeminence as a protective material to this fact. More positive elements would corrode too rapidly with the evolution of considerable hydrogen, while less positive metals would not adequately protect a reasonable area of iron.

If any such combination of dissimilar conductors is connected up so as to measure the current flow, or to show, by indicators or otherwise, anodic and cathodic areas, these points are very clearly brought out. The point at which the hydrogen is removed will show up by a passage of current from the solution to the metal and by the production of alkali (by using up H^+ ions), both characteristic of a cathode. This same reaction may take place on nonmetallic conductors, such as mill scale, which is the reason for the illogical reference to these or other oxides as being "electronegative" to iron—any insoluble conductor at which hydrogen can be oxidized would be electronegative in the same sense, but the reported values of potential or current flow are meaningless in the true electrochemical sense, and instead of referring to such accelerating agents as "setting up galvanic action due to their electronegative character," they should be considered merely as furnishing conducting surface on which hydrogen can plate out and be oxidized, with the necessarily resulting flow of current.

In this connection, ferroxyl tests are somewhat misleading in another respect—the existence of the sharply defined

16 A neutral jelly containing ferricyanide and phenolphthalein indicators to indicate where iron goes into solution and where alkali is produced. See Friend, "The Corrosion of Iron and Steel," p. 248.

blue and red areas is generally taken to indicate that the two parts of the corrosion reaction $Fe \rightarrow Fe^{++}$ and $2H^+ \rightarrow 2H$ must occur at finite distances apart, with the formation of fairly large anodic and cathodic areas. The writer feels certain, however, that only the solution of the iron is localized and that the diffusion in of oxygen, which controls the rate of corrosion, is taking place *over the whole surface*. If the electropositive areas which pass into solution first are small compared with the total surface, the oxygen diffusion (in the absence of ferricyanide) in these regions may be largely or wholly consumed in oxidizing ferrous ions to ferric before they can reach the surface, but as soon as iron begins to pass into solution over a large proportion of the area—as usually happens in a fairly short time—the oxidation of hydrogen is undoubtedly taking place over the whole surface. The existence of a red or cathodic area simply means that in this region the oxidation of hydrogen is taking place more rapidly than the production of ferrous ions, but when the two take place simultaneously the hydroxyl ions consumed in precipitating $Fe(OH)_2$ just balance the hydrogen ions consumed in making gaseous hydrogen.

In all cases of two metals in contact, as the acid concentration is increased corrosion will pass from the region where the rate of diffusion of oxygen is controlling to the region where the rate of evolution of hydrogen, as determined primarily by overvoltage phenomena, becomes determining. If the second metal in contact with iron has a lower overvoltage, this transition will come at a lower acidity than otherwise, and the same thing is true if a more electropositive element is in contact with iron, on account of its greater solution pressure. As a result, the overvoltage of small amounts of impurities and of metals in contact becomes important even in slightly acid natural waters, and especially so in more strongly acid solutions. Here the accelerating action of a small amount of impurity is no longer proportional to area, as a single spot of platinum, for example, may liberate tremendous quantities of hydrogen as gas. As a result, it is in the case of corrosion by acid solutions where the difference between different kinds of iron and steel becomes pronounced.

CALCULATION OF SPECIFIC RATES OF CORROSION IN NATURAL WATERS

The remainder of this paper considers only the intermediate range of corrosion corresponding to most natural waters at temperatures below 200° F. where no hydrogen is evolved. In order to study the effect of various factors and to compare the results of different investigators within this range, it is desirable to correct for all factors—such as area, time and oxygen concentration—whose effect is known *quantitatively*.

In the past it has been customary to define the rate of corrosion by the loss of weight per unit area per unit time. This factor, of course, varies greatly with changes in the oxygen content of the water, and in order to study the effect of other factors, such as temperature and velocity, it seems highly desirable to take advantage of the known laws of corrosion in this region, and correct for the fact that corrosion is practically directly proportional to the oxygen concentration. This would give a *specific* rate of corrosion in terms of *loss of weight per unit area per unit time per unit concentration of oxygen*. In other words, the measured rate of corrosion should always be divided by the average oxygen concentration of the water in order to find the *specific* rate of corrosion.

For specific units the writer suggests that k, the *specific rate of corrosion*, be expressed as milligrams loss per square centimeter per year per cubic centimeter oxygen in 1 liter

of water. This generally gives figures of a convenient order of magnitude.

In cases where the rate of corrosion is being measured in a long pipe and the oxygen content is greatly different at the exit from that at the entrance, it can readily be shown that the effective average oxygen content is not the arithmetic mean of initial and final values, because it drops more rapidly at first, and therefore the greater portion of the length is subject to a concentration lower than the arithmetic mean. For such cases the "logarithmic mean" is mathematically the correct one to use. This value may be calculated by means of the formula:

$$\text{Log mean concn.} = \frac{\text{initial concn.} - \text{final concn.}}{2.303 \log \frac{\text{initial}}{\text{final}}}$$

or more readily from the chart in Fig. 3, which gives the logarithmic (and to make the method general, the geometric)
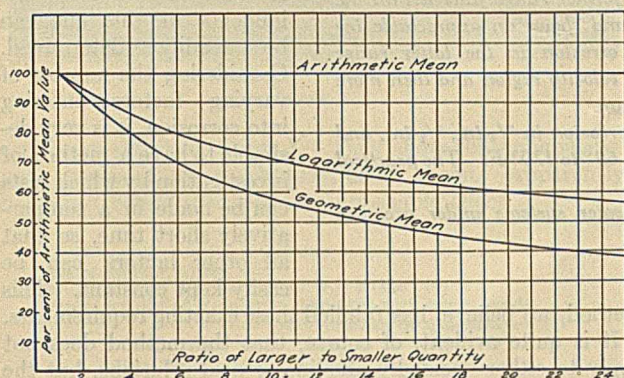

FIG. 3

mean in terms of per cent of the arithmetic mean, for various ratios between the initial and final concentration.

To calculate k in the units above, from data on the *depth* of corrosion of iron or steel, since 1 cm. depth equals about 7800 mg. per sq. cm., the formula becomes

$$k = \frac{7800 \times \text{measured depth in cm.}}{\text{time in years} \times \text{cc. } O_2 \text{ per liter}}$$

In cases where the rate of corrosion is studied by measuring the *drop in oxygen* in passing through a pipe or sheet-iron deactivator, as in the following paper by Speller and Kendall, it is merely necessary to make use of the fact that the ratio of cubic centimeter SO_2 to milligrams Fe in Fe_2O_3[17] is 1:3.32. We may then write:

$$k = \frac{\text{cc. } O_2 \text{ consumed per year} \times 3.32}{\text{area of iron surface in sq. cm.} \times \text{av. concn. } O_2}$$

$$= \frac{3.32 \, (\text{initial conc. } O_2 - \text{final conc. } O_2) \times \text{liters water per min.} \times 1440 \times 365}{\text{area of iron surface} \times \dfrac{\text{initial concn. } O_2 - \text{final conc. } O_2}{2.303 \log \dfrac{\text{initial concn. } O_2}{\text{final concn. } O_2}}}$$

$$= \frac{4,020,000 \times \text{liters water per min.} \times \log \dfrac{\text{initial concn. } O_2}{\text{final } O_2}}{\text{area of iron surface in sq. cm.}}$$

$$= \frac{16,400 \times \text{gal. water per min.} \times \log \dfrac{\text{initial } O_2}{\text{final } O_2}}{\text{area of iron surface in sq. ft.}}$$

[17] Iron does not always corrode to give Fe_2O_3. Indeed, samples of rust taken from the inside of pipes generally analyze around $1/3$ FeO to $2/3$ Fe_2O_3. Most of the ferrous iron, however, is in the layer nearest the steel surface which has not yet had an opportunity to oxidize completely, and, when steady conditions are established, practically all the iron corroded eventually goes to form Fe_2O_3. At any rate, the correction to the conversion factor above is not over 10 per cent.

It is interesting to note that, other things being equal, the specific rate of corrosion is proportional to the logarithm of the *ratio* of the initial oxygen to the final. It is important to keep this relationship in mind because there is much loose thinking with respect to the effect of the rate of corrosion on the oxygen content. For example, under one set of conditions the oxygen content of water passing through a given deactivator or pipe might drop from an initial value of 8 cc. per liter to a final value of 1 cc. per liter, whereas under slightly different conditions it might drop from 8 to 0.3 cc. per liter. This is a tendency to say that the rate of corrosion in the second case is $\dfrac{8 - 0.3}{8 - 1}$, or 1.1 times that in the first, whereas actually the *specific* rate of corrosion, as defined above, is more than 1.5 times as great, although the amount of metal corroded is only 1.1 times as great.

The formula also brings out the fact that accurate results on rates of corrosion by the drop-in-oxygen method can only be obtained under conditions such that the $\log \dfrac{\text{initial } O_2}{\text{final } O_2}$ is accurate, which is only true where the ratio is not too near unity or infinity. The method is most accurate where the amount of oxygen removed is between 25 and 80 per cent, and should not be used for rate determinations outside the limits of 10 and 96 per cent removed.

It is thus possible to correlate specific rates of corrosion obtained in a variety of ways. A few typical sets of results from the literature have been calculated by this method and are presented in the following paper.

The considerations pointed out in preceding sections show that, in order for corrosion data in natural waters to be of value, the composition of the water is not important, save for its oxygen content, and its tendency to form protective films, while the usually neglected factor of velocity should be carefully measured and specified.

The author appreciates fully the fact that reasoning as to reaction rates is a rather dangerous proceeding, and that a number of the deductions herein presented have not as yet been adequately verified by experiment; but the great need for such simplification and correlation of corrosion data, and the fact that the writer is now forced to terminate his present investigations along these lines, seem to justify a somewhat detailed presentation of what he believes to be the essential mechanism of underwater corrosion.

Staff Correspondents

Since our previous publication of the list of staff correspondents representing the various local sections, the following additional correspondents have been appointed for THIS JOURNAL and the News Edition:

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In connection with Cancer Week, the State of New York and the City of Philadelphia each bought two grams of radium for the use of its citizens.

A New Method of Measuring Corrosion in Water[1]

By F. N. Speller and V. V. Kendall

RESEARCH LABORATORY, NATIONAL TUBE CO., PITTSBURGH, PA.

Further data are given confirming previous work that corrosion is directly proportional to dissolved oxygen concentration.

A new method of measuring corrosion, especially applicable to the solution of practical problems, has been developed. It is based on the fact mentioned above and consists in cooling the water under pressure, and determining the amount of dissolved oxygen by the Winkler method.

The effect of velocity upon corrosion is determined for the range 0.0043 ft./sec. to 8.0 ft./sec. The range 0.0043 ft./sec. to 0.10 ft./sec. is covered by a small-scale deactivator. The range 0.10 ft./sec. to 8.0 ft./sec. is covered by experiments in ¼-in., ½-in., and ¾-in. steel pipe. Corrosion in the former range falls within the very low velocity range of the pipe and shows an appreciable increase with increase of velocity. Corrosion in the latter range increases rapidly through the critical velocity region and then more gradually, finally reaching a maximum.

Comparative curves are given for corrosion in ¼-in., ½-in., and ¾-in. steel pipe at temperatures from 60° to 170° F. The practical use of these curves is pointed out.

The rate of corrosion in closed water systems under pressure increases directly with temperature.

I T HAS BEEN quite clearly realized for some time that the dominating influence in corrosion difficulties in natural waters is the content of dissolved oxygen. This was first experimentally demonstrated by Walker[2] and his co-workers, and followed up a few years later by some work by one of the authors in which the loss of weight of weighed test pieces at various oxygen concentrations was determined.

In the latter experiment, water was passed through three small laboratory "deactivators"[3] arranged in parallel, each containing diminishing amounts of expanded steel sheets, thereby reducing the oxygen content to a definite amount in proportion to the time of contact. Special care was taken to keep the temperature constant at 162° F. (72° C.). In this way it was possible to keep an almost constant oxygen content in the water in each deactivator. Test pieces were then inserted at places indicated, and allowed to remain for 150 days while water was flowing through the three deactivators at the same rate. The loss of weight was then determined (Fig. 1) and it was found that corrosion is almost directly proportional to the dissolved oxygen content.

This being the fact, it should be possible, then, to determine the amount of corrosion by measuring the amount of oxygen used. Arndt[4] used an oxygen-absorption method based on measuring the oxygen gas removed from moist air in which the samples of metal under observation were exposed in a closed vessel. While this is an approximation of atmospheric corrosion, it cannot be applied to underwater corrosion. Moreover, in piping installations and service lines the most important factor is the concentration of the dissolved oxygen. A measurement, then, of the decrease or drop in dissolved oxygen through any system becomes a measurement of the amount of corrosion in that system. This is manifested in a practical way by the early failure of portions of the system near the water inlet and the comparatively long life of other parts farther away. The dissolved oxygen is removed in the first lengths of pipe so that the pipe farther away is furnished with water almost free from dissolved oxygen. It would seem, therefore, that, by using an iron pipe of convenient size and measuring the oxygen concentration in the water which was caused to flow through such a pipe, rapid and accurate measurement of the corrosion could be made.

The main factors which influence corrosion, aside from oxygen concentration, are temperature, velocity of flow, composition of the water, and protecting influence of films of oxides or other matter formed on the surface of the metal. By keeping all factors constant except the one to be measured, the influence of this one can be readily determined. Considering the number of varying factors entering into corrosion, it is very desirable to have a method of investigation by which tests can be made in a comparatively short time, so that all other factors can be easily kept constant. This method, we believe, has fulfilled these exacting requirements.

It is quite evident, of course, that the method does not apply to either decidedly alkaline or acid solutions, but the majority of natural waters fall within the range pH 5 to pH 11, and it is in this range that oxygen concentration is the dominating factor.[5]

The following investigation consists essentially of two parts—the first, experiments on commercial, uncoated steel pipes of various diameters covering velocities from 0.1 ft./
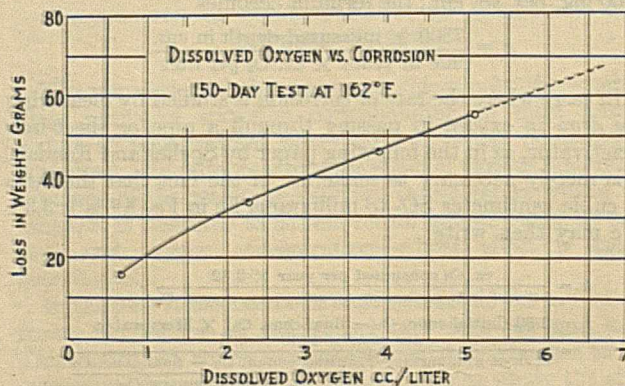
FIG. 1

sec. to 8.0 ft./sec. and temperatures from 60° to 170° F.; and the second, experiments on a small deactivator covering the range from 0.0043 ft./sec. to 0.1 ft./sec.

EXPERIMENTAL METHOD

Some preliminary work was first carried out by C. R. Texter[6] on ¼-in. pipe using 12 lengths of 19 ft. each, connected by return bends with sampling taps at the end of the 1st, 2nd, 3rd, 6th, and 12th lengths; the whole enclosed

[1] Presented before the Division of Industrial and Engineering Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

[2] *J. Am. Chem. Soc.*, **29** (1907), 1251.

[3] This term was adopted to denote a tank carrying a large surface of metal serving to fix the free oxygen in water.

[4] *Chem.-Ztg.*, **24** (1910), 425, 1078.

[5] See paper by Robert E. Wilson on page 127 of this issue.

[6] National Tube Company Research Staff.

within a 6-in. pipe with steam connection. Velocities of from $\frac{1}{3}$ to 4 ft./sec., with 57 sec. time of contact and temperatures of 110° and 140° F., were obtained. These
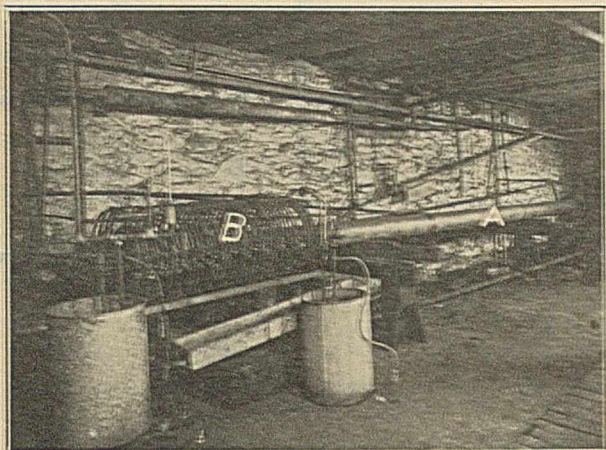
results are shown in Table I. They show the same shaped curve as was afterward obtained using a coil. Apparently, the return bends produced no appreciable effect.

TABLE I

Time of contact, 57 sec.
Average number of runs, 6 (110° F.), 3 (140° F.)
Straight lengths of $\frac{1}{4}$-in. pipe connected with return bends

TEMP., °F.	SPECIFIC RATE OF CORROSION—K	
	110	140
Velocity Ft./Sec.		
0.33	123	357
0.66	335	602
1.00	309	713
2.00	639	1352
4.00	676	.....

An apparatus was then constructed consisting of a coil about 18 in. in diameter of 200 ft. of $\frac{1}{4}$-in. black pipe placed within a drum. The coil was tapped every 5 ft. up to 30 ft., then at 40, 50, 75, 100, 150, and 200 ft. Fig. 1a shows the essential connections. In order to maintain constant time of contact at different velocities, the length of pipe was varied. For example, at a velocity of 1 ft./sec. the water had a time of contact of 50 sec. when it was passed through 50 ft. of pipe. When the velocity was raised to 2 ft./sec. the water was passed through 100 ft. of pipe. In this way

the only variable at any given temperature was the velocity. A gas heater was connected with the apparatus so that the water could be heated to any desired temperature. At the higher temperatures, to maintain an even temperature throughout the entire system, steam was introduced into the drum. All connections and pipes from the gas heater to the coil and also the cooling coils and connections were of brass. At the entrance to the coil a small amount of water was by-passed through a cooling coil and the dissolved oxygen content determined by the standard Winkler method.[7] The water after passing through the experimental coil was cooled to normal temperature and its oxygen content determined. All samples were cooled under pressure so that the gas would not separate when the pressure was lowered. The initial pressure varied from 40 to 75 lbs. Under no conditions was the exit pressure less than 10 to 20 lbs. Each curve is the average of at least two complete runs. The pipe used was "National" standard pipe. Plate 1 shows the $\frac{1}{4}$-in. straight-line system (A) and the $\frac{1}{4}$-in. coil (B). In the latter, the drum has been removed to show the coil.

To insure that the coil was representative of actual pipe installations, 200 ft. of $\frac{1}{4}$-in. pipe were laid out in a straight line and the pressure drop measured at taps corresponding to those in the coil. The coil did not increase the frictional loss appreciably except for the last two lengths.

TABLE II

Time of contact, 50 sec.   Coil of 200 ft. of $\frac{1}{4}$-in. pipe

TEMP., °F.	SPECIFIC RATE OF CORROSION—K					
	60	80	95	110	120	150
Velocity Ft./Sec.						
0.1	58.5	36.8	45.6	75.1	75.1	70.8
0.2	103.0	58.5	129.0	99.1	189.0	206.0
0.3	122.0	36.8	107.0	99.1	302.0	278.0
0.4	83.1	95.4	276.0	187.0	343.0	595.0
0.5	70.8	91.1	392.0	273.0	550.0	873.0
0.6	225.0	87.3	539.0	336.0	765.0	1075.0
0.8	87.3	384.0	366.0	526.0	577.0	1868.0
1.0	423.0	431.0	670.0	675.0	1083.0	1789.0
1.5	379.0	271.0	528.0	902.0	1389.0	1890.0
2.0	334.0	436.0	724.0	938.0	1684.0	.....
3.0	386.0	450.0	845.0	1059.0	.....	.....
4.0	442.0	623.0	1272.0	1323.0	.....	.....

After this series of tests was run, the $\frac{1}{4}$-in. pipe was replaced by $\frac{1}{2}$-in. and later by $\frac{3}{4}$-in. pipe (Plates 2 and 3). Because of the large volume of water required for obtaining high velocities on the last two sizes of pipe, it was found necessary to insert an auxiliary cooling coil consisting of 30 ft. of copper pipe at the discharge from the experimental coil. This cooled all the water to a temperature of 50° to 110°

[7] "Standard Methods of Water Analysis," American Public Health Association, 1920, 65.
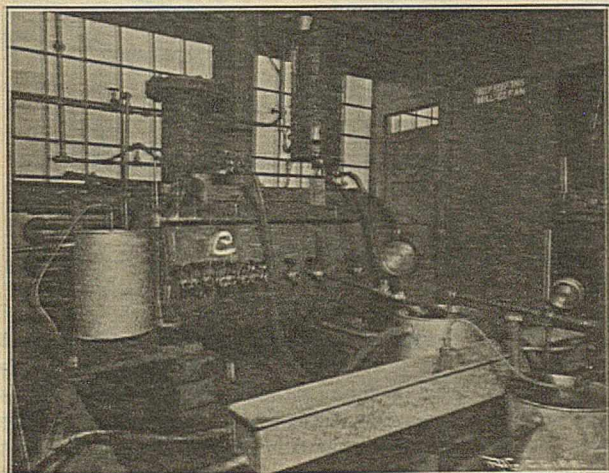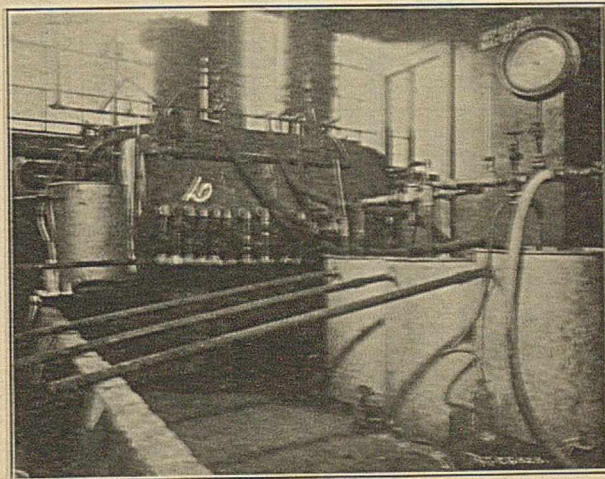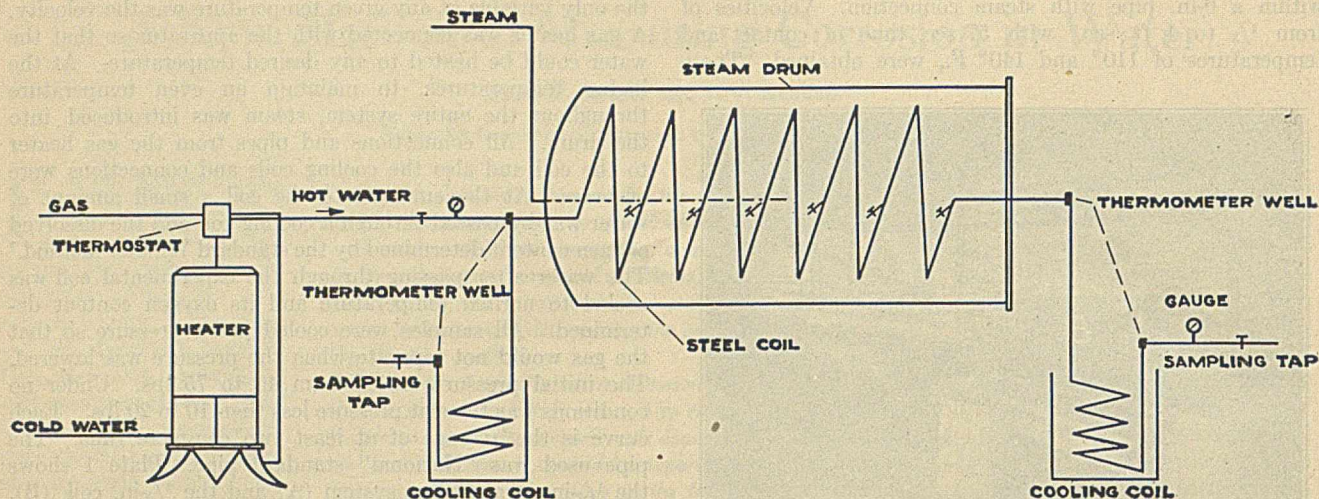
FIG. 1a

F., depending on the working temperature. The discharge was then split, part passing through another cooling coil which brought the temperature down to between 40° and 60° F., and then sampled for dissolved oxygen and the remainder wasted. Each rate of flow was set by a stop watch. Particular pains were taken to hold the temperature absolutely constant throughout the entire length of the coil. The condition of the surface of the test pipe was determined at frequent intervals to make sure that the rate of corrosion had not changed materially by reason of adhering rust films. The data for the $1/4$-in. pipe are given in Table II; for the $1/2$-in. pipe, Tables III, A and B; for the $3/4$-in. pipe, Table IV.

TABLE III-A
Time of contact, 50 sec. Coil of 200 ft. of $1/2$-in. pipe

		SPECIFIC RATE OF CORROSION—K		
TEMP., ° F..... 80		120	150	171
Velocity Ft./Sec.				
0.1	24.6	79.4	131	238
0.2	71.8	172.0	268	417
0.3	138.0	262.0	475	622
0.4	166.0	381.0	577	799
0.5	206.0	471.0	664	1055
0.6	262.0	586.0	896	1129
0.8	370.0	676.0	1034	1600
1.0	485.0	793.0	1140	1840
1.5	602.0	895.0	1485	1935
2.0	743.0	1125.0	1654	2628
3.0	594.0	1318.0	2629	3286
4.0	750.0	1472.0	3248	3770

TABLE III-B
Time of contact, 25 sec. Coil of 200 ft. of $1/2$-in. pipe

	SPECIFIC RATE OF CORROSION—K		
TEMP., ° F..... 80	120	150	
Velocity Ft./Sec.			
0.2	81	233	174
0.4	174	262	304
0.6	174	331	463
0.8	290	584	687
1.0	290	730	894
1.2	399	709	1016
1.6	549	875	1061
2.0	500	1147	1204
3.0	631	1425	1763
4.0	933	1624	2147
6.0	998	2100	2999
8.0	962	2735	2987

TABLE IV
Time of contact, 50 sec. Coil of 150 ft. of $3/4$-in. pipe

	SPECIFIC RATE OF CORROSION—K		
TEMP., ° F..... 80	120	150	
Velocity Ft./Sec.			
0.1	27.2	21.6	53
0.2	152.0	84.2	294
0.3	171.0	93.8	243
0.4	181.0	114.0	359
0.5	199.0	243.0	367
0.6	243.0	252.0	413
0.8	226.0	420.0	506
1.0	269.0	492.0	671
1.5	375.0	499.0	968
2.0	405.0	682.0	995
3.0	413.0	711.0	1037

DISCUSSION

In using the drop in oxygen concentration as a measure of corrosion, one objection must be raised. There are two reactions involving the dissolved oxygen—one removing the polarizing film of hydrogen on the surface of the iron, and the other oxidizing the ferrous iron already formed. To determine if the oxidation of ferrous iron was constant under all conditions of temperature and velocity, an analysis was made of the iron rust formed in the $1/4$-in. pipe, as follows:

Velocity, Ft./Sec.	Temp., ° F.	Per cent Fe^{++}
0.2	80	32.0
		32.4
		32.7
		Av. 32.4
0.2	165	36.9
		36.1
		37.1
		Av. 36.7
4.0	80	29.0
		27.0
		Av. 28.0
4.0	165	34.0
		33.0
		Av. 33.5

FIG. 2

The effect of velocity is apparently to decrease the amount of ferrous iron. At low temperature this decrease seems to be slightly greater than at high temperatures. This means somewhat less corrosion at higher velocity, since more oxygen will be used to oxidize the ferrous iron. The effect of temperature, on the other hand, is to increase the per cent of ferrous iron, which means increased corrosion per unit of oxygen. This effect is also slightly greater at high tem-

peratures. With increase of temperature and velocity, these variations would balance each other. In any case the variation is sufficiently small to come well within an experimental error of 10 per cent.

The entire investigation covered several months. The water used was Pittsburgh city water, the average analysis of which follows:

	December 1921	January 1922	February 1922
Turbidity	0	0	0
Total solids	103.0	127.9	134.4
Alkalinity	10.0	10.8	10.5
Total Fe	0.2	0.3	0.3
Insoluble residue	3.6	2.2	1.5
SiO_2	4.2	4.2	3.8
Al	0.7	0.6	0.7
Ca	16.7	17.3	18.5
Mg	5.2	4.4	5.4
Na and K as Na	4.7	5.9	5.5
SO_4	45.2	49.8	52.2
Cl	7.7	10.6	10.2
HCO_3	12.2	13.1	12.8
NO_3	0.9	1.0	1.0

The oxygen content of the entering water varied from 5.50 to 9.50 cc./liter.

To allow for this variation, the data were calculated according to the formula suggested by R. E. Wilson.[8] In this article he expresses the specific rate of corrosion as the loss of weight per unit area per unit time per unit concentration of oxygen, or K = mg. loss per sq. cc. per year per cc. oxygen in 1 liter of water =

$$\frac{4,020,000 \times \text{liters water per min.} \times \log \frac{\text{initial oxygen}}{\text{final oxygen}}}{\text{Area of iron surface in sq. cm.}}$$

This formula has the double advantage of allowing for variations in oxygen concentration and also a varying volume-area ratio, the effect of both of which is approximately calculable. After making these corrections, we can plot the specific rate of corrosion against velocity and temperature and study their effect.

Figs. 2 and 2a give the results for $1/4$-, $1/2$-, and $3/4$-in. pipe at various temperatures. In varying the velocity it has been shown[9] that the flow at low velocity is viscous, at high velocity, turbulent, with a critical range between in which the flow may be either viscous or turbulent. This critical range for each temperature is marked in each case. For example, in $1/4$-in. pipe at 80° F. the critical region is from 0.3 ft./sec.

[8] *Loc. cit.*
[9] Wilson, McAdams, and Seltzer, THIS JOURNAL, **14** (1922), 105.

to 1.0 ft./sec.; at 120° F., 0.20 ft./sec. to 0.65 ft./sec. Below these points the flow is entirely viscous or straight-line; above it is entirely turbulent. It is quite evident that in straight-line flow most of the water does not come in contact with the pipe, and that in turbulent flow the water is thoroughly mixed, thus allowing a maximum opportunity for diffusion of the oxygen to the pipe. In the critical
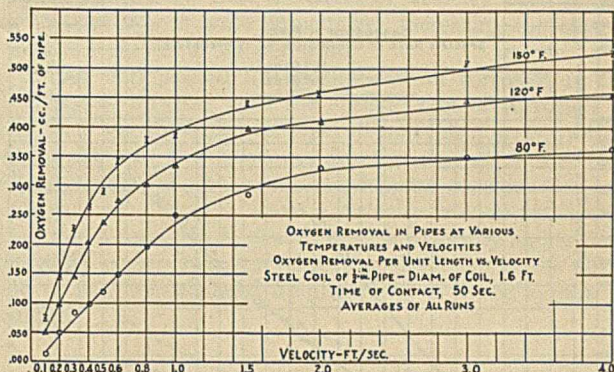
FIG. 2b

range, therefore, it will be seen that there is a rapid rise in the specific rate of corrosion. Above this range it continues to rise, but not as rapidly except at high temperatures. Below this range corrosion it is low at all temperatures. As the size of pipes increases viscous flow vanishes, within the range of velocity included in this study, and the flow is entirely turbulent. The $1/2$-in. and $3/4$-in. plots show a gradual rise, since in these the flow is turbulent almost from the beginning. In all cases at the higher temperatures corrosion *increases* with velocity and at the lower temperatures reaches a maximum and does not diminish. This is contrary to the results obtained by Heyn and Bauer,[10] and Friend.[11] The former passed water across iron plates immersed in beakers, determined the loss in weight, and found a diminution of corrosion beginning at 0.007 ft./sec. The latter passed water from the service mains through glass tubing in which

[10] "Mitterlungen Königlichen Materialprüfungsant," Berlin, **28** (1910), 62.

[11] "The Corrosion of Iron," Carnegie Scholarship Memoirs, **11** (1922).
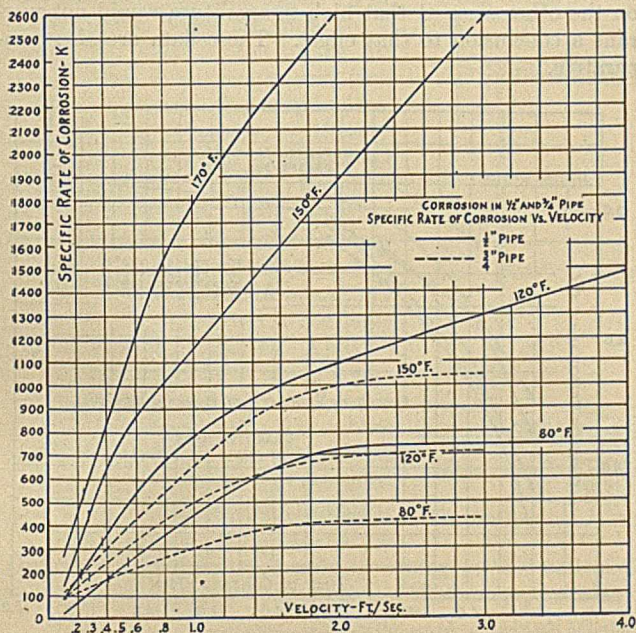
FIG. 2a
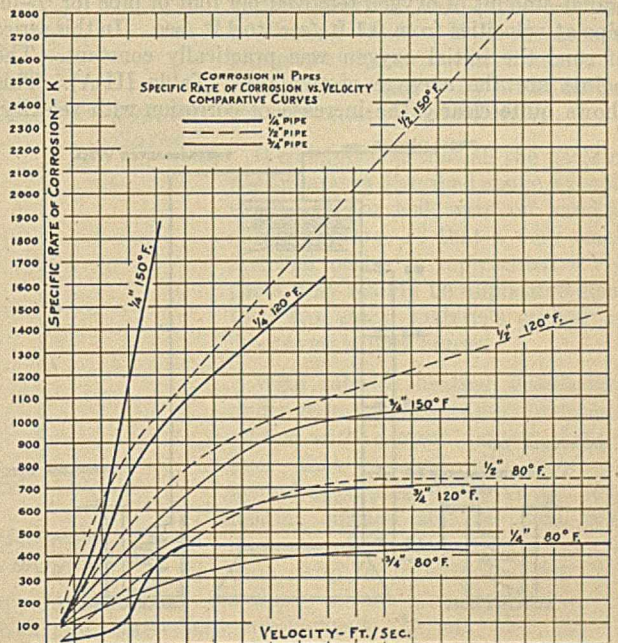
FIG. 3

was suspended iron foil, determined the loss in weight, and found a diminution of corrosion starting at 1.1 ft./sec. In spite of the fact that both report a diminution of corrosion with increase of velocity, yet the difference between 0.07

FIG. 4

ft./sec. and 1.1 ft./sec. is so great that the results cannot be considered as checking each other. In order to investigate fully the effect of velocity, the time of contact (in the $\frac{1}{2}$-in. pipe) was halved, and the velocity thus increased to 8 ft./sec., covering the range from 0.2 ft./sec. to 8.0 ft./sec. These results at 80°, 120°, and 150° F. are given in Table III-B. They show an increase to a maximum but no diminution.

This can be illustrated a little differently by a slightly different method of calculation. In Fig. 2b is shown the actual amount of oxygen removed per foot of pipe for $\frac{1}{2}$-in. pipe at velocities from 0.1 ft./sec. to 4 ft./sec. In this series of runs the initial oxygen was practically constant. The points are the average of two runs (Table III-A). This shows quite clearly the increase of corrosion with velocity.

While the work reported by Heyn and Bauer, and Friend was evidently at relatively low temperatures, yet the 60° F. line in the $\frac{1}{4}$-in. pipe and the 80° F. lines in the $\frac{1}{2}$-in. and $\frac{3}{4}$-in. pipe (Fig. 3) show merely a maximum. The data
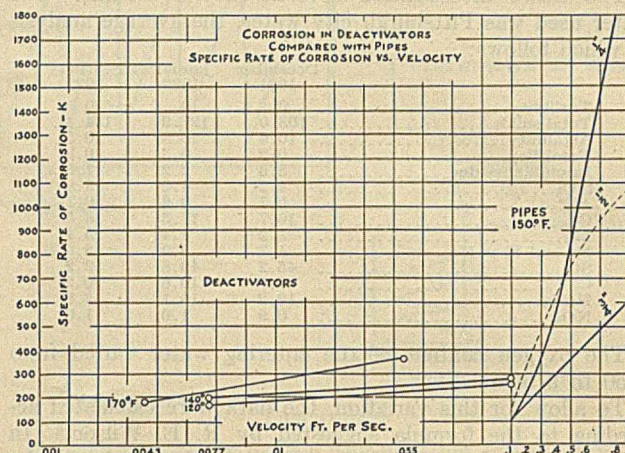
FIG. 6

of this investigation were obtained at pressures from 40 to 75 lbs./sq. in. with Pittsburgh city water, thus reproducing actual operating conditions.

Fig. 3 is a comparison of the three sizes of pipe at three temperatures. This shows a decreasing rate of corrosion with increase of size. These results are comparative and can be applied to the solution of the many practical problems which arise in piping installations. For example, the rate of corrosion at 2 ft./sec. at 120° F. is 2.4 times as much for $\frac{1}{4}$-in. as for $\frac{3}{4}$-in. pipe. Also, the rate of corrosion in $\frac{1}{4}$-in. pipe at 120° F. at a velocity of 0.2 ft./sec. is $\frac{1}{8}$ that at 1.5 ft./sec. It would therefore be better from a corrosion standpoint to use an oversize of pipe, thereby increasing the life of the pipe both by increase of thickness and diameter and by decrease of velocity.

In Fig. 4 the specific rate of corrosion is plotted against temperature for velocities of 0.5, 1.0, and 2.0 ft./sec. and for the three sizes of pipe. The rate of corrosion is directly proportional to temperature. The points at 170° F. in the $\frac{1}{2}$-in. pipe show a much more rapid rise, but the lack of data on the other sizes at that high temperature would not warrant a conclusion to that effect. These data are also comparative.
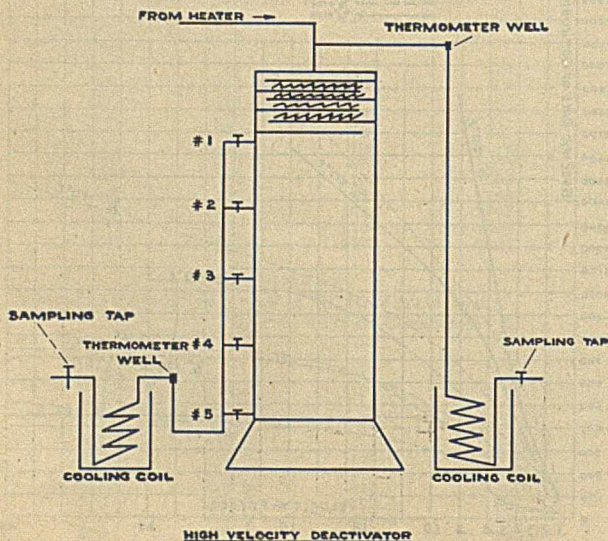
FIG. 5
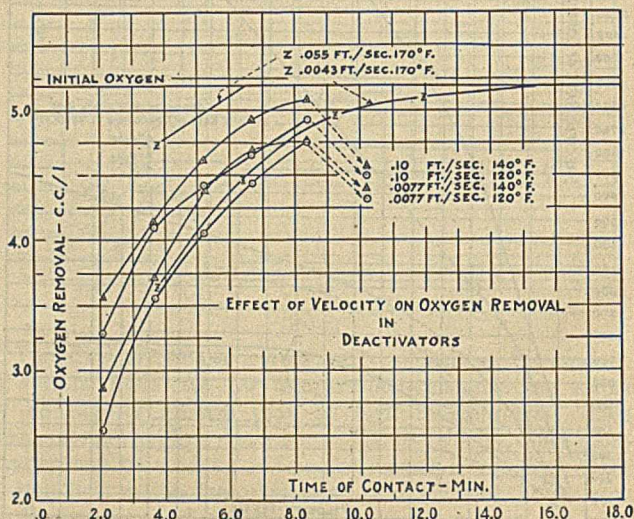
FIG. 7

At Low Rate of Flow

While 0.1 ft./sec. is extremely slow for pipe flow, it is very rapid compared to the customary velocity at which water passed over a number of closely spaced steel sheets, as in the deactivator now used for removal of free oxygen from water. Also, if velocity increases the rate of corrosion so rapidly, the efficiency of a deactivator should be considerably increased if the velocity can be increased. The following apparatus was therefore constructed: A small experimental deactivator (Fig. 5) 8 in. in diameter and 4 ft. in height was used. In order to obtain a higher velocity with the same time of contact, a system of alternate baffles was employed, composed of 26-gage black iron, between each of which was one of the regular soft steel sheets used for deactivation purposes. These baffles fitted very closely to the inside of the deactivator so that the water was compelled to pass over them. By this means the velocity could be increased about 13 times, covering the range 0.0043 to 0.10 ft./sec. All the sheets were freshly pickled in sulfuric acid and thoroughly washed before use. After a series of runs was made the sheets were removed, recleaned, and the deactivator filled in the usual way without the baffles. Duplicate runs were then made. Five valves giving outlets from various sections of the deactivator enabled various times of contact to be included in the same run. Thus was the time of contact as well as the temperature kept constant for various values, the only variable being the velocity. Fig. 7 gives the experimental results, which show that the effect of velocity even at this low rate of flow is quite pronounced, increasing the oxygen removal from 10 to 25 per cent.

In Fig. 6 is plotted the specific rate of corrosion in the deactivator, together with the specific rate of corrosion at 150° F. of the three sizes of pipe. From this it is shown that the specific rate of corrosion in deactivators falls in the lower velocity range of pipe corrosion when we consider the specific rate of corrosion from a velocity standpoint alone. The rate of corrosion in deactivators is naturally higher than we would expect from the velocity of the water as the direction of flow was changed frequently by a closed system of baffling.

An Internally Heated Laboratory Vacuum Pan[1]

By J. F. Brewster

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THE ORDINARY laboratory arrangement for vacuum distillations consisting of two round flasks, one heated externally serving as still or pan, the other cooled by running water serving as a condenser, is unwieldy and slow in action. In order to test the efficacy of internal heating the apparatus described herein was devised.

The body of the pan consists of an inverted bell jar 6 in. in diameter, with ground flange and wide mouth; this is supported by an asbestos ring resting on a tripod. The mouth of the body is closed by a rubber stopper through which pass the feed and draw-off tubes of glass and the leads of the flat-wound heating coil of $^3/_{16}$-in. copper tubing. When the spiral coil is wound the ends of the tubing are brought close to the center and bent at right angles to the spiral plane, being left long enough to pass through the rubber stopper and to provide for connection, one to the drain, the other to the source of heat. The top of the pan is the glass dome of the ordinary vacuum distilling apparatus shown in the catalogs of dealers in laboratory apparatus. This is fitted to the body by means of a rubber gasket. A second bell jar or the tubulated top of a vacuum desiccator may very well serve as the dome of the pan. The rubber stopper closing the mouth of the dome carries the thermometer and the glass exhaust tube leading to the condenser.

The pan coil may be connected by means of brass unions or rubber tubing to the coil of a Fletcher instantaneous water heater. With a good working pump a vacuum of 27 to 28 in. of mercury may be maintained; consequently it is unnecessary for the pan coil to be brought to a very high temperature and the Fletcher heater may be replaced by a helix of copper tubing heated by a Bunsen flame. The temperature of the water entering the coil may be controlled by varying water or gas pressure.

Several types of condenser are suitable for vacuum distillation. The Soxhlet ball condenser is small and efficient, or a closely wound helix of block tin or copper tubing $^1/_2$ in. in diameter with water jacket may be used. The latter is supported in a vertical position and discharges into a filtering flask. If a mechanical pump is at hand the distillation may be made continuous by withdrawing the condensate when necessary.

It so happened that all the parts of the apparatus described above, excepting the copper coil, were on hand in our laboratory, so that a very small financial outlay is represented. The parts may readily be duplicated since they are stock materials carried by laboratory supply houses.

With interior heating, distillations under reduced pressure may be accomplished with a great saving of time over that required with externally heated apparatus, owing to the large heating surface and the heat conductance of the coil. The boiling of cane sirup to massecuite with this apparatus requires one-third or less time than with the flask and water-bath arrangement. It has also proved very satisfactory for reducing the volume of alcoholic plant extracts.
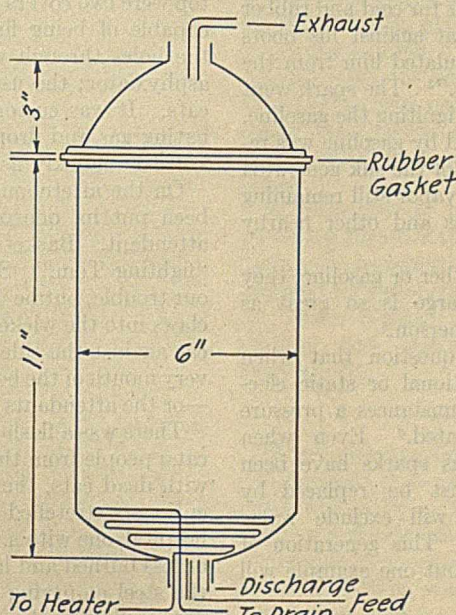
Labels in figure: Exhaust — Rubber Gasket — 3" — 11" — 6" — To Heater — Discharge To Drain — Feed

Curious Causes of Gasoline Fires and Gas Explosions[1]

By Augustus H. Gill

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THE ENORMOUS and ever-increasing use of gasoline and of hydrocarbon gases has caused many mysterious and disastrous explosions and fires. The reports of these are widely scattered throughout the daily press, and are more or less distorted and exaggerated, but very few get into scientific literature.

This article is a study and investigation of some of the typical and well-authenticated cases, combined with a plausible or perhaps probable explanation of their cause. It may be useful to those who from time to time have occasion to look into such matters, particularly in connection with legal cases.

One of the most mysterious of these fires, which was attended with fatal results, was the "Hair-Dresser's Accident" of June 26, 1897, in London, cited by Dr. Munroe.[2] A petroleum-containing hair wash was being applied as a shampoo when it suddenly ignited, burning the woman. Bearing in mind the familiar experience of lighting gas by shuffling across a rug and applying the knuckle to the open gas jet, there is no doubt but that frictional electricity was here generated in sufficient quantity to ignite the petroleum vapor. It has been reported from New York, but not verified, that a woman recently set fire to her hair by an electric spark while walking on a Brussels carpet, after indulging in a shampoo containing alcohol. The electrophorus, after being rubbed with a catskin, is sometimes used to explode gaseous mixtures in the small Hempel gas-explosion pipet. Inasmuch as ordinary ether is a constituent of hair washes at the present time, it seems that they should be rendered noninflammable by mixing with chloroform—or better, when applied, the patient should grasp a metal handle which should be carefully grounded.

An automobile was destroyed and its owner, a naval surgeon, severely burned, through the firing of the gasoline by a spark produced by frictional electricity. "The surgeon had walked some distance to his garage in his fur coat and rubber boots. The friction of the flapping coat against his boots generated the electricity, while they insulated him from the ground and allowed his body to store it."[3] The spark went hence through the grounded automobile igniting the gasoline.

A silk dress that had just been cleaned by gasoline was removed from a basket. This movement of the silk generated an electric spark that fired the gasoline vapor still remaining in the dress after cleaning. The dress and other nearby garments were burned.[4]

When woolen fabrics are washed in ether or gasoline, they become electrically charged. This charge is so great as to produce sparks when touched by a person.[5]

It has been demonstrated beyond question that when gasoline is pumped through hose, frictional or static electricity is generated—under certain circumstances a pressure of 400 to 500 volts has been generated.[6] Even when poured through chamois skin dangerous sparks have been produced.[7] This chamois strainer must be replaced by 80- to 90-mesh wire gauze which will exclude water when first wetted with clear gasoline. This generation of electricity has been shown repeatedly, but one example will

illustrate: A chauffeur hung an ordinary 5-gal. can on the hook of a common gasoline pump. The bail of the can had a wooden handle which insulated the can from the pump. A gallon had been pumped when a spark jumped from the can to the pump and fired the gasoline. After putting out the fire—as it was desired to fill a car, and the reason for the fire not being understood—the filling of the can was repeated and it caught fire a second time.

In filling a can or motor-car tank, care must be taken that good metallic contact is made between the nozzle of the hose and the article filled. If a funnel is used, it should not be blocked up with wood or paper, but metallic contact should be made. A chain or wire should connect the hose nozzle with the filling tank so that all electricity generated may pass to the ground as it is produced.

Gas Explosions

The explanation given of the cause of the hair-dresser's accident—the generation of frictional or static electricity by rubbing of hair or fur—will undoubtedly explain the two following incidents:

It is the custom of dog (and cat) catchers to asphyxiate their catch in a "tank" or "dispatch" with ordinary illuminating gas. In 1914 the dog officer in Providence[8] threw a cat into the lethal tank; on turning on the gas it exploded, singeing the officer's hair and injuring another. This was the third time such an accident had occurred—many dogs had been disposed of without trouble.

In New York the Society for the Prevention of Cruelty to Animals reports that in the course of twenty-five years there have been half a dozen minor explosions; the last one, however, was so serious that they have decided to adopt other means.

Their "dispatch" was a steel tank 10 × 4 × 4 ft.; on the top were two covers of heavy plate glass set in steel frames and capable of being firmly fastened down. Thin lids covered the holes through which the animals were passed into this asphyxiator; the usual charge was about six cubic yards of cats. It was customary to charge it somewhat with illuminating gas and drop the victims into it, that they might be killed as quickly as possible.

On the afternoon in question three basketsful of cats had been put in, one of the glass covers being held up by an attendant. Basket four contained, among others, a black "fighting Tom." Several of his companions dropped without trouble, but he wanted to stay where he was. He dug his claws into the wickerwork and hung on, even holding another cat against the side of the basket. It was put down to the very mouth of the hole and shaken hard; the two cats dropped —or the attendants think they did.

There was a flash—an explosion, a shower of plate glass and cats; people from the office rushed in to find the place strewn with dead cats, the black Tom included, and the three executioners stretched out on the floor. Two were sent to the hospital, one with a possibly fractured skull, and all were more or less burned and lacerated. The explosion had blown open the steel emptying door and wrecked the plate-glass covers. The ceiling of the room was torn open for several feet and showed where the cats had been blown against it. All are positive that there were no lights burning in the room and that no one was smoking, it being strictly prohibited in the building.

[1] Received January 8, 1923.

[2] *J. Am. Chem. Soc.*, **21** (1899), 330.

[3] *Boston Traveller*, January 11, 1917.

[4] *New York World*, February 28, 1915.

[5] *Ber.*, **47** (1914), 3239.

[6] *Quart. Nat. Fire Protection Assoc.*, October, 1914.

[7] *Safety Eng.*, October, 1914.

[8] *Boston Herald*, January 31, 1914.

Pyrex Glass as a Material for Chemical Plant Construction[1]

By A. E. Marshall

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ANYONE who has undertaken construction work on chemical plants, whether for the manufacture of mineral acids or less corrosive products, will admit that no available material gives satisfactory service under all conditions.

Materials in general use have specific advantages for specific work, and the chemical engineer utilizes a number of different materials in one piece of construction in order to develop maximum durability under varying conditions. Incidentally, durability is in many cases synonymous with resistance to corrosion.

Glass, because of its insolubility in acids, has always found uses in the chemical industry, but its limitations in the way of temperature resistance have restricted the field of application.

Ordinary glass, if desired to withstand moderate temperature changes, has to be made into shapes with thin walls, and such shapes when thin enough to survive slight heat shocks are much too thin to stand up under ordinary plant usage, or in many cases to survive rough handling during erection.

The desire to make use of the noncorrosive properties of glass has led to its being tried out under a variety of plant operating conditions, but the inherent disadvantages of ordinary glasses so far outweigh the useful features that it is difficult to point to successful applications in plant-scale work except under special circumstances.

Some years ago I made a survey of materials used in the construction of gas conveying lines from hydrochloric acid pots and muffles. One plant at the time of my visit was using 15-in. slip-joint glass pipes on the pot line. Very good results were being obtained because of the thorough cooling of the gas in its passage through the thin-walled pipes to the absorption tower. Later inquiries indicated rather heavy breakage during the winter months, the cause being ascribed to leakage of melted snow through the roof and onto the pipes, or to the considerable difference in temperature between the atmosphere and the gas inside the pipes.

There was a purely local reason for the use of glass on this line. The chemical plant adjoined a glass factory, and the glass pipes were thin cylinders from the plate glass department.

When wire glass was introduced it seemed to offer favorable possibilities to the chemical industry, and it was tried out for various uses without any great measure of success. I was interested in sulfuric acid concentrators at that time, and substituted some wire-glass plates for the acid-proof cover slabs on a cascade concentrator. The glass cracked in the

At the 1921 meeting of the Institute at Baltimore, the author read a short paper on uses of glass in chemical plant construction, and pointed out certain desirable features of glass equipment. Reference was made to the properties of Pyrex glass, and to a prospective investigation of the possibility of manufacturing Pyrex shapes suited to the needs of the chemical industry.

In the intervening period, development of the necessary manufacturing operations has proceeded satisfactorily, and it has also been possible to follow the behavior of the finished articles under actual working conditions in a large number of plants.

As the Richmond meeting was mainly devoted to a symposium on plant materials, it seemed desirable to elaborate last year's note into a more formal paper giving a summary of the development work, of the present status of Pyrex as an industrial material, and of its future possibilities.

The following paper describes in detail the present status of industrial Pyrex, and carries a suggestion of future possibilities. It is believed that Pyrex will in a short time occupy a definite place along with the other materials used for plant construction. It is not a universal panacea for construction ills, but, like everything else in our practice, it demands thought in its application and care in its use.

course of a few hours and thereafter final collapse was merely dependent on the time required for the acid fume to attack the wire reinforcement.

Other engineers have endeavored to utilize glass in various ways, and where temperature resistance and mechanical strength have not been essential, the material has proved satisfactory. I have in mind, as an instance, the glass-packed Gay-Lussac and absorption towers introduced in England about 1909 by Carmichael. These towers, usually of square section, are packed with annealed plate-glass sheets, set on edge and spaced fairly closely. Each successive layer of packing is placed at right angles to the row below, thus giving excellent surface contact and good gas distribution.

Mention has been made of attempts to use and the actual use of ordinary glass in plant construction, because such attempts afford evidence of a desire on the part of the chemical industry to utilize the valuable noncorrosive properties of glass.

With the introduction of Pyrex as a laboratory material and as a domestic utility in the form of baking ware, the possibilities of using glass in plant construction assumed a more promising outlook. Chemical manufacturers tried out Pyrex baking ware for small-scale chemical operations, drawn Pyrex tubes were used in Hart nitric acid condensers, and many other minor uses were discovered for the standard shapes which were being produced for the laboratory or the home.

In December of last year the idea of the desirability of gathering together these sporadic developments and investigating the possibilities of producing a line of Pyrex products designed for the chemical industry was suggested to the Corning Glass Works. The field appeared promising and a decision was reached to establish an Industrial Pyrex Department.

Characteristics of Pyrex

Before entering into a description of the present state of development, it is necessary to set forth the essential characteristics of Pyrex and the difference in its properties and those of ordinary glass.

Pyrex is a low-expansion borosilicate glass of simple chemical composition, containing no metals of the magnesia-lime-zinc group and no heavy metals. A comparison of the linear expansion coefficients of Pyrex and a number of materials is given in the attached table, and, as will be seen, Pyrex has a smaller coefficient than porcelain, ordinary glass, or any of the usual metals. The low coefficient of expansion

introduces a marked distinction from ordinary glass whether of the lead or lime-soda type.

The melting point of glass is not particularly valuable as an engineering consideration, as there is usually a fairly wide range between the initial softening point and final melting point. In the case of Pyrex the softening point is about 800° C., but the material will soften slightly, especially under pressure if maintained for a long time above 600° C. In connection with the softening point it is useful to remember that devitrification, which is a serious factor in the use of some materials, does not affect Pyrex in its working range.

LINEAR EXPANSION COEFFICIENTS
(PER ° C.)

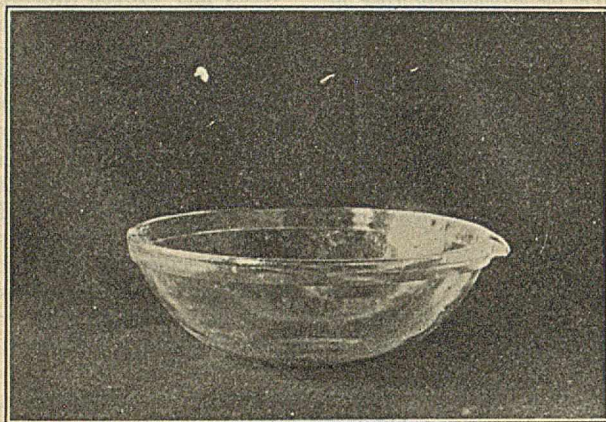|	
Pyrex Glass	0.0000032
Porcelain	0.0000036
Hard Glass	0.0000077
Soft Glass	0.0000085
Cast Iron	0.0000102
Wrought Iron	0.0000119
Portland Cement	0.0000120
Copper	0.0000167
Brass (66 Cu : 34 Zn)	0.0000190
Zinc	0.0000258
Lead	0.0000276

FIG. 1

Acid resistance is not usually given much thought in the case of glass, the general assumption being that all glasses are equally resistant. *Bulletin* 107 of the Bureau of Standards gives considerable data on the acid-resisting qualities of Pyrex and other glasses, and is well worth study. Researches have also been conducted in the Corning laboratories on the resistance of Pyrex to perchloric, phosphoric, constant-boiling hydrochloric, and concentrated sulfuric acids under a variety of conditions. The action of hydrochloric and sulfuric acids is imperceptible, constant-boiling hydrochloric acid attacking Pyrex at a rate of 0.000006 g. per sq. cm. per hr. Concentrated sulfuric acid in 4 hrs. at the fuming temperature shows an attack of 0.000002 g. per sq. cm. per hr. Both figures relate to initial surface attack, as after the lapse of a few hours a state of practical stability is reached.

Work on the coefficient of heat transference is being carried out at Corning but has not been completed. Preliminary results on the relative efficiencies of Pyrex, porcelain, and stoneware indicate Pyrex and porcelain as equal, whereas stoneware shows slightly less than one-half the Pyrex value.

It can be said that while Pyrex is superficially a glass, its physical characteristics justify consideration from the engineering standpoint as a special and distinct material adapted to a variety of industrial uses to which ordinary glass cannot be applied.

DEVELOPMENT OF SHAPES

Proceeding from a consideration of useful properties to the development of definite industrial shapes, it is obvious that the upper limit of size is a factor of great importance. If the sizes had to be restricted below the usual standards in other materials, then the field of application would also be restricted. It was not practicable to pick out very large pieces and concentrate on them, because failure in manufacture might be caused by lack of dexterity in handling such large shapes. The history of most plant materials, stoneware, fused silica, high silicon irons, etc., has been one of gradual enlargement of product. In the case of Pyrex the existing laboratory and domestic shapes could be used as a starting point and a stage selected which would represent useful commercial products, without going out to sizes which would call for the introduction of new methods of handling.

The starting points selected were, therefore, an 18-in. evaporating dish (Fig. 1), a 6-in. bore socket pipe 39 in. over-all, and a cylindrical pot 12 in. in diameter by 20 in. high. It was expected that difficulties would develop in the manufacturing process; but, contrary to expectations, production was worked out with not more than the usual minor troubles.

With proof that manufacture was possible it was then necessary to test out the product under working conditions. These tests were made on single pieces in various plants, and following satisfactory reports distribution was started on a small scale. The application of these first available shapes brought along a demand for other forms of Pyrex equipment, and as a consequence new items have been added in the last few months, while others are approaching the production stage. Reference is directed to the 72-liter capacity retorts designed for distillation and reaction work, various sizes of pots up to 9-gal. capacity, and large separatory funnels of 8-gal. capacity (Fig. 2), as articles now available. Pyrex glass is also being produced in sheets 14 x 18 in., and it is anticipated that much larger sheets can be made if there is the necessary demand.

In addition to these items a 25-in. diameter dish of 30-liter capacity is about ready for distribution, 12-in. socket pipes will follow in a few weeks, and other shapes of equivalent size, such as a drier tray, cascade dishes, etc., will be put in production as soon as a demand is assured.

Incidentally, the use of Pyrex in forms developed specially for the chemical industry has created interest in the possibilities of equipment made up from Pyrex tubing. Condensing equipment made up of S-bends, pipe lines with socket or butt joints, etc., is becoming standardized.

An interesting piece of Pyrex equipment was constructed recently for the du Pont Company. This was in the form of an experimental denitrating tower 6 in. in diameter by 8 ft. high (Fig. 3). All parts, including distributor, and inlet and outlet connections, were Pyrex. It is understood that the tower has given satisfactory service, despite rather strenuous conditions.

SEPARATORY FUNNEL
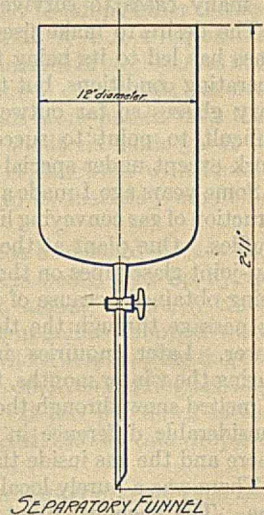
FIG. 2

ADVANTAGES OF PYREX

The use of Pyrex in actual plant work has developed some interesting side lights, not only on applications, but on a phase of excessive cost created by a lack of standardization. This point will be discussed later.

It had been anticipated by users that there would be a higher handling breakage with Pyrex dishes than with porcelain. Experience has been entirely contrary to this idea, and the reason apparently lies in the province of psychology.

One plant, which is now completely equipped with Pyrex dishes, reports handling breakages as nil, and states that the men treat the dishes as glass, setting them down with care and so obviating breakages through dropping. It has been the experience of every user of Pyrex, irrespective of the shape of the article, that transparency creates care in handling. It is a natural assumption that an opaque object will withstand shocks and that a transparent one will not, so a transparent material which is at least equal to stoneware and porcelain in mechanical strength has a much better chance to survive at the hands of a workman. Transparency has other advantages which are not psychological. The first and most important is that a transparent article cannot have blow holes or other hidden flaws. Even strains can be detected by the use of a special polariscope, this being one of the routine tests to which every piece of Pyrex equipment is subjected in the factory.

FIG. 3

EXPERIMENTAL DENITRATING TOWER

Next comes the question of cleanliness. Opaque equipment may or may not be clean, but transparent equipment always supplies its own positive answer on this point. Finally, there is the feature of controlling reactions through direct observation.

Another interesting feature which has been brought forward by users is in relation to the process of manufacture. Pyrex is to a certain extent competitive with chemical stoneware. The process of making stoneware is quite lengthy, the time required being about two months. Breakage of a special piece of stoneware, provided there is no duplicate in the plant storeroom or at the stoneware manufacturer's works, means a long delay in starting up after the shutdown. If a mold exists for the piece in Pyrex, manufacture can be completed in three days at a minimum, although factory conditions might necessitate a delay of a few additional days on account of prior routing of work.

Touching on the phase of excess costs of construction materials, it seems very desirable to emphasize the lack of standardization in the chemical industry. Molds are costly, whether they are intended for stoneware, silica, Pyrex, or other materials. The manufacturer of the equipment has to charge up his mold cost to the user, and there seems to be too great a demand for "specials" which may vary only $1/8$ in. from a stock mold. Some concerted effort to standardize shapes would cheapen the products, and, of equal importance, would enable producers to carry representative stocks. A striking example of the lack of standardization is shown by the Corning Glass Works list of sight glass molds. Continuous efforts have been made to keep down the number of sizes, but the success can be judged when it is shown that between the range of $2^{1}/_{2}$ in. diameter by $1/_{4}$ in. thickness to $8^{1}/_{2}$ in. by $3/_{4}$ in. it has been necessary to provide 41 molds.

In the case of plant equipment, a further effort is being made to work out shapes that will suit a variety of uses, and it is hoped that a full measure of coöperation will be extended by plant managers and engineers, through the use of stock rather than special molds.

INSULATORS

The industrial use of Pyrex is spreading into many fields, and, while not a strictly chemical application, decided interest attaches to the development by the research laboratories of the Corning Glass Works of Pyrex high-tension insulators.

The generally accepted causes of failure of porcelain high-tension insulators are: (1) change in structure of porcelain with time and absorption of moisture; (2) breakage due to thermal changes; (3) flaws in the porcelain body causing dielectric and other failures; (4) failure due to expansion of cements used in attaching hardware to the insulator; (5) mechanical weakness. These failures may be generally classified as failure due to the properties of the insulator and failure due to design.

Pyrex glass seems to have ideal properties for an insulator for it apparently is not subject to any of the intrinsic weaknesses of the porcelain insulator. It does not change in structure, can be inspected for any defects thus assuring a uniform product, has a sufficiently high dielectric strength, a great resistance to thermal changes (its thermal expansion coefficient being low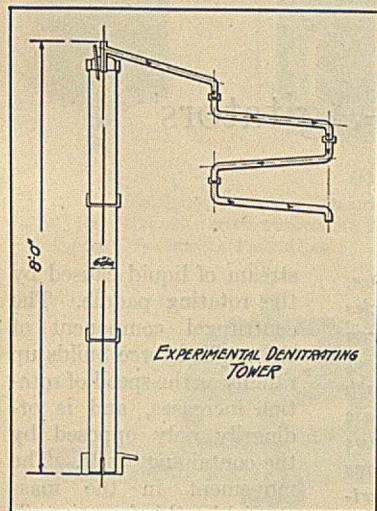er than that of porcelain), and in addition is not heated by direct solar radiation as much as porcelain. Consequently, if a Pyrex glass insulator could be built free from the design defects of the porcelain, there is no question but that it would be a better insulator.

The drawing shows the construction of the Pyrex insulator (Fig. 4). It is evident at a glance that this construction and design gives a cement-free, all metal and glass insulator, and that the design is one of great resistance to tension as the material of the insulator is largely under compression.

Considerable data have been collected showing the relative properties of Pyrex which show the increase in temperature due to solar radiation to be 3.65 times as much for the porcelain as it is for the glass. The glass is transparent and the porcelain absorbs the heat radiation. This proves that in service the glass is not subjected to anywhere near as severe heat changes as is porcelain.

One of the large manufacturers of electrical equipment says: "The tests on Pyrex suspension insulators show quite conclusively that the material has good characteristics. The uniformity of electrical puncture is a distinct advantage over porcelain."

It is evident that Pyrex glass has very good dielectric properties, more than ample for the service, as well as being uniform.

FIG. 4

Tensile strength tests of the better grades of porcelain insulators show that they will not stand over 10,000 lbs. load as a maximum, and many break below that. It is therefore evident that the glass insulator has a strength far superior to anything yet developed. This property should allow for longer spans, and in many cases where two strings of porcelain are used in parallel one of Pyrex will be ample to carry the load.

There are other points of probable superiority of the glass insulators which will have to be proved by service tests. Pyrex glass has a great resistance to water absorption and
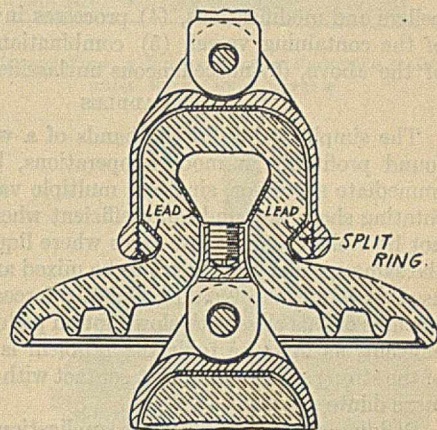
surface attack, and it is therefore durable under long exposures to severe atmospheric conditions, as, for instance, around chemical plants. It is probable that glass insulators will not be as attractive to birds and spiders for nesting sites since they will not have the dark shadows that exist in a string of porcelain insulators.

The chief advantages of the Pyrex insulator are the facts that it does not absorb heat as does porcelain; has no cement in its construction to gradually absorb water and expand, ultimately fracturing the insulator; and has a mechanical strength that will average twice as high as any porcelain insulator yet on the market.

Tools of the Chemical Engineer.　I—Agitators[1]

By D. H. Killeffer

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Agitation, as the term is applied to chemical engineering practice, may be defined as the operation causing mutual movement of particles of matter for the purpose of bringing about intimate contact between them. In general practice the term is applied to the mixing of different liquids, different solids, and liquids and solids, although in a strict sense its application to mixtures involving a gas phase is equally logical. The purpose of the present article is to discuss some of the fundamental principles of agitation and the means available for putting them to work in the chemical plant. Experimental evidence of the effectiveness of any particular form of agitator is sadly lacking, and nothing better than the old "cut and try" method is available to the prospective user of such apparatus. There is no method at present in use by which the effectiveness of any particular type of machine may be compared with any other, either as to speed of mixing or power consumed to accomplish it. The result is that chemical engineers generally are inclined to instal tools which will give greater mixing than is actually necessary with consequent waste of power. It is to be hoped that the generalizations put forth here may lead to a closer study of the subject by those best equipped to undertake it.

FUNDAMENTALLY, agitation is accomplished by applying force to a more or less fluid mass and then opposing the resulting movement in such a way as to alter its direction or otherwise emphasize its selective action on various parts of the mass. Movement must be brought about in parts of the mass in such a way as to force changes in the relative positions of its various particles. The means by which this result is accomplished in practice may be roughly classified into six groups: (1) simple paddles and modifications, (2) turbines and modifications, (3) propellers and modifications, (4) processes involving movement of the containing vessel, (5) combinations of two or more of the above, (6) miscellaneous unclassified types.

PADDLES

The simple paddle in the hands of a workman is seldom found profitable in modern operations, but frequently its immediate successor, single or multiple vanes mounted on a rotating shaft, is found quite efficient where movement need not be violent, as in those cases where liquids of very nearly the same specific gravity are to be mixed and where mixing is used as a means of aiding osmotic forces. Dissolvers and leachers of this class with slow-motion paddles are found to be efficient, as in these tools the problem is really the mixing of the strong solution in direct contact with the solute with the more dilute solvent.

Paddle agitators involve the application of force with two directional components, one in the direction of rotation and a second centrifugally and at right angles to the first. The rotating force is comparatively greatest and the centrifugal force least when the movement of the paddle is slow and tends to bring the mass as a whole into rotation at a speed approximating that of the paddle. Actual mixing in this event is comparatively slight. The inertia of the mass, as well as the resistance to rotation offered by the walls of the containing vessel, tends to start cross currents of various kinds and thus promotes some mixing. Increases in the resistance to this rotational motion are made by introducing stationary paddles or simple vanes projecting from the sides of the containing vessel in various ways which break up the otherwise solid

stream of liquid caused by the rotating paddle. The centrifugal component of the applied force builds up rapidly as the speed of rotation increases, and is ordinarily only opposed by the containing walls. The movement in the mass caused by this force is utilized more or less incidentally in the ordinary paddle mixer but becomes the principal force in turbine mixers which will be considered later. Motion from the center toward the walls of the containing vessel is changed in direction at that obstruction into up or down motion following the wall, and is largely influenced by the strong rotational movement which is especially rapid at the periphery of the vessel. Few machines are now built which are of the simple paddle type, as most builders incline the paddles in such a way as to add a force component in the direction of the paddle's axis.

Combinations of paddles are frequently used. Two paddles mounted to revolve in the same direction at the focuses of an elliptical vessel, three paddles in a clover-leaf vessel, etc., generate conflicting currents in the liquid and bring about very efficient mixing in many processes. The mounting of two sets of paddles on the same axis to revolve in opposite directions has been found to consume a disproportionate amount of power. The use of single or multiple sets of paddles mounted off-center in cylindrical tanks gives economical mixing in many cases where a centrally mounted paddle would result in a simple rotation of the mass without real mixing. Inclining the axis of a cylindrical vessel with a simple paddle revolving in its center produces a marked increase in mixing by utilizing gravitational force.

TURBINES

The turbine type agitator is really a special case of the paddle type, but since the principal force used is centrifugal rather than rotational, it must be considered separately. In this type of agitator the rotating unit is so designed as to minimize the rotational component of force and increase the centrifugal component to a maximum. Its operation is in all respects similar to that of a centrifugal pump, with the exception that the motion of the liquid is permitted in every radial direction instead of being forced in a single direction by a casing or pipe. The radial currents are directed toward
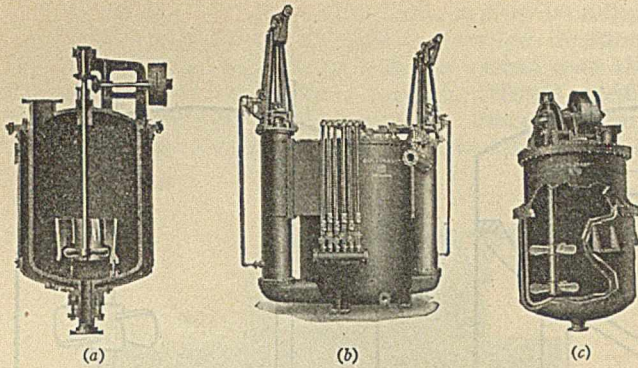
(a) Propeller Type with Draft Tube (Patented)
(b) Nitrator with Propeller in Independent Tube
(c) Off-Center Propeller
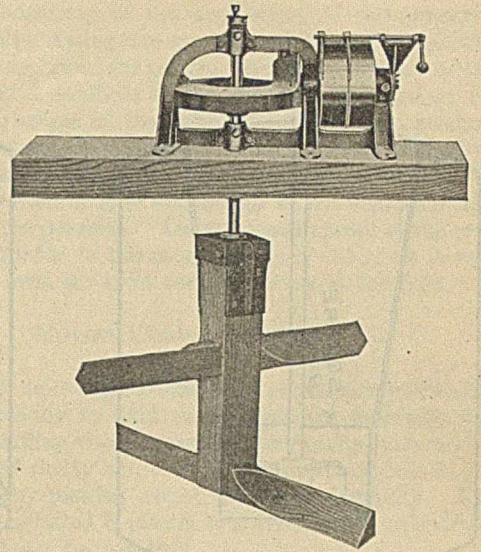
Slow-Speed Propeller. Virtually a Combination of Propeller and Paddle
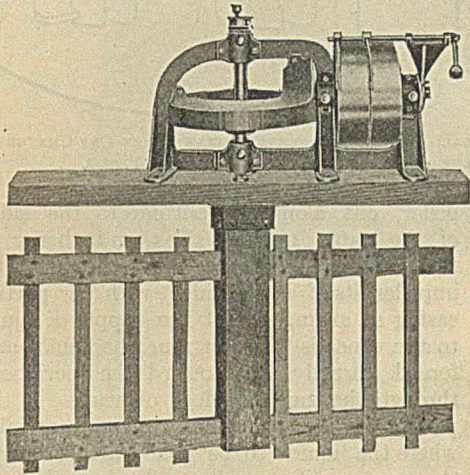
Multiple Type Simple Paddle
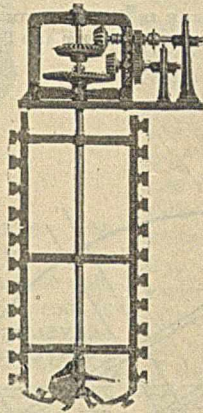
Combination Propeller and Paddle Scraper
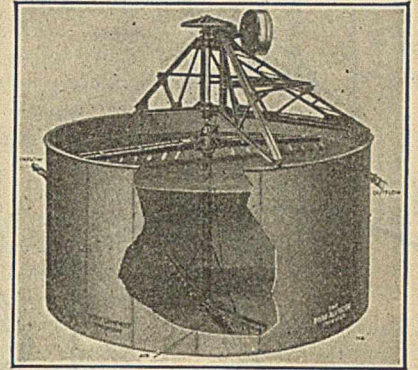
Modification of Simple Paddle Principle Combined with Liquid Stream
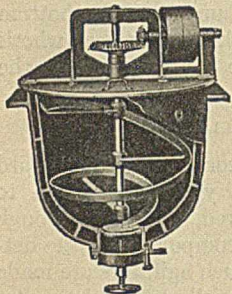
Combination Propeller and Screw Type

Simple Paddle Scraper
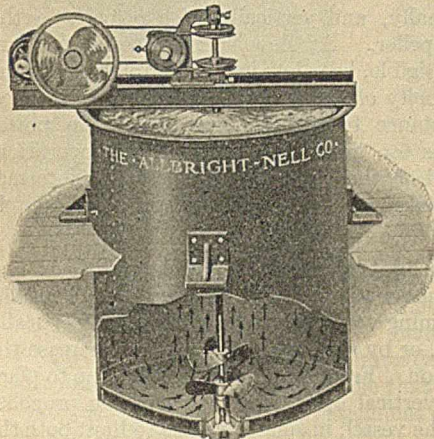
Two Propellers Rotating in Opposite Directions on the Same Shaft
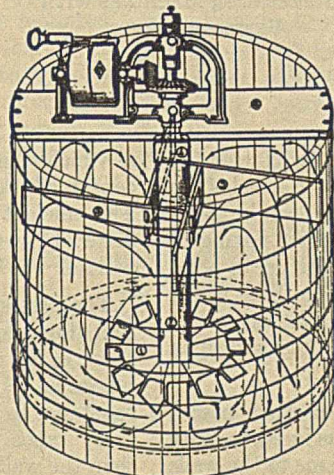
Combination Propeller and Turbine Type Mixer

Combination Paddle and Propeller of Stoneware

PROPELLER IN SQUARE DRAFT TUBE

SIMPLE PADDLE IN VESSEL WITH HELICAL VANES. EFFECT OF PADDLE AND PROPELLER

MULTIPLE PROPELLERS SET OFF-CENTER IN CYLINDRICAL VESSEL

SIMPLE TURBINE MIXER

SIMPLE PADDLE IN INCLINED VESSEL

STIRRERS FOR MACHINES WITH VERTICAL SHAFTS

peller, out along the bottom to the sides of the tank, up the sides and thence to the center at the surface of the liquid. The impeller itself is provided with a partial casing so arranged that the supply of liquid to the vanes is taken in near the center and forced directly out toward the periphery through the guiding effect of vanes in the partial casing. In some cases, especially where the liquids to be mixed are of nearly the same specific gravity and where the volume to be mixed is large, it is advantageous to elevate the impeller unit from the bottom to the center of the tank, as here two whorls are started, one above and one below the impeller.

PROPELLERS

Ship-propeller agitators introduce a third force component in a vertical direction to those already considered, and it is through the emphasis of this component to the detriment of others that such agitators are made efficient. A simple propeller set in the center of the mass of liquid imparts motion to it in each of three directions, horizontally, rotationally, and vertically with respect to the propeller. At slow speed these effects are negligible, but they increase rapidly with the velocity of rotation, until a point is reached at which the resistance to motion, and hence the power consumed, becomes too great to permit efficient operation. The efficient speed of the propeller is ordinarily intermediate between those of the turbine and the simple paddle.

The first step in limiting the effects of the rotational and centrifugal components was to reduce the first by altering the shape of the containing vessel by vanes more or less vertically placed on its sides, or by otherwise altering it to increase the resistance to rotation. From this it was an easy step to place these vanes in a vertical open tube closer to the propeller than the walls of the vessel, in such a way as to limit both the rotational and centrifugal forces to action on a small part of the mass while permitting the vertical component to act

and up along the walls of the containing vessel by placing the turbine itself close to the bottom. In general, the speed of the rotating member is high and sufficient force can be communicated to the liquids to bring about efficient mixing of liquids of widely differing specific gravities. Its use is practically limited to liquids of low viscosity and to those which do not contain solids except in very finely divided form. Its efficiency depends upon the mobility of the liquid and upon giving it a high velocity.

Ordinarily, turbine mixers are most efficient when placed in the center of the bottom of cylindrical tanks in such a way as to permit free movement of the radial streams to the walls of the vessel where they are turned in a vertical direction. The flow of liquid in this case is down in the center to the im-

freely on the whole.[2] These draft tubes, as they are called, force high-velocity streams of liquid in a vertical direction, and it has been generally found that this method gives the greatest mixing of two liquids of markedly different specific gravities, such as acids and hydrocarbons. Since such reactions as nitration are strongly exothermic, the mass of liquid
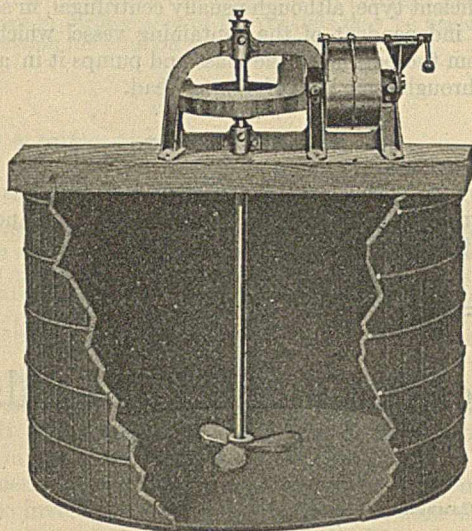
SIMPLE PROPELLER

must be moved rapidly past large cooling surfaces. One type of agitator has been developed especially to accomplish this end. Here the propeller is placed in a tube outside the main container and a great mass of cooling coils is located in the main vessel. The inlet and outlet of this tube are so arranged that the stream of liquid through it causes a more or less pronounced swirl in the main volume around and through the mass of cooling coils. The effect of the marked difference in specific gravity of the liquids to be mixed is largely offset by introducing one of them, usually the hydrocarbon, at a point in the draft tube just before the stream comes to its point of greatest agitation at the propeller.

Still other makers of agitators find a propeller provided with a narrow ring around its circumference highly efficient in producing a maximum vertical component, with little energy wasted in the other two directions. Another type has two propellers mounted on the same shaft in such a way as to revolve in opposite directions, yet producing parallel vertical components. Here the rotational component is minimized by the action of the two opposed propellers, and a pronounced vertical flow is achieved, while the centrifugal component is neglected. The neglect of the latter feature is generally considered of little consequence, but it is conceivable that it might be more efficiently used than in present machines of this type.
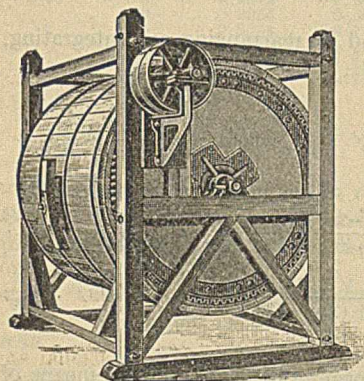
ROTATING BARREL TYPE MIXER

[2] The use of a cylindrical draft tube with vanes inside it has been patented. Other forms, such as a square tube, while possibly less efficient, are available without patent interference.

Other modifications of the application of the propeller principle involve setting one or more off-center in much the same way as described for paddle stirrers, inclination of the containing vessel, multiple blades, propeller mounted on the same shaft to rotate in the same direction but to produce vertical components in opposite directions, continuous screws set in less fluid masses, and so on through every conceivable variation as varied in type and design as the engineers who have studied the question. The universal appeal of the propeller type agitator to the imaginations of designers is well borne out by even the most cursory survey of the field.

MOVING VESSEL AGITATORS

The types of agitating devices so far considered lend themselves most readily to fluid masses but are decidedly less efficient in handling viscous masses. Ordinarily such masses must be mixed slowly and it is frequently found best to accomplish this by making use of the force of gravity. The mixture to be agitated is placed in a more or less cylindrical vessel which can be rotated about a horizontal axis. In this case the rotation of the container raises the mass by degrees, and its fall from slight elevations brings about the desired mixing. The vessel may be cylindrical, in which case it is ordinarily provided with projections toward the center from its inside periphery, or it may assume a variety of shapes from spherical to cubical that will assist the operation of raising parts of the mass and allowing them to fall back into the original mass, their relative positions being thus altered. Cement kilns and barrel dissolvers used

COMPLETE SCREW MIXER FOR VISCOUS MATERIALS

in shellac manufacture are the simplest practical tools of this type. The ball mills are modifications of the same principle since they include balls to assist the motion in the mass as well as to perform the grinding operation.

The majority of agitators for mixing viscous masses—aside from those above, the application of which is not limited to this use—are modifications of the simple paddle mixer with some propeller action so altered as to permit the application of the greater forces required. In general, the principles involved are the same after allowance is made for the lack of fluidity of the mix and the consequently greater power requirement. As an engineering problem, however, viscous mixing presents many problems not involved in mobile mixing.

COMBINATION AGITATORS

Combinations involving two or more of the foregoing types of agitating devices may be found in most tools as commercially used. The combinations and their applications are as numerous as the uses to which they are put, as it is seldom that the operating engineer finds a tool ready built to suit his particular need, in spite of the variety offered by makers. Combinations of simple paddles with propellers and of turbines with propellers in greatest variety are to be found in most plants, yet the principles underlying them are much the same. One of the force components possible is emphasized at the expense of others. This practice has become so common that it is indeed difficult at present for one

to find tools made in which the agitation is accomplished by a device which does not involve a variety of principles.

MISCELLANEOUS TYPES

Various types of devices are encountered in special fields which do not involve any of the principles so far discussed. Blowing a gas through a liquid mass is often used for agitation where the interaction of the gas with the mass is either desired or not objectionable, as in the cases of the aeration of sewage and mixing of strong mixed acids, where it is desirable to blow out oxides of nitrogen. Many combinations of fluid streams, either liquid or gas, with paddles and propellers are met in practice. The stirring of a liquid being electrolyzed in an electrolytic cell by surrounding it with a magnetic field has been found to be very highly efficient in many electrolytic operations where the presence of any foreign substance in the electrolyte is objectionable. The cascade principle is often applied to operations not ordinarily considered agitation, as where it is desired to dissolve a solid in a liquid in the lixiviation of ores. Still another form which agitation takes is well illustrated in washing an immiscible liquid with water by pumping the heavier, in a stream more or less broken, into the lighter, as in washing nitrobenzene with water to free it from acid. The circulation is accomplished by a pump of any efficient type, although usually centrifugal, in a system virtually independent of the containing vessel which draws liquid from the bottom of the mass and pumps it in again at the top through some kind of a spray head.

ACKNOWLEDGMENT

The writer wishes to acknowledge the kindness of the various manufacturers who have lent us the cuts and drawings for this article.

Effect of Agitation on the Rate of Solution of Crystals[1]

By E. V. Murphree

MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASS.

ONE OF the problems in which agitation plays an important part is the solution of crystalline materials. It is possible to develop formulas for this case in which the only unknown quantity is the specific solution rate. This constant depends upon the effectiveness of agitation, and it is possible to test out experimentally an agitator suited for this work by determining this constant for the case of a given material dissolving in a given solvent. Comparison of the constant thus obtained with that found on other equipment used for the same purpose gives a measure of the relative agitation efficiencies of the two types of equipment.

Assume a definite weight of crystals of size uniform or nearly so, added to a solvent and agitated at a uniform rate. Assume also that the volume of the solution remains substantially constant. The rate of solution is proportional to the area of crystals exposed and to the degree of agitation. Furthermore, as has been shown by A. A. Noyes,[2] the rate of solution at any particular time is proportional to the difference in concentration of the saturated solution and that of the main body of the solution. This is because the solution in absolute contact with the crystal is saturated and the crystals dissolve only by diffusion of the solute through the stationary film of liquid around the crystals. This diffusion is of course proportional to the concentration difference. Since the diffusion rate will be inversely proportional to the thickness of this film, and since this film thickness is determined by the effectiveness of agitation, being approximately inversely proportional to the velocity of the liquid past the crystal, diffusion rate—i. e., the constant which represents the specific rate of solution for unit area of crystal surface—is a good measure of agitation efficiency.

GENERAL FORMULA

NOMENCLATURE

V = volume of solution.
Θ = time.
c_s = concentration of saturated solution as weight per unit volume.

c = concentration of solution at time Θ in same units.
x_o = linear dimension of crystal at zero time.
x = linear dimension of crystal at time Θ.
W_o = total weight of crystals at time zero.
W = total weight of crystals at time Θ.

n = number of crystals = $\dfrac{W_o}{a x_o{}^3}$.

$a x_o{}^3$ = weight of one crystal.
$b x_o{}^2$ = surface of one crystal.
a and b are constants, the numerical value of which depends upon the form of the crystal grains.

It is assumed that when $\Theta = 0$ the solvent contains no solute.

$$V \frac{dc}{d\Theta} = K (c_s - c) x^2 bn \qquad (1)$$

$$W_o - W = V_c \qquad (2)$$

$$n (a x_o{}^3 - a x^3) = V_c \qquad (2a)$$

$$- 3 a n x^2 dx = V dc \qquad (2b)$$

On substituting for c and dc, rearranging, and integrating, Equation 1 takes the form

$$3 \frac{V}{nb} \int_x^{x_o} \frac{dx}{A + x^3} = K\Theta \qquad \text{where } A = \frac{V c_s}{na} - x_o{}^3$$

$$\frac{Vk}{nAb}\left[\frac{1}{2} \ln \frac{(k + x_o)^2 (k^2 - kx + x^2)}{(k + x)^2 (k^2 - kx_o + x_o{}^2)} + \right.$$
$$\left. \sqrt{3} \tan^{-1} \frac{k \sqrt{3} (2x_o - 2x)}{3k^2 + (2x_o - k)(2x - k)}\right] = K\Theta \qquad (3)$$

where $k^3 = A$.

The value of x in this formula can be found by means of Equation 2a.

SPECIAL CASE I—When there are not enough crystals originally present to saturate the solution, the time for complete solution is found from Equation 3 by making $x = 0$. This gives

$$\frac{Vk}{nAb}\left[\frac{1}{2} \ln \frac{(k + x_o)^2}{k^2 - kx_o + x_o{}^2} + \sqrt{3} \tan^{-1} \frac{x_o \sqrt{3}}{2k - x_o}\right] = K\Theta \qquad (4)$$

[1] Received January 5, 1923.
[2] Noyes and Whitney, Z. physik. Chem., **23** (1897), 689.

SPECIAL CASE II—When there are just enough crystals to saturate the solution, the time for complete solution is found from Equation 4. In this case, however, A = 0, so the time becomes infinite.

SPECIAL CASE III—When there are more than enough crystals to saturate the solution, the time for saturation is given by Equation 3 and is infinite.

SPECIAL CASE IV—When the amount of crystals is very large compared with the amount necessary to saturate the solvent, the change in surface area of the crystals may be neglected and the expression for solution rate reduces to

$$V \frac{dc}{d\Theta} = K\ (c_s - c)\ B$$

where B = surface area.

Hence, $ln\ \dfrac{c_s}{c_s - c} = \dfrac{KB\Theta}{V}$

This condition might well be used where it is desired to test the agitation efficiency of a given type of agitator for a thick mixture of solids suspended in liquid. Where the agitator is to be used for a relatively small amount of solids in the liquid, this condition should obviously not be employed, because it greatly changes the character of the mixture.

To measure rate of solution any of the standard methods can be employed for analysis of the solution at any specific time. If instantaneous readings are desired, it might be worth while to use conductivity methods of analysis.

The general equation is applied to the following data. Since the investigator did not determine the number of particles, they were assumed to be spherical. This can introduce no serious error. The value for c_s was taken as the last reading in the table.

DATA FOR RATE OF SOLUTION OF $K_2Cr_2O_7$ CRYSTALS[3]

Volume of solution, 4000 cc.   Weight of crystals, 500 g.
Size of crystals, 0.6314 cm.   Temperature of solution, 23° C.

Time in Min.	Concn. in Equivalents per Liter
0	0.00
1	0.60
5	1.60
10	1.93
15	2.06
25	2.18
40	2.26
60	2.30
80	2.34

From these data the following was calculated:

c_s = 0.1147 g./cc.		n = 235	
a = 8.450		A = −0.0218	
b = 3.142		k = −0.2794	

Θ	x	f	Θ (calcd.)
0	0.6314	0.0	0.0
1	0.5780	0.0162	0.5
5	0.4552	0.333	6.3
10	0.3954	0.566	10.6
15	0.3654	0.759	14.5
25	0.3340	1.272	24.0
40	0.3083	1.702	32.5
60	0.2936	3.710	70.0

$$f = \frac{1}{2}\ ln\ \frac{(k+x_o)^2\ (k^2 - k_x + x^2)}{(k+x)^2\ (k^2 - x_o + x_o^2)} + \sqrt{3}\ \tan^{-1} \frac{k\ \sqrt{3}\ (2x_o - 2x)}{3k^2 + (2x_o - k)\ (2x - k)}$$

According to Equation 3, the result of plotting f against Θ should be a straight line, and the experimental results justify this conclusion. The slope of the straight line is

$\dfrac{K}{Vk} \Big/ nAb$. The value of K for this case is therefore 0.366 g. per

sq. cm. per min. per unit concentration difference.

The difference between Θ observed and calculated for one minute may be due to error in determining zero time. A small error in analysis will make a large error in the case of Θ for 40 and 60 min.

It is evident that results analogous with those given here can be obtained for any similar case of heterogeneous equilibrium.

[3] H. Braude, M. I. T. thesis, June, 1913.

The Stability of an 0.01 N Sodium Oxalate Solution[1]

By Edward S. Hopkins

BALTIMORE CITY WATER DEPARTMENT, BALTIMORE, MD.

In this laboratory the usual oxygen-consumed test[2] is made as daily routine practice. This is an acid permanganate digestion and subsequent titration with sodium oxalate. Frequent standardization of the oxalate solution was necessary as decided deterioration was encountered after the first week of use. In fact, upon titrating a solution 17 wks. old it required only 7.4 cc. of permanganate instead of 10 cc. This condition is well known in chemical literature.[3,4]

The addition of 100 cc. of 1:4 sulfuric acid per liter to the oxalate solution will prevent this deterioration for at least two months (actual experiment), even when the solution is stored in *clear glass bottles on the laboratory shelf exposed to daylight.*

Weekly tests were made upon our laboratory solutions, and 10 cc. oxalate always equaled 10 cc. permanganate. The permanganate was checked at the time of each titration against a weighed amount of standard oxalate and found to be correct. These laboratory solutions are stored in the usual clear glass tincture bottles with glass tube connections to the usual siphon buret and no precaution is taken to exclude light or treat them in any particular manner.

This addition of sulfuric acid to a standard oxalate solution has been presented by one authority[5] who discussed the behavior of an 0.1 N solution of oxalic acid, without describing storage conditions.

[1] Received December 20, 1922.
[2] "Standard Methods for the Examination of Water and Sewage, American Public Health Association," **1920**.
[3] Blum, *J. Am. Chem. Soc.*, **34** (1912), 129.
[4] *Bur. Standards, Circ.* **40** (1920).
[5] Treadwell and Hall, "Quantitative Analysis," 599.

Gypsum Decision

By a decree of the Federal District Court issued on January 3, the Gypsum Industries Association, which comprises practically all the manufacturers of gypsum products in the United States, was ordered dissolved as a combination in restraint of trade and commerce in gypsum products. The terms of the decree virtually destroy the trade association and prohibit its regular weekly or monthly meetings, at which opportunities were offered, as the government contended, for open or illicit price-fixing by the group, for arrangements for the curtailment and limitation of production, and for devising other abuses which are alleged to have resulted from the meetings. In its place is substituted a non-profit-making corporation for the joint welfare of the members, with powers limited expressly by the decree, and by its charter to certain well-defined and concededly lawful activities. The decree is said to be of far-reaching importance because for the first time in the history of the Sherman Law there is clearly set forth a code of principles governing trade associations and outlining definite restrictions, with certain provisions in this specific case for what they may be permitted to do.

The main injunctive provisions of the decree prohibit agreement to fix or establish prices for gypsum products, to establish or maintain uniform prices, to advance or decrease prices, to limit or otherwise control the production of gypsum products, to fix boundaries of sales territories open only to certain members, and to effect any discrimination in prices. Activities which are held to be lawful include advancing or promoting the use of gypsum products by all legitimate means, including research, publicity, and advertisement, dealing with engineering and trade problems pertinent to the industry, carrying on educational work, maintaining a traffic bureau to furnish information, dealing with improved methods of plant and mine operation, and maintaining a credit bureau. The decree is the result of a nation-wide investigation conducted by the Government, and of a Grand Jury hearing lasting more than a month, at which a large amount of evidence was accumulated.

Integral Waterproofings for Concrete[1]

By Alfred H. White

University of Michigan, Ann Arbor, Mich.

This paper will deal with the properties of concrete and of integral waterproofings, not as used under conditions where the concrete is always kept wet, but where the concrete is frequently dry and may never have had adequate opportunity to have its colloid developed. It limits itself quite closely to a discussion of the rate of absorption of water by capillary action and the effect of integral waterproofings on the rate of water absorption. The results set forth were obtained by observations on blocks 4 x 4 x 6 in. made from a single lot of sand and with cement from well-recognized commercial brands. The sand was clean, natural sand of good quality. The blocks were all made from a 1:3 mix with about 10 per cent of water. The tests are selected from a total of ninety-eight involving differing materials and different methods of treatment.

THE conception of concrete held by the majority of engineers and users is that it is a mixture of portland cement and inert aggregate which on reaction with water becomes a dense and hard mass, expanding and contracting with changes of temperature in about the same ratio as steel but otherwise unalterable in volume and permanent if properly made and not exposed to any action other than that of water and air. It is now definitely established that concrete shrinks whenever it becomes dry and expands whenever it becomes wet, irrespective of its age when tested, and that, furthermore, these changes in volume are much larger, more rapid, and more frequent than those due to temperature changes.[2] These changes when concrete is alternately wet and dried may amount to as much as the equivalent of a temperature change of 200° F.

Reactions of Portland Cement and Water

The process of hardening portland cement is as follows: Each grain is surrounded by liquid water which attacks the surface of the grain, decomposes it, and forms hydrated compounds—silicates, aluminates, and hydrated lime—some of which are amorphous and some crystalline. The amorphous bodies are colloids, which swell in contact with water and shrink when water is abstracted.

Concrete retains these properties of a colloid to an undiminished extent for at least twenty years. The reaction between the grains of cement and the water is so slow that it requires months or years for its completion. In a rich cement mortar the reaction stops only because the colloid has swollen to such an extent that no more water can force its way in to react with the unchanged kernels of cement. The pressure of this swollen colloid is enough to cause an increase in length of 0.15 per cent in bars of neat cement, and of expansion one-half as great in mortars of 1:3 composition. This expansion in 1:3 mortars is equivalent to a compressive stress of 1500 lbs. per sq. in. Concrete that is properly made in a fairly rich mixture and thoroughly hardened under water will not permit any water to pass through it, because the swollen colloid closes all the capillary pores. Such a concrete when thoroughly swollen will contain no liquid water, but only colloid water, or water of crystallization. If one surface of this concrete is in contact with water and the other in contact with freely circulating air, as frequently happens in a dam or reservoir, the concrete will appear absolutely tight. No water will seep through it. If, however, the air should be relatively dead, as in a cellar or basement, it would be found that the humidity of the air in the cellar was very high. Moisture would evaporate from the apparently dry surface of the concrete and be replaced by

moisture diffusing through the colloid of the concrete. If the water were drained from the reservoir, in the case cited above, the concrete wall would lose water by evaporation from the colloid and shrink so that after a few weeks it would be porous. If the concrete wall were several feet in thickness this phenomenon might not be noticed, but in a cellar wall about 12 in. thick it might be very apparent. If water should again be brought in contact with one side of the wall, the pores in the concrete would rapidly fill with water, owing to capillary action, and the inside of the wall would appear damp. It might even allow water to percolate through it for a few days until the dehydrated colloid had again absorbed water and become swollen so as to shut out further ingress of water. It has been the tendency of engineers to test concrete when it is wet and most of the results that have shown concrete to be waterproof have been made on concrete with its colloid fully swollen.

Water Absorption by Mortars with No Waterproofing Agent

The behavior of a block of 1:3 mortar without waterproofings is shown in Fig. 1. This block, 160 B, was made from 1 volume of Universal cement, 3 volumes of sand, and 1 volume of water. It was mixed by hand and placed in a metallic mold 4 in. square and 6 in. deep. After 12 days in the mold it was removed and allowed to dry 21 days in the air, during which period it lost 3.87 per cent in weight. It was then placed in a box containing a layer of damp sand with a constant water level $1/4$ in. below the surface of the sand. The

Fig. 1

block was placed on end on the surface of the sand and the box was covered with a cloth so that evaporation was largely restricted. During 13 days on damp sand the block gained 8.1 per cent in weight. Detail 1 in the lower part of Fig. 1 indicates the rise of moisture in the block. After 9 hrs. moisture had risen 4 in. out of the total 6, and at the end of 24 hrs. the top of the block was moist. At this time the weight was 0.54 per cent less than the initial weight of the block when it was removed from the form. The capillaries were not, however, completely filled with water, for the block continued to gain weight at a decreasing rate, until after 13 days its weight had increased to +3.75 per cent.

[1] Presented before the 15th Annual Meeting of the American Institute of Chemical Engineers, Richmond, Va., December 6 to 9, 1922.

[2] White, *Proc. Am. Soc. Testing Materials*, **14** (1914), 203; "Materials of Construction," *Trans. Inter. Eng. Congr.*, **1915**, 242.
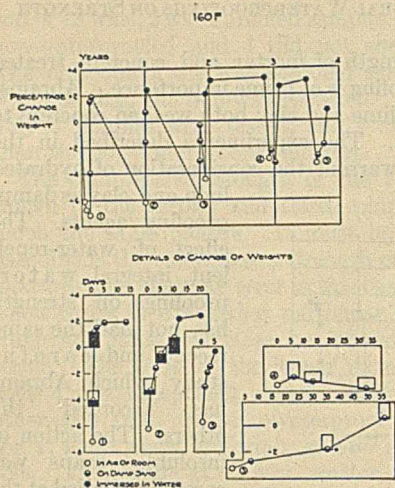
Fig. 2
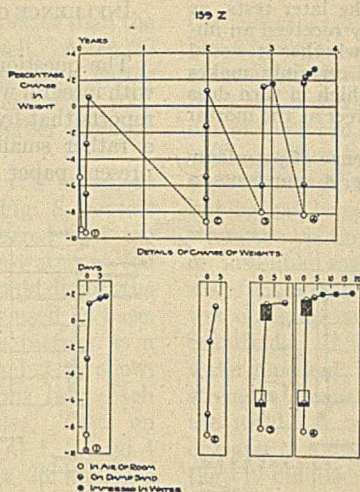
Fig. 3
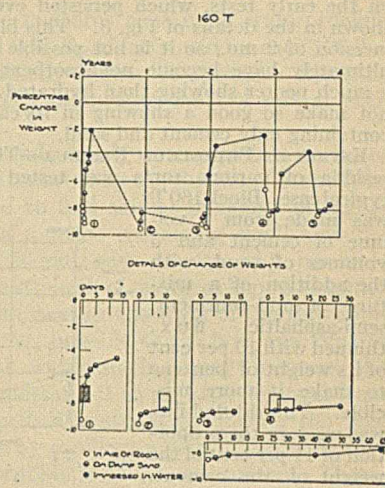
Fig. 4

It was then immersed in water and in 10 days increased only 0.5 per cent more. It is thus apparent that a cement mortar, even as rich as 1:3, which is allowed to dry out when removed from the forms, is highly absorptive.

This block was then allowed to stand in the air of the laboratory for 9 mo., when it was again placed on damp sand. Its dry weight was practically the same as in the previous year, but it only absorbed a little over one-half as much water and the moisture only climbed $4\frac{1}{2}$ in. in 10 days, whereas in the preceding year it had climbed 6 in. in one day. On immersion in water for 10 days the weight increased to an even slightly higher figure than it had reached in the preceding year.

This block was then again dried for 10 mo. in the air, when it returned to nearly the same dry weight which it had shown originally. When placed on damp sand it absorbed moisture at substantially the same rate as before.

It was then determined to try the effect of a longer immersion in water. During this immersion its weight increased slowly through hydration of cement that had not been previously attacked. When dried 25 days in the air after 11 mos. immersion in water, it retained almost as much moisture as it had held when it was first removed from the mold. This is a clear indication that the colloid had developed by the 11-mo. immersion in water. When this block was now placed on damp sand, the moisture climbed only $\frac{3}{4}$ in. in 6 days. The block was then laid on its side instead of its base, but the water climbed only $\frac{1}{2}$ in. The block was again immersed in water for 5 mo. and then kept in air for 45 days, when it was again placed on damp sand. The moisture only rose $\frac{1}{2}$ in. in 40 days and the change in weight was almost negligible. It was evident that for some reason the moisture was no longer rising in the block. The question then arose as to whether the resistance to the absorption of water was in the skin of the block or was uniform throughout the entire mass. To determine this point, about $\frac{1}{8}$ in. was rasped off the bottom of the block and it was again placed on damp sand. Its behavior is shown in Detail 5 of Fig. 1. The block now absorbed moisture slowly until its total increase in weight was greater than it had been on its first test when the water had reached the top of the block. Notwithstanding this fact, the surface of the block remained entirely dry except for the damp line about $\frac{1}{4}$ in. wide at the bottom of the block. The conclusion is that the nonabsorptive properties resided largely in the skin of the block. The earlier test had shown that the side of the block was not more permeable than the base of the block so that it could not

have been due to any accidental contamination with oil or other water-repellent material on the base of the block.

The explanation may be easily found from consideration of the theory. One of the products formed by reaction of portland cement and water is hydrated lime, which is relatively soluble in water. When the block with its pores filled with water is allowed to dry in the air, it is not pure water but a saturated solution of calcium hydroxide that travels to the surface of the block. This becomes converted to calcium carbonate through reaction with the carbon dioxide of the air and the calcium carbonate thus deposited seals the capillary openings just as on a larger scale it stops up the tubes in a steam boiler. The surface of fairly rich concrete which is alternately wet and dried will therefore waterproof itself in time through deposition of calcium carbonate. The waterproofing will, however, reside mainly in the skin, and the center of the mass will still have capillary openings. These capillary openings will be smaller in old concrete which has had long immersion in water, because they have become partly filled with colloid. Dry concrete will, however, always have capillary canals.

EFFECT OF WATERPROOFING MATERIALS

HYDRATED LIME—The effect of hydrated lime is shown in Fig. 2, which is a study of a block made from 1 volume cement and 3 volumes of sand, to which was added 0.1 volume of high, calcium hydrated lime for each volume of cement. This block, 160 F, was kept two days in a metal mold, then dried in the air of the laboratory for 38 days and placed on damp sand as before. The absorption of water was about three times as rapid as in the case of the mortar to which no lime had been added. After 10 mo. in air the test was repeated and the absorption found to be distinctly slower than at first. After the block had stood 11 mo. in water and had been afterwards dried for 28 days in air, a repetition of the absorption test showed very little increase in weight. (Detail 4 of Fig. 2.) When the block was placed on its side instead it actually lost weight because of the better conditions for evaporation. After another period of 5 mo. in water and subsequent drying, there was very slow absorption. When, however, after 35 days on damp sand the outer skin of the base was rasped off, the weight increased much more rapidly. (Detail 5 of Fig. 2.) The final waterproofing was due largely to deposition of calcium carbonate in the pores of the surface, as in the previous case. The first effects of hydrated lime are distinctly unfavorable from the waterproofing standpoint. Hydrated lime is a water-absorbent colloid and the addition of this material promotes absorption of water until such time as the surface pores become filled with calcium carbonate.

CLAY—The effect of clay is shown in Fig. 3, where the history of Block 159 Z is traced. This was made from 1 volume of cement and 3 volumes of sand, with the addition of a plastic clay to the extent of 15 per cent of the weight of the cement. The clay caused an absorption even more rapid than hydrated lime

on the early tests, which persisted even on the later tests, as shown in the details of Fig. 3. This block only received an immersion of 2 mo., so it is not possible to say whether it would ultimately have become nonabsorbent. Clay certainly makes a much poorer showing than hydrated lime, which in turn does not make so good a showing in its earlier career as the mortar containing only cement and sand.

EFFECT OF PETROLEUM RESIDUA—The influence of petroleum residua of various sorts was tested and Fig. 4 represents a typical case. Block 160 T was made from 1 volume of cement and 3 volumes of sand, with the addition of a mixture of mid-continent, semi-asphaltic flux, thinned with 10 per cent of its weight of benzene to make it more miscible. This diluted flux was used in the proportion of 11 per cent of the weight of the cement. The block was dark in color and had a petroleum odor.

The water absorption on the early tests was distinctly slower than in the cases previously discussed, although the moisture rose to the top of the block on the first test. The second and subsequent tests showed very efficient damp-proofing. Even after the bottom of the block was rasped off on the fifth absorption test, the increase in weight was very small. An objectionable feature was noted in the diffusion of the oil out of the block. After the block had stood for several days on damp sand, the sand would be black from diffused oil for a depth of $1/4$ in. below the block.

EFFECT OF INSOLUBLE SOAPS—The insoluble soaps tested as waterproofing agents were prepared in the laboratory by precipitation, washing, and drying. This had the advantage of the use of a definite product but the disadvantage of the difficulty in mixing it with the water. The soaps were distinctly water-repellent and did not lend themselves as well to incorporation as some of the commercial compounds specially prepared to emulsify readily with the mixing water.

The behavior of calcium oleate as a damp-proofing agent is shown in Fig. 5, which shows the behavior of Block 159 B made from 1 volume cement, 3 volumes of sand, and calcium oleate to the extent of 1 per cent of the weight of the cement. This dry calcium oleate was flocculent and did not emulsify readily. The water-absorption tests showed distinctly less absorption than the blocks that did not contain water-repellent material. This block did not receive any immersion to develop its colloid until the end of the third year, and then it was kept only 30 days in water. After drying it was again tested for water absorption and it increased in weight slowly until, after 7 days, the water reached the top of the block. It was then put into water for a longer time, but unfortunately the test had to be interruped at that point.

The effect of aluminium stearate is shown in Fig. 6. Block 159 F was made, like the others, from a 1:3 mix, with the addition of aluminium stearate to the extent of 1 per cent of the weight of the cement. An attempt was made to emulsify the aluminium stearate with dilute ammonia, but with only partial success. The tests parallel those with calcium oleate shown in Fig. 5, but are in general more favorable, perhaps due to the better emulsification of the aluminium soap.

COMPARISON OF WATER ABSORPTION

A comparison of the behavior of these blocks during their first absorption period is given in Fig. 7, where the rate of water absorption of the air-dried blocks when placed on wet sand is plotted. It will be noted that the three blocks with the insoluble soaps and with petroleum incorporated show roughly only half the absorption of the plain mortar, which in its turn makes a distinctly better showing than the blocks containing hydrated lime or clay.

FIG. 5

FIG. 6

INFLUENCE OF INTEGRAL WATERPROOFINGS ON STRENGTH

The question of strength of mortar and concrete treated with integral waterproofing is of prime importance. Abrams[3] reports that hydrated lime and clay both weaken concrete to a rather small extent. The experiments described in the present paper do not warrant the consideration of hydrated lime and clay as damp-proofing agents. The effect of water-repellent, integral waterproofings on strength has not had the same recent and careful study which Abrams has accorded the others. The action of insoluble soaps was carefully studied at the Bureau of Standards.[4] Both tensile and compressive strengths of mortar of varying richness containing commercial waterproofings, whose chief constituent was an insoluble soap mixed with dry hydrated lime, were included in this report. These investigators drew the conclusion that the strength was not seriously affected by the compounds used. There were seven of these waterproofings containing insoluble soaps and the amount of fatty acid varied from 0.064 to 0.78 per cent of the weight of cement used. It is very difficult to get a clear picture of the effect of these compounds from the long tables given in this paper, and in order to give a visual picture of this effect the results have been plotted in Fig. 8. In this figure the compressive strength of the non-waterproofed specimen has been shown by horizontal lines. The variation of the samples containing waterproofings is shown by rectangles extending above or below these horizontal lines. The waterproofing agents are arranged in increasing order according to their fat-acid content. The figure may be further explained as follows: The first column of Fig. 8 shows the compressive strength of blocks of 1:4 mix kept damp for varying periods. The average compressive strength of the non-waterproofed specimens tested when one week old was 750 lbs. per sq. in. Six of
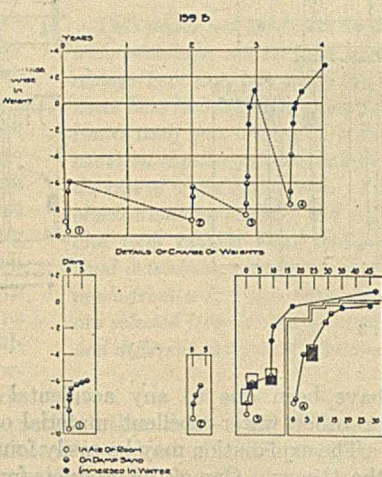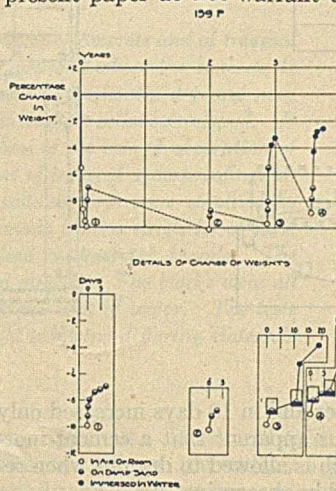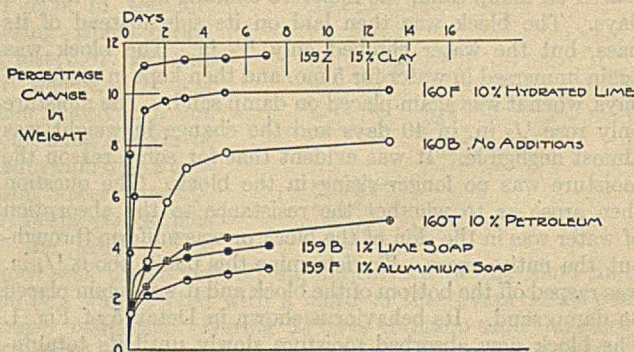
FIG. 7

the seven waterproofed specimens showed a higher compressive strength than the mortar with no additions. The highest figure, for No. 32, was 1096 lbs. A similar picture was presented at the end of 2 wks. and of 4 wks. In testing at the

[3] Proc. Am. Soc. Testing Materials, 20 (1920), II, 149.
[4] Bur. Standards, Tech. Paper 3 (1911).

end of 13 wks., 2 waterproofed samples showed better than the non-waterproofed and 4 did not show so well. After 26 wks. only one of the waterproofed samples showed a better strength than the non-waterproofed. At the end of 52 wks. only 5 samples were tested, and 4 showed higher strength than the non-waterproofed mortars.

The compressive strength of the 1:6 and 1:8 mixes, as shown in the second and third columns of Fig. 8, reveals much the same picture. It must be remembered that the base line is the compressive strength of the non-waterproofed mixtures amd that any error in this base line would distort the whole series in which that particular test was used as base. Judgment must therefore be formed on the picture as a whole. The tests on the leaner mixes 1:6 and 1:8 show, with a few exceptions, rather slight variations from each other and from the non-waterproofed samples. Tests on the 1:4 mix show uniformly greater strength at 1, 2, and 4 wks. The results at 13 wks. scatter, those at 26 wks. are inferior to the non-waterproofed samples, while 4 out of the 5 waterproofed samples tested after 52 wks. were stronger

COMPRESSIVE STRENGTH

FIG. 8

The horizontal line shows the strength of the concrete to which no additions have been made. The rectangles show the differential strength of the specimens containing waterproofings

than those not waterproofed. This considers all the different waterproofings as being of equal merit, which, however, is hardly fair. The mixtures containing waterproofing No. 30 only contained 0.066 lb. of fatty acid for each 100 lbs. of cement. This mixture No. 30 gives inferior results.

On the other hand, the mixtures containing waterproofing No. 32, which contained 0.75 lb. of fatty acid for each 100 lbs. of cement, showed distinctly higher compressive strengths than the non-waterproofed samples of the 1:4 mix at each one of the 6 test periods.

The author has not made nearly as complete a series of tests of strength as those reported by the Bureau of Standards, but he has been puzzled to find similar instances of higher strengths on the part of mortars containing small amounts of insoluble soaps. It is not easy to see why insoluble soaps should increase the strength of mixtures kept constantly wet or damp, as was the case in the tests of the Bureau of Standards. It is, however, possible to see how any type of water-repellent, integral waterproofing may increase the strength of concrete or mortar left in air after removal from the mold. A water-repellant material diminishes the flow of water to a dry surface by capillary action in the same way that it diminishes absorption from a wet surface. Therefore a block of mortar containing a water-repellent material will not dry out as rapidly as one which does not contain such a material. It should, therefore, have a better opportunity to develop its colloid and should show higher strengths, especially at the end of 7 and 28 days in air.

Note on Dispensing Bottle for Concentrated Alkali Solution[1]

By Walter J. Geldard

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A convenient arrangement for dispensing concentrated alkali solution as used in the Kjeldahl nitrogen determination is shown in the accompanying diagram. A stock bottle is equipped with a siphon-pipet, 32 mm. in diameter and 150 mm. long, which has a capacity of 90 to 100 cc. The tubing used is of 6 to 7 mm. inside diameter.

Air pressure from the laboratory line is applied at A. The tube B is closed with a finger until the solution, rising in C and filling D, flows over the bend in the delivery tube F and completes the siphon, when the finger on B is released. The solution also rises in E, and this tube should be made high enough to permit the siphon to be completed without having the tube overflow. The delivery tube F is constructed at such an angle that the solution will run down the neck and side of the flask without mixing excessively with the acid solution in the flask.
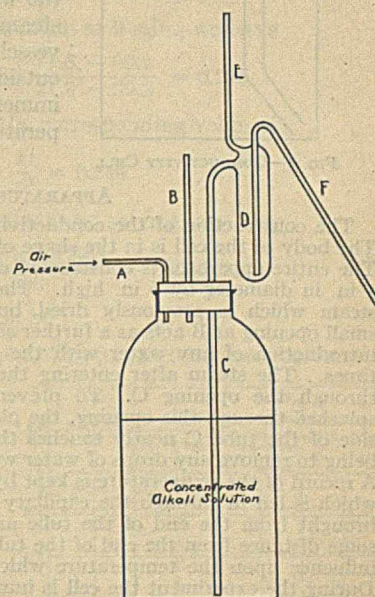
Thermal Properties of Various Pigments and of Rubber[1]

By Ira Williams

RESEARCH LABORATORIES, FIRESTONE TIRE & RUBBER CO., AKRON, OHIO

The thermal conductivity and diffusivity of rubber may be determined by two methods. A method for the determination of the conductivity of pigments is given and the values have been determined for the most common pigments used in rubber compounding. A method is shown by which the thermal conductivity and diffusivity of any rubber compound may be calculated from an analysis of the stock.

WHILE values for the thermal insulating power of rubber compounds are often desired, no adequate table of values is available, nor is it possible to construct a reliable table for such variable material as rubber. Practically, the only table containing values by which the thermal conductivity or diffusivity might be calculated is that published by A. A. Somerville.[2] This table, besides being rather inaccurate, does not present the material in a readily usable form. It was with the idea of obtaining the data necessary for the calculation of thermal conductivities that the following work was undertaken. Two separate methods of determination were used, one of which gave the conductivity directly, while the second gave values for the diffusivity. Either could then be converted into the other through the relation:

$$\text{Diffusivity } k = \frac{\text{conductivity K}}{\text{specific heat} \times \text{specific gravity}}$$
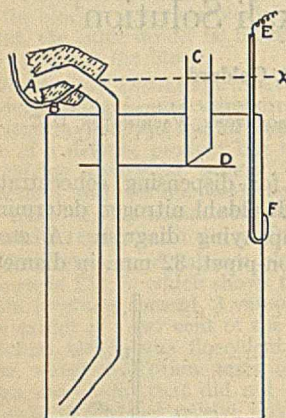
METHOD I

A cell method was used for the direct determination of conductivity of the stock examined. This consisted essentially in covering a closed cylindrical vessel with the material to be studied and measuring the water which collects when steam is passed through the vessel, the temperature of the outside being controlled by immersion in a constant temperature bath.

FIG. 1—CONDUCTIVITY CELL

APPARATUS

The construction of the conductivity cell is shown in Fig. 1. The body of the cell is in the shape of a cylinder with flat ends. The entire apparatus is constructed of thin sheet copper and is 4 in. in diameter by 5 in. high. The pipe A serves to lead in steam which is previously dried, but not superheated. The small opening at B acts as a further safety device to prevent the introduction of any water with the steam, and is open at all times. The steam after entering the cell is allowed to escape through the opening C. To prevent any water from being splashed through this opening, the plate D is introduced. One side of the tube C nearly touches the baffle plate, the purpose being to remove any drops of water which collect on the tube C. A record of the temperature is kept by means of a thermocouple which is led in through the capillary tube E. The junction is brought from the end of the tube and fastened at F, which is some distance from the end of the tube to avoid any disturbing influence upon the temperature which might be caused by E. During the experiment the cell is immersed to the point X in a thermostat.

It is necessary that no water be carried into the cell with the steam. To prevent this, the apparatus shown in Fig. 2 is used. Steam generated at a few ounces pressure is led in at the opening

[1] Presented before the Division of Rubber Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

[2] *Rubber Age*, **9** (1921), 131.

will be deposited on the sides of the chamber and finally blown out through the opening E. The stream used is drawn off through the opening F, which is connected as closely as possible to the opening A in Fig. 1. The entire drying apparatus is constructed of glass and heavily insulated with rubber.

METHOD OF PROCEDURE

The sample to be studied is calendered into a thin uniform sheet which is used to cover the outside of the conductivity cell. The thickness of each piece of material used is measured in several places and an average thickness determined. The ends of the cell and the pipes A, C, and E (Fig. 1) must also be covered. If the stock is freshly prepared and the cell slightly warmed the stock will adhere firmly to the cell. The length of the stock should also be carefully measured before it is applied, and when applied the edges should meet to form a smooth joint, in order to prevent a change in dimension of the stock with the corresponding change in thickness. After the covering has been built up to the desired thickness, the weight of the cell and rubber is taken. This, together with the known weight of the cell, gives the weight of the sample taken. The covered cell is then placed in the thermostat and clamped in such a manner that the level of the water lies at the line X (Fig. 1), and is tilted slightly so that the steam always enters under the water which condenses. The accuracy of the experiment depends largely upon a careful determination of the time-temperature curve covering the first few minutes of the experiment. Therefore, as soon as steam is admitted by opening the stopcock G (Fig. 2), readings should be started and taken at short intervals until a constant temperature is reached. After the experiment has continued for a known time (10 to 20 min.), the cell is removed and weighed to determine the amount of water collected inside.
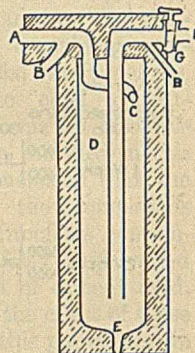
FIG. 2—WATER TRAP

A sample data sheet is as follows:

CONDUCTIVITY STOCK P3, LARGE CELL, No.1   12/7/20

Weight of cell	466.8 g.
Weight of cell + rubber	618.8 g.
Area of cell	583.0 sq. cm.
Specific heat of sample	0.502
Weight of cell + rubber + water	701.8 g.

Thickness of sample:

0.060 in.	0.058 in.	0.055 in.
0.059 in.	0.057 in.	0.063 in.
0.056 in.	0.055 in.	0.053 in.
Average thickness	0.0573 in.	

Number of layers used to cover cell	2
Thickness of cover	0.1146 in. or 0.291 cm.
Time of experiment	20 min.

Temperatures are shown in Fig. 3.

CALCULATION OF WORKING FORMULA FOR CONDUCTIVITY CELL

Steam is condensed inside the cell from two causes—(1) the conduction of heat, and (2) the heat capacity of the material used for constructing the cell and for covering the cell.

Let X = water condensed by the cell in changing from the original to the final temperature,

M$_c$ = the mass of copper,

M_x = the mass of the covering,

T_0 and T_1 = the original and final temperatures, respectively.

Then $X = \dfrac{M_c \times \text{specific heat Cu} \times (T_1 - T_0)}{\text{latent heat of condensation of water}}$, or substituting

in the respective values, $X = \dfrac{M_c \times 0.0931\,(T_1 - T_0)}{537}$.

Let y = water condensed by the material covering the cell. Here the rise in temperature at different parts of the stock is unequal. The inside evidently assumed the temperature of the cell, while the outside assumed the temperature of the bath. If we assume the temperature gradient to be a straight

line, the temperature rise will be $\dfrac{T_1 - T_b}{2}$, where T_b is the final

temperature of the bath. This assumption may be made as long as the covering remains fairly thin, but as the thickness increases, the error becomes correspondingly larger.

Then $y = \dfrac{\text{weight of material} \times \text{specific heat of material}\ \dfrac{T_1 - T_b}{2}}{\text{latent heat of condensation of water}}$;

or, if we represent weight of material by M_x and the specific heat by S,

$$y = \frac{M_x \times S\ \dfrac{T_1 - T_b}{2}}{537}.$$

If W_c = water condensed by conduction, and

W = total water condensed,

then $W_c = W - (X + y)$.

But the coefficient of conductivity $= \dfrac{\text{cal. through 1 sq. cm. in 1 sec.}}{\text{fall in temperature per cm.}}$.

Let A = area of cell, and

t = time in minutes during which heat flows.

Then thermal conductivity $K = \dfrac{\dfrac{537\ W_c}{60 t A}}{\dfrac{T}{l}} = \dfrac{537\ W_c\, l}{60\ t A\ T}$,

where l = thickness of covering (material studied), and

T = average temperature difference between the bath and cell.

This is obtained from the area between the curves repre-

Fig. 3
Temperature Rise of Cell
Stock P3 #1
Area 1047 degree minutes
Minutes

senting temperature of bath against time and temperature of cell against time, by dividing the area so obtained by the length of time over which the experiment extended. If we now substitute the value of W_c in the equation above we have

$K = \dfrac{537\ (W - (x + y))\, l}{60\ t A\ T}$ cal./cu. cm./sec. as the expression

for thermal conductivity when using the present apparatus.

Sample Calculation by First Method

In Fig. 3 the line ACD represents the temperature of the cell while the line AB represents the temperature of the thermostat. The area is 1047 degree minutes and the time of the experiment was 20 min. The average temperature difference attained is then $\dfrac{1047}{20}$, or 52.3° C. This is the value of T.

The water condensed by the cell =

$X = \dfrac{466.8 \times 0.0931 \times (99.2 - 45.5)}{537} = 4.35\ \text{g.}$

The water condensed by cover =

$y = \dfrac{(618.8 - 466.8)\ 0.502\ \left(\dfrac{99.2 - 45.5}{2}\right)}{537} = 3.81\ \text{g.}$

We may now substitute in Formula 1, and

$K = \dfrac{537\,[83 - (4.35 + 3.81)] \times 0.291}{60 \times 20 \times 583 \times 52.3} = 0.000319\ \text{cal./sec./cu. cm.}$

for a difference in temperature of 1° C.

Method II

The second method involves the determination of the diffusivity constant from which conductivity may be calculated. The method follows the work of Williamson and Adams,[3] and consists in measuring the temperature rise at the center of a cylinder when the surface is subjected to a uniform temperature. The stock to be studied is first calendered thin and a uniform cylinder obtained by rolling it to the desired size. Before rolling the sheet into a cylinder a thermocouple was placed at the edge so that it would be rolled into the center of the cylinder. The cylinders measuring $3/4$ to 1 in. in diameter were wrapped in aluminium foil and immersed in boiling water. The temperature was recorded by the use of a potentiometer.

A sample data sheet is as follows:

Stock P3

Time Min.	Temperature ° C.	Temperature Bath ° C.
0	21.3	99.2
5	51.5	99.2
9	77.6	99.2
12	88.2	99.2

Diameter of Cylinder, 2.44 cm.

Specific Heat, 0.502   Specific Gravity, 0.92

Calculations

The calculations are quite simple if we make use of Fig. 4, which is taken from data by Williamson and Adams.

Here Θ = temperature at the center.

Θ_0 = original uniform temperature.

Θ_1 = new surface temperature.

t = time in seconds.

a = radius of cylinder.

k = diffusivity constant.

If we choose the data taken at 9 min., we have

$$\frac{\Theta - \Theta_1}{\Theta_0 - \Theta_1} = \frac{77.6 - 99.2}{21.3 - 99.2} = 0.275$$

From Fig. 4 we find the corresponding value of

$$\frac{kt}{a^2} = 0.244$$

Substituting in the values and solving, we have

$$k = \frac{0.244 \times (1.22)^2}{540} = 0.000674$$

and the conductivity will be

$K = 0.502 \times 0.92 \times 0.000674 = 0.000310$ cal./sec./cu. cm./° C.

The corresponding value found by the cell method was 0.000317. A single determination by the cylinder method may vary more than that above if different values of Θ are used in the calculation. For

Fig. 4
Temperature Relation
at Center of Infinite
Cylinder
kt/a^2

this reason intermediate values of Θ were chosen so that the corresponding value of kt/a^2 would fall on the part of Fig. 4 that is most easily read.
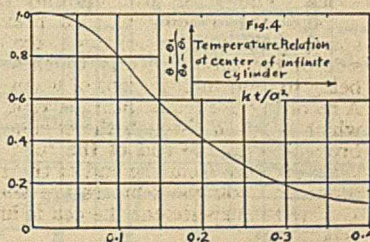
[3] *Phys. Rev.*, **14** (1919), 99.

Conductivity-Cell Method

(Temperature Range, 45° to 100° C.)

Stock	Specific Heat of Stock	Wt. of Cell[1] G.	Wt. of Cell and Rubber G.	Wt. of Cell, Rubber, and Water G.	Thickness of Rubber Cm.	Time Min.	Av. Temp. Rise Degrees	K × 10³
P35	0.251	468.5	660.6	928.4	0.166	20	50.4	0.658
			660.7	953.8			54.8	0.663
			660.7	872.8			52.0	0.668
P3	0.502	466.8	618.8	701.8	0.291	20	52.3	0.319
			619.1	701.4			51.9	0.319
			619.0	707.1			55.0	0.322
			619.0	705.1			54.0	0.321
P36	0.385	464.0	572.3	715.0	0.153	15	53.3	0.399
			572.2	717.2			53.7	0.403
			572.3	719.1			54.6	0.402
P37	0.190	463.9	697.8	915.0	0.153	10	50.8	0.968
			698.2	925.6			53.0	0.976
E1	0.383	464.0	555.2	656.0	0.295	10	52.2	0.396
			555.4	658.3			51.4	0.408
			555.2	654.8			51.8	0.394
			555.3	655.8				0.397
P5	0.422	466.7	567.5	647.1	0.326	10	51.6	0.368
		464.0	568.1	681.3		15	51.4	0.360
		466.7	667.6	759.5		20	56.7	0.364
		464.0	568.5	646.6		10	51.6	0.361
Frictioned cord fabric	0.418	179.3	239.8	282.9	0.280		59.9	0.503
			239.8	281.9			57.6	0.510
			239.9	282.7			58.9	0.507
P51, cured 45 min. at 29° C.	0.411	462.1	590.0	673.7	0.203		52.8	0.301
			594.2	672.8			51.7	0.309
P51	0.411	463.7	535.8	662.4	0.123		52.2	0.297
			536.5	664.1			52.2	0.299
P53	0.378	462.3	567.9	707.0	0.149	15	52.8	0.381
			568.0	710.5			52.8	0.390
			568.0	712.2			52.8	0.388
P54	0.431	462.2	554.0	680.5	0.142		52.0	0.334
			554.0	683.0			52.3	0.340
P55	0.241	462.3	619.6	790.8	0.138		50.7	0.462
			620.0	793.5			51.2	0.462
P56	0.324	462.0	575.1	718.2	0.140		50.8	0.387
			575.2	717.4			50.8	0.386

[1] Area of the cell is 583 sq. cm. in all cases except that of frictional cord fabric, where the area of the cell is 220.3 sq. cm.

Conductivity-Cylinder Method

Stock	Specific Heat	Specific Gravity	Temp. Bath °C.	Diameter Cylinder Cm.	Time Min.	Temp. Center Cylinder °C.	K × 10³
P3	0.502	0.92	99.2	2.440	0	21.3	....
					5	51.5	0.316
					9	77.6	0.310
					12	88.2	0.306
E1	0.383	1.170	99.2	2.080	0	22.3	....
					3	56.8	0.407
					4	68.8	0.397
P35	0.251	2.06	99.2	1.903	0	24.6	....
					2	60.6	0.640
P51	0.411	1.082	99.1	1.800	0	26.6	....
					2	41.1	0.294
					3	56.2	0.293
P51	0.411	1.082	99.1	1.680	0	23.4	....
					2	46.1	0.314

Should the conductivity of a stock be an additive property, as the filler is varied we should obtain a curve of volume per cent plotted against conductivity, which is a straight line between the value for the conductivity of rubber and the value for the pigment used. Since the values for the different pigments are not known, we must obtain the curve by varying the amount of filler in the compound. Once the curves are established as straight lines, the values for the conductivity of the pigment may be obtained by extrapolation. That the curves assume straight lines is shown by Fig. 5.

Fig. 5. Thermal Conductivity of rubber pigment mixtures.
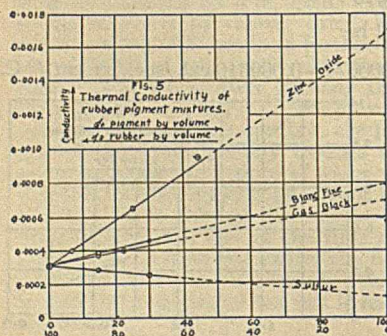
In the following table the values for the conductivity of the different pigments were obtained by extrapolation. The values for the specific heat were taken from the Landolt and Börnstein tables, with the exception of the specific heat of rubber and gas black, which was determined in this laboratory.

Pigment	Specific Gravity	Specific Heat	Diffusivity 45°–100° C.	Conductivity 45°–100° C.	Methods of Determination
Zinc oxide	5.50	0.125	0.00241	0.00166	Cylinder and cell
Sulfur	2.00	0.175	0.00034	0.00012	
Whiting	2.68	0.201	0.00156	0.00084	
Litharge	9.25	0.052	0.00106	0.00051	
Lithopone	3.95	0.115	0.00207	0.00094	
Talc	2.70	0.209	0.00116	0.00058	Cylinder
Antimony sulfide[1]	3.20	0.085	0.00077	0.00021	
Red oxide	4.70	0.160	0.00175	0.00132	
Gas black	2.00	0.204	0.00164	0.00067	
Blanc fixe	4.35	0.114	0.00157	0.00078	Cylinder and cell
Dixie clay	2.60	0.200	0.00112	0.00058	
Magnesium carbonate	3.00	0.303	0.00114	0.00103	Cylinder
Rubber, smoked sheet, pale crepe, etc., including cured rubber	0.92	0.502	0.00069	0.00032	Cylinder and cell
Cord fabric[2] (approximate)	1.50	0.324	0.00168	0.00082	Cell

[1] Contained 15.6 per cent free sulfur.
[2] Value calculated from determinations made on frictioned fabric.

Since thermal conductivity is an additive property and depends upon the volume per cent, the calculation of the value of the conductivity constant is extremely simple. It is only necessary to take the sum of the volume per cent of each material times its conductivity. Let us illustrate with the compound containing smoked sheet, zinc oxide, and gas black. Multiply each per cent (expressed as hundredths) by the conductivity of the corresponding pigment, and take the sum as follows:

PIGMENT	Volume Per cent	Conductivity	Conductivity × Volume
Smoked sheet	70	0.00032	0.000224
Zinc oxide	15	0.00166	0.000249
Gas black	15	0.00067	0.000100
TOTAL			0.000573

The total is the conductivity coefficient in calories per cubic centimeter per second.

An actual determination of this stock (P50) by the cell method gives the value 0.000572, which is even closer agreement than can be expected in most cases.

The diffusivity cannot be calculated in this manner, but must be found by the relation given before, that $k = \dfrac{K}{\text{specific heat} \times \text{sp. gr.}}$. Taking values from the table above, the specific heat of the compound is found as follows:

PIGMENT	Per cent by Weight	Specific Heat	
Smoked sheet	0.365	× 0.502	= 0.183
Zinc oxide	0.465	× 0.125	= 0.058
Gas black	0.17	× 0.204	= 0.035
TOTAL			0.276

The specific heat is then 0.276 cal. per g. per ° C.

The gravity is found by calculation to be 1.76 and by substitution in the formula, the diffusivity constant

$$k = \frac{0.000573}{0.276 \times 1.76} = 0.00118$$

As an example of the agreement which may be attained

between different determinations, tables of compounds and experimental data are included.

No.	COMPOUNDS PIGMENT	Per cent by Weight
P3	Smoked sheet	100.0
P5	Smoked sheet	73.5
	Gas black	26.5
P35	Smoked sheet	33.5
	Zinc oxide	66.5
P36	Smoked sheet	69.0
	Zinc oxide	31.0
P37	Smoked sheet	17.3
	Zinc oxide	82.7
P51	Smoked sheet	72.3
	Sulfur	27.7
P52	Smoked sheet	51.7
	Sulfur	48.3
P53	Smoked sheet	58.6
	Dixie clay	41.4
P54	Smoked sheet	76.1
	Dixie clay	23.9
P55	Smoked sheet	33.0
	Blanc fixe	67.0
P56	Smoked sheet	54.4
	Blanc fixe	45.6
E1	Smoked sheet	60.5
	Gas black	39.5

Of the two methods described, the cell method probably gives more accurate figures because difficulty is experienced in obtaining a uniform cylinder with the couple exactly in the center. The cylinder method is, however, much more rapid and the results are generally sufficiently accurate for the purpose at hand.

Hard-Rubber Lined Steel Tanks for Transporting Hydrochloric Acid[1]

By F. C. Zeisberg

E. I. DU PONT DE NEMOURS & CO., INC., WILMINGTON, DEL.

ON May 24, 1920, a meeting of handlers of hydrochloric acid was called by Col. B. W. Dunn, chief inspector of the Bureau of Explosives, to consider specifications for hydrochloric acid tank cars. The necessity for action resulted from the classification, according to the Interstate Commerce Commission Regulations, of hydrochloric acid as a dangerous article, which made the Bureau of Explosives responsible for developing specifications for containers used in its transportation. At this meeting a sub-committee was formed, consisting of A. J. Lüpfert, General Chemical Co.; Otto Rissman, National Zinc Co.; M. M. Neale, American Steel and Wire Co.; J. M. Rowland, Hooker Electrochemical Co.; and Thos. S. Grasselli, Grasselli Chemical Company. This committee held several meetings in 1920, with a view to gathering and correlating the available information on the transportation of hydrochloric acid. At one of these meetings it was decided to have certain companies gather additional information which past experience had not developed.

Since E. I. du Pont de Nemours & Company had already had under consideration the lining of a steel tank with hard rubber, and had carried on considerable correspondence

Note: Several months after the following paper was read, the tank in question was opened for inspection and it was found that several joints in the hard-rubber lining had opened up. The soft-rubber cushion next to the steel was, however, intact, since the tank had shown no sign of leaking. No inspection of the tank had been made since it was first put in service; consequently, it is impossible to tell just when the hard rubber failed.

with the American Hard Rubber Company in regard thereto, it was decided to ask that such a tank be built as speedily as possible and put into actual service. This the du Pont Co., with the coöperation of the American Hard Rubber Co., agreed to do.

Owing to one delay and another, the tank was not actually put into service until the fall of 1921. The first shipment of acid was made from our Paulsboro plant on October 5, 1921. On the first trip the tank shifted endwise on the car, but this was remedied by tightening the holding-down bands and providing two wooden end braces. Since that time the tank
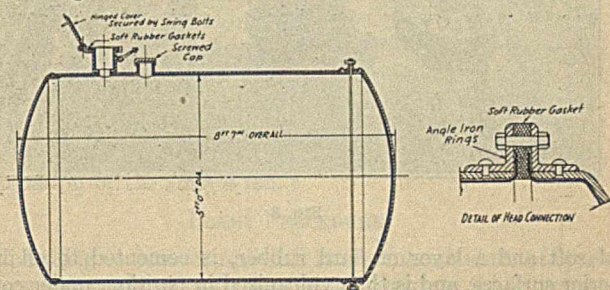
FIG. 1

has been in constant use for interplant shipments between Paulsboro, Newark, and the Dye Works, without any further

repairs except occasional painting, and it seems to be in as good condition to-day as the day it was installed. There is no reason why it should not continue its satisfactory service for a long time.

Fig. 1 shows a cross section of the tank, which has an over-all length of 8 ft. 7 in. and a diameter of 5 ft. 0 in. The
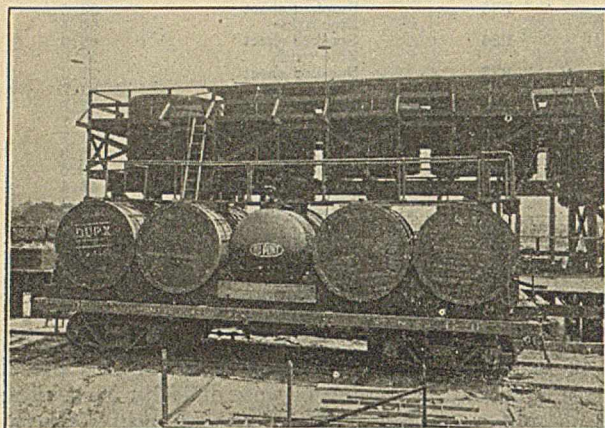
FIG. 2

heads are bumped outward, and the capacity of the tank is about 15,000 lbs. of 20° Bé. hydrochloric acid. It is mounted transversely on a flat car, as may be seen from Fig. 2. Fig. 3 is a close-up of the openings in the tank.

The joint between the head and the body is made tight with a soft-rubber gasket, which has given no sign of leaking. In the case of a larger tank, entrance to which could be gained through a manhole, this gasket would be unnecessary, the lining of the whole tank being continuous. However, during the process of lining one end has to be removed, but after being replaced the joint between it and the tank could be vulcanized, thus eliminating one possible source of leakage.

Since the method of making the lining adhere and of taking care of the differences in the coefficients of expansion of the hard rubber and the steel is of interest, these points will be briefly discussed. A laminated lining, consisting of a layer
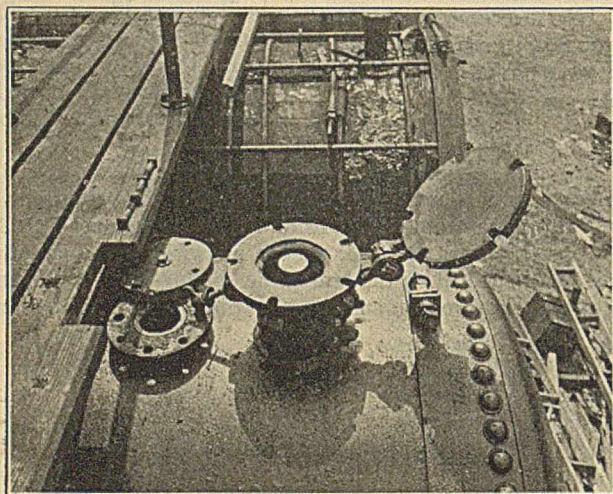
FIG. 3

of soft and a layer of hard rubber, is cemented to all interior surfaces, and is then vulcanized in position, under considerable pressure. The outer layer of hard rubber then comes in contact with the liquid to be handled, while the under layer of live, soft rubber, so firmly bonded to it and to the tank that

it is practically impossible to pull it off, exerts a cushioning effect between the two harder layers. This cushion not only allows for differences in the rate of expansion of the two hard layers, but protects the inner lining in case the outer one is subjected to a blow. In the extreme event of the inner lining being broken as the result of an extraordinary shock, such as might be experienced in a train wreck, the soft-rubber backing will still hold, even if the tank is dented, allowing the acid to be drawn off at leisure without damage to the steel of the tank or car.

This experimental tank was built as simply as possible and is emptied with a soft-rubber siphon. There would be no difficulty in providing a tank with a permanent hard-rubber standpipe, for emptying with compressed air, provided the steel tank was designed to stand the necessary pressure. This tank also, while designed primarily for hydrochloric acid, can be used with any other liquid which does not attack hard rubber, such as acetic acid, citric acid solution, caustics, etc. Moreover, because of the nonabsorptive properties of the lining, a single tank can be used for a number of different materials, as it is very easily cleaned by simply flushing out with water.

At present it is impossible to give even approximate cost figures, though if such a tank is adopted as the standard shipping container for hydrochloric acid, and specifications are drawn up for it, it should not be difficult to arrive at a cost figure shortly.

Our present feeling is that, if continued service with this tank proves as satisfactory as our experience to date, there is little doubt but that the du Pont Company will ultimately go to this type of construction entirely.

The Detection of Salt in Stock Feeds[1]

By H. E. Gensler

BUREAU OF CHEMISTRY, PENNSYLVANIA DEPARTMENT OF AGRICULTURE, HARRISBURG, PA.

In the microscopical examination of stock feeds difficulty is often experienced in finding or identifying actual crystals of salt when salt is claimed to be one of the ingredients. Various modifications of the silver nitrate test may be applied, but, except under certain conditions, such tests will only indicate the general presence of chlorides usually present in most feeds, but will not conclusively show the presence of common salt itself. For example, a molasses feed will give a free test for chlorides, although salt as such may not be present.

After studying the problem, a simple and accurate procedure was devised which required less than a minute to perform: Transfer 2 cc. of a 5 per cent solution of silver nitrate to a small test tube of 1-cm. internal diameter. Carefully add to this liquid an equal volume of the feed, which has previously been ground to pass a millimeter sieve, so that most of the sample floats or remains above the liquid. Upon gradually inclining the tube, the liquid is absorbed and white patches of silver chloride appear wherever the minutest crystal of salt may lie or be in contact with the side of the test tube. These patches may easily be observed with a lens or even with the naked eye.

A deposit of diatomaceous earth in Calvert County, Maryland, has been opened and the product is being refined by the Dashiell Mining & Refining Company. It is stated that the deposit is pure white and free from foreign matter, and that tests have been made which indicate that brick made from this earth possess high insulating qualities.

Potash from Kelp. VII—The Manufacture of Potash Salts[1,2]

By J. W. Turrentine, H. G. Tanner, and P. S. Shoaff

Experimental Kelp-Potash Plant, Bureau of Soils, Summerland, Calif.

POTASH SALTS, as a kelp product, followed the sequence in this plant of dry kelp, kelp charcoal, and kelp ash, each marketed as a potash carrier, and each produced as a stage in the development of the technic of processing kelp. The preparation of the crude or refined salt had to await the solution of the practicable leaching of the potash from the kelp.

It was determined that this could be accomplished most satisfactorily—m o s t nearly completely, with a brine of the greatest concentration,[3] and in the purest state—if the kelp were first reduced to charcoal.

As the manufacture of potash salts from kelp involves the separation of those salts from the other saline constituents of kelp, the original saline constituents are shown and the changes which they undergo in processing are outlined.

The methods devised and employed for the crystallization of potassium chloride are described as consisting essentially of an alternate evaporation to the point of saturation with respect to potassium chloride, and cooling in a vacuum crystallizer for the precipitation of that salt. The main impurity, sodium chloride, is eliminated through hot crystallization on evaporation. The details of construction of the apparatus and the methods of operation are described.

The advantages of vacuum crystallization are such that a discussion of that method is deemed warranted.

Kelp-potash brines, while relatively pure, contain saline materials, the elimination of which is desirable. The manner in which the rectification of the brines is accomplished is mentioned.

Composition of Kelp Brines

Table I shows the composition of a typical sample of unrectified kelp brine as developed by the countercurrent lixiviation of kelp charcoal. The combinations are conventional, although the ions present may be K, Na, Ca, Mg, Fe, NH_4, Cl, I, SO_4, SO_3, S_2O_3, CN, CNO, CNS, S, CO_3, and OH.

Table I—Analysis of Kelp-Potash Brine

	G./100 Cc. Soln.
KCl	25.80
NaCl	6.40
Na_2SO_4	2.60
Na_2CO_3	0.10
NaI	0.11
CaO	0.15
MgO	0.35
Other solids, by difference	0.85
Total	35.36

Note: All sulfur here has been calculated to sodium sulfate. The present analysis shows an occurrence of both calcium and carbonate, while others may show either one or the other absent. Magnesium is generally present, but on heating is precipitated as the hydrated oxide.

It is not to be expected that the composition of kelp brines is constant. There is a seasonal variation in the composition of kelp itself, likewise, in the quantity of calcareous organisms which inhabit its surface, and any pronounced variation in the temperature or time of treatment of the kelp in its processing at high temperature may be expected to result in a variation in the amounts of the compounds formed by heating.

This analysis shows that the components requiring consideration from the manufacturer's point of view are principally the potassium, sodium, chloride, iodide, and sulfate ions, inasmuch as these constitute 96 per cent of the total solids. The others require attention only in case their concentration is largely increased through evaporation. Some eliminate themselves through voluntary precipitation. Where iodine is to be recovered, most of the others are removed as a preliminary operation to the liberation of iodine.

[1] Received August 1, 1922.

[2] Parts I to VI, This Journal, 11 (1919), 864; 12 (1920), 682, 786; 13 (1921), 605; 14 (1922), 19, 441.

[3] Turrentine and Shoaff, *Ibid.*, 13 (1921), 605.

brine saturated while hot with these two salts precipitates only potassium chloride on cooling; if saturated while cold, it precipitates only sodium chloride on evaporation—to the point, of course, where it becomes saturated again with the potassium chloride. This simple principle has been made the basis of the process devised for the manufacture of high-grade potassium chloride from kelp brines.

The equilibria on which this process is based being upset by the presence of other ions in considerable concentrations, their elimination is necessary. The principal impurity is the sulfate ion, which is precipitated by calcium chloride. Sufficient to effect this precipitation may be produced as a by-product of iodine manufacture, as a part of the operating cycle. Other anions which form insoluble salts with calcium are likewise precipitated, and the naturally alkaline nature of the brine causes the elimination of the magnesium, iron, and ammonia.

In the manufacture of iodine the oxidation method is employed. The mother liquors containing the accumulation of iodide likewise contain the accumulation of soluble impurities. The anions containing sulfur, except the sulfate ion, are oxidizable by the reagents usually employed to oxidize the iodide. Their elimination, accordingly, is desirable. For this purpose the mother liquors are acidified and heated to volatilize some of the objectionable ingredients and decompose others—a preliminary operation to the liberation of iodine.

Calcium hypochlorite is an acceptable oxidizing agent and is added together with hydrochloric acid, and the iodine steam-distilled. The resulting brine is still a concentrated solution of potassium chloride, and contains a large proportion of calcium chloride. Its potassium content would warrant its conservation, and its calcium chloride content makes it a convenient carrier for the addition of that amendment. Thus, unrecovered potassium and iodine are returned to the system together with calcium chloride to effect the elimination of the sulfate ion.

Rectification of Brine

The problem of the crystallization of pure potassium chloride from kelp brines is essentially that of the separation of potassium and sodium chlorides and this is reduced to its simplest terms when only the chlorides are dealt with. The wide differential existing between their respective temperature coefficients of solubility permits their easy separation by alternate evaporation and cooling—the hot-cold process. A

Plant Procedure

The thing to be accomplished in the manufacture of crystalline potassium chloride from potash brine is the evaporation of rectified brine to approximately the point of saturation with respect to potassium chloride and its transference to a crystallizer where it is made to boil and give up its heat and
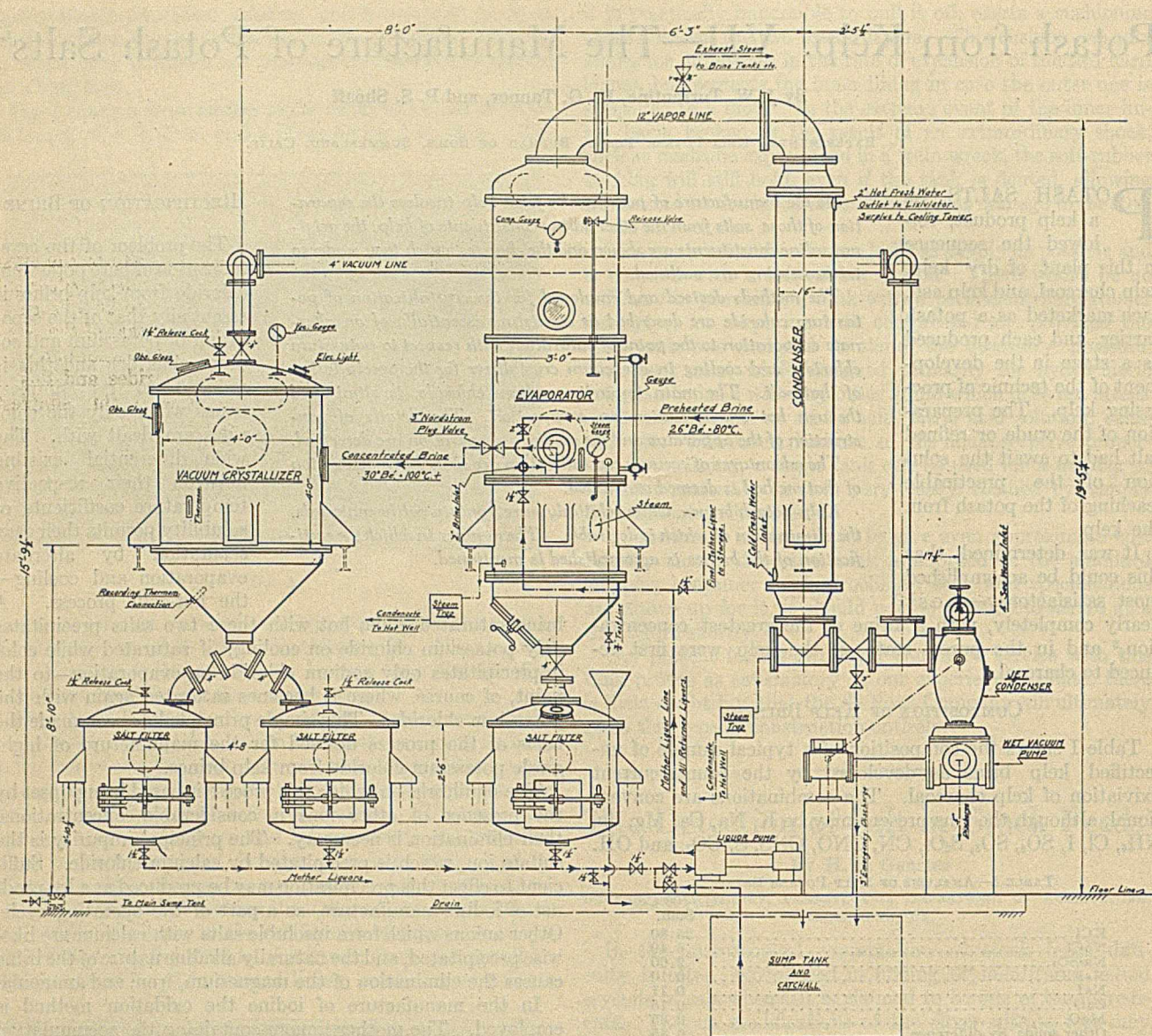
FIG. 1—EVAPORATING AND CRYSTALLIZING APPARATUS

simultaneously deposit its potassium chloride. Thereupon it is returned to the evaporator together with a fresh portion of brine to restore the original volume, and the cycle is repeated. When the brine through evaporation reaches saturation with respect to sodium chloride, that salt is deposited as long as evaporation continues. The greater part of the evaporation taking place in the evaporator, most of the sodium chloride is deposited there; but, inasmuch as cooling is effected in the crystallizer by boiling (evaporation), a small but corresponding amount of salt is deposited there. Thus, potassium chloride is deposited in the crystallizer and sodium chloride in the evaporator, while the brine is alternately cooled and evaporated. The cycle is repeated until the concentration of iodide justifies processing for the recovery of iodine.

APPARATUS

The apparatus for the separation and recovery of potassium and sodium chlorides consists essentially of a vertical crystallizing evaporator with a salt filter connected to the bottom, and to the top a vapor line leading to a surface condenser; a vacuum crystallizer with two salt filters connected

to the bottom and to the top a vacuum line running to a jet condenser and wet vacuum pump.

Iron, particularly cast iron, is a desirable material of construction where there is exposure to the action of the kelp-potash brines; the latter being neutral or slightly alkaline and containing reducing substances, there is practically no corrosion in the absence of air and electrolytic couples. Copper or copper alloys are not durable, principally on account of the ammonium salts present, and should not be used. The use of all-iron gate valves and the self-lubricating Nordstrom plug valves is particularly advantageous.

APPLICATION

The apparatus was designed for continuous evaporation and crystallization by circulating the brine through the system. The brine was to be led into the crystallizer in a continuous stream and at such a rate as to keep the solution therein boiling, the level of the brine in the evaporator to be maintained through the addition of fresh portions of brine in a continuous stream from the preheater. As the brine was to be drawn off from both the evaporator and crystallizer at a point beneath the salt filters, it was to be

freed from the crystals forming in each and a continuous separation of potassium and sodium chlorides thus effected. However, less careful regulation was required, and it was found to be more convenient to employ the intermittent method, and that manner of operation was adopted for the time being.

To start, the evaporator is filled with 900 liters of brine, and this volume is maintained until, through evaporation, the density reaches 30° Bé. at the temperature obtaining. A portion of about 575 liters is then transferred to the crystallizer. This transfer can be made by gravity, but is generally facilitated and the time required greatly shortened by maintaining about 15 in. of vacuum in the crystallizer, accomplished by partially opening the air-release valve on the crystallizer. With the transfer effected, the vacuum is raised to about 28 in. and so maintained for 15 min., the time required for cooling the mass from the initial temperature of 106° C., at which it leaves the evaporator, to 60° C., at which it is returned. About 53 liters of water are evaporated to effect this cooling. The time required is 15 min., 85 per cent of the cooling taking place in the first 7 min., as illustrated by Fig. 2. Immediately on discharging the evaporator a fresh quantity of brine of equal volume is added from the preheater, and the density is raised to 30° Bé. by the time the crystallizer is ready to be discharged. To discharge, the valve connecting the crystallizer to the salt filter beneath is opened, and the entire charge of crystalline salts permitted to flow into it by gravity. There the crystals settle upon the perforated plate in the bottom. A second charge from the evaporator is now transferred to the crystallizer, as before, and the cooled brine from the salt filter, now freed by filtration from its crystals, is pumped to the preheater, and thence it flows back to the evaporator. This cycle is repeated until the salt filters are filled with the crystalline product, whereupon they are discharged. Two filters on the crystallizer are provided, so that one may be filling while the other is being emptied.
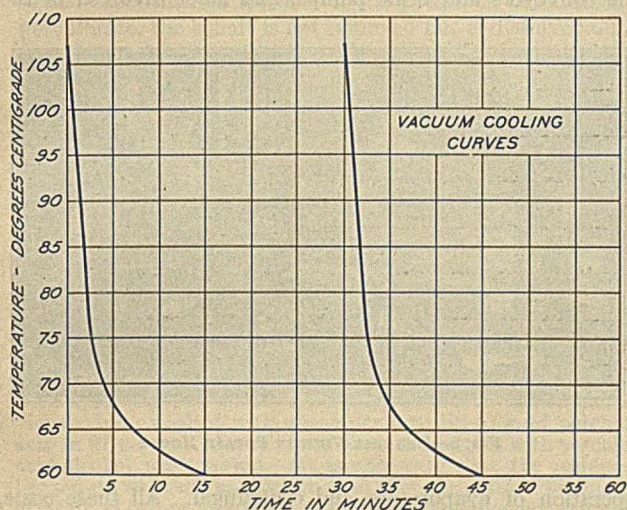
FIG. 2

The potash salts are washed on a centrifugal with small volumes of cold, concentrated brine to remove mother liquor carrying iodine, and are then delivered into a rotary, cylindrical, countercurrent, hot-air drier, flowing thence into sacks.

For the manufacture of a fertilizer grade of potash salts and where no effort is made to separate potassium and sodium salts, the saturated brine is transferred from the evaporator to the crystallizer from the body of the evaporator itself, instead of from the salt filter beneath, with the crystals of sodium chloride still in suspension, and the two salts are

collected together in the salt filter of the crystallizer. This somewhat simplifies the procedure to be observed and at the same time yields a product containing 80 per cent potassium chloride.

DISCUSSION

The results obtained with the apparatus and procedure described above are essentially satisfactory, although experience has pointed out improvements that can be introduced.

EVAPORATION—The sodium chloride obtained from the salt filter of the evaporator contains potassium chloride in proportions varying with the skill of operation. In this instance too much is left to skill of operation, and results are correspondingly uncertain. Evaporating beyond the saturation point with respect to potassium chloride precipitates that salt with the sodium chloride. Any cooling of the brine in the salt filter of the evaporator gives the same result. To prevent the latter, since complete insulation is hard to attain, steam-jacketing is advantageous. But since potash mother liquors must be washed from the sodium chloride, any crystalline potash may be simultaneously removed.

PREHEATING—Better utilization can be made of the steam generated in the evaporator than is here described. It would be advantageous to operate a second effect under vacuum, using this both as a preheater and to effect some evaporation—though on account of the high concentration of the brine delivered by the lixiviator, very little work is required even of the present evaporator. Even with a single effect, as here operated, a satisfactory utilization is possible if the evaporator is built so as to withstand several pounds internal pressure, sufficient to facilitate the delivery of the steam there generated into such heating coils as may be found advantageous. For example, in a preheater for rectified brine and for brine returned from the crystallizer, for fresh water going to the lixiviator, for heating the lixiviator agitators and the air used in the salt dryer, and for use in other departments—all combined effecting a practically complete utilization of the heat here available. Evaporation under pressure would result in a superheated brine with the advantage that it would make cooling and crystallizing possible over a wider range of temperatures.

VACUUM CRYSTALLIZATION—Vacuum crystallization has been found to be very satisfactory, as it is rapid, utilizes the heat of crystallization, results in additional evaporation, and obviates caking of cooling coils or other cooling surfaces. In a thoroughly insulated system all the heat put into the brine is utilized in the evaporator and crystallizer in the evaporation of water. The cost of operation is low, being only that required to maintain a vacuum. The cooling being effected by boiling, the transfer of heat takes place through a relatively enormous surface film, the cooling surface being represented by the combined surfaces of the innumerable bubbles of water vapor forming throughout the entire volume of brine. The formation of a cake of crystals over cooling surfaces and the consequent prevention of a further heat transfer is, therefore, entirely obviated—an advantage not possessed by any other method of rapid cooling. A comparison of the degree of crystallization by vacuum cooling and cooling by conduction shows an increase of 40 per cent of the former over the latter.

A disadvantage is found in the fact that cooling cannot be carried below the boiling point of the brine under the maximum vacuum practicably obtainable, and that the rate rapidly falls off as this point is approached. However, this in itself is not a
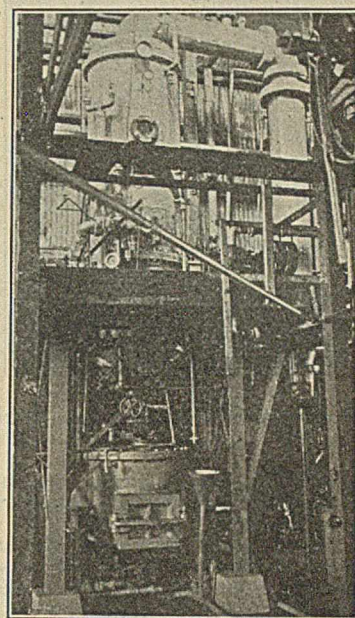
FIG. 3—EVAPORATOR AND PREHEATER

serious matter, since, for example, cooling twice over a range of 10 degrees is equivalent to cooling once over a range of 20 degrees; but it happens that in cooling from 106° to 60° C. that region of temperatures is passed through which some sodium chloride is precipitated together with the potassium chloride, and that at lower temperatures potassium chloride of greater purity is thrown down. Likewise, a brine of lower concentration and consequently higher vapor pressure would be delivered to the evaporator. Additional cooling could be effected in a spray pond, but this would require an additional sequence of operations with compensation of doubtful adequacy.

A difficulty was encountered in maintaining a constant stream of hot brine flowing into the crystallizer while the latter was under full vacuum, owing to the fact that the hot brine boiled and cooled in the delivery pipe and as a consequence precipitated salts which plugged the line. Putting this line in a steam jacket relieved but did not entirely obviate the condition. Therefore, the plan of charging the crystallizer with vacuum reduced to 15 in. was resorted to as a complete though temporary solution of the difficulty. This point requires further investigation and its solution would be of great benefit.

FIG. 4—VACUUM CRYSTALLIZER AND SALT FILTERS

WASHING OF SALTS—In the manufacture of a fertilizer grade of potash salts, the only washing of the salts required is that necessary to remove the mother liquor, and the consideration here is not the further purification of the salts, but the recovery of the iodine which otherwise would be lost. For this washing rectified brine is employed, since, as it is already highly concentrated in potassium chloride, it displaces the mother liquor without redissolving large quantities of salts. The return of the wash waters to the system can be accomplished without upsetting the balance there maintained.

To remove sodium chloride from the potassium chloride for the preparation of chemical grades of potash, the mother liquors must be displaced with wash water containing no sodium chloride. Usually this is sufficient, since the chilling of the salts in contact with their mother liquor does not precipitate sodium chloride as it does the potassium salt. The wide difference in the temperature coefficients of solubility of the two prescribes the use of cold wash water in this case.

The removal of potassium chloride from the sodium salt presents greater difficulties, since the former takes the crystalline form more readily and its removal represents more than the displacement of mother liquor. It may be removed most readily in the salt filter, before any cooling and consequent crystallization of potassium chloride have taken place, as an operation preliminary to discharging. Thus, when the filter is full of sodium chloride and the brine has been pumped out, wet steam should be blown in above the salts and forced through them, thus effectually displacing the mother liquor without permitting it to cool, and supplying some hot water to dissolve any potassium chloride that may be in the solid form. This may be followed, if desired, with hot-water washing on the centrifugals.

The by-product, sodium chloride, may be yielded as the crude salt for local industrial use, or by a simple method it may be purified for table use. Since it is free from deliquescing substances and is finely crystalline, it is especially adaptable to this purpose.

Costs

Since the countercurrent lixiviation of kelp charcoal yields a brine of high concentration in potash, the costs involved in manufacturing potash salts are very moderate. Principal among these is fuel oil for the generation of steam, other items being centrifuging, drying, and sacking—items

involved in the small-scale processing of kelp. Of these the only ones that are at all proportional to output are steam and sacks, and of these the former is transferable to other products and the latter may be eliminated.

The small amount of evaporation required to precipitate potash salts from kelp brines may easily be accomplished with the use of exhaust steam. Thus, the power requirements of a kelp-products plant may be so distributed between a steam plant and electric motors that the former can be made to yield the desired amount of exhaust steam. The cost of the steam, therefore, may be charged to the other departments of the plant and the potash relieved therefrom.

Likewise in the manufacture of kelpchar and iodine, dilute hydrochloric acid is employed in such a quantity that it is highly advantageous to manufacture this acid as a part of the plant procedure. This side operation is further warranted by the fact that if potassium chloride with sulfuric acid is used in its manufacture, the muriate is converted into sulfate—a more acceptable form of fertilizer potash, as expressed in a materially higher price consistently offered for the sulfate and a less localized market. The required amount of sulfuric acid is obtained at a fraction of the price per pound which must be paid for the equivalent of hydrochloric, and less is required for freight, unloading, and storage.

For the manufacture of hydrochloric acid the potash salts as delivered by the centrifugal are sufficiently dry. Thus may the item of cost incident to drying be eliminated.

The potash salts as delivered by the rapid cooling of potash brines, as described above, are finely divided, and therefore require packing in sacks for safe shipment. The coarser particles of sulfate, on the other hand, as delivered by the hydrochloric acid kiln, can be shipped in paper-lined cars, thus obviating the additional expense for sacks, or, if ground before shipment, can be screened to sizes which still can be so shipped.

Thus are eliminated the costs for steam (evaporation), drying, and sacking, leaving only centrifuging, operation of the conveyors and brine pumps, and labor involved in the
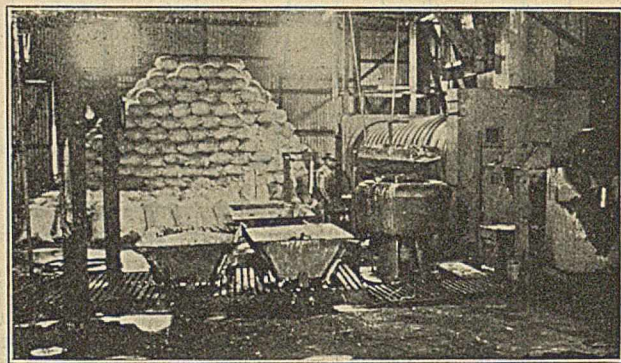
FIG. 5—GENERAL VIEW IN POTASH HOUSE

operation of evaporators and centrifugal. All these costs, instead of being proportional to output, are practically fixed charges and become of less and less importance as output increases. In the large plant, therefore, they are such as to afford potassium salts a highly strategic position as a by-product.

The distribution of costs among by-products is to an extent a matter of bookkeeping, with the limitation that a situation may arise where it has to be decided whether it is profitable to manipulate or to entirely discard an intermediate material from which a by-product is to be obtained. Were such a question to arise in connection with the manufacture of potassium salts from kelp brines, as a by-product of the

kelpchar industry, consideration would have to be given the iodine (contained in the brine with the potash), which alone is able to bear the costs here entered against the potash and still leave a profit on the iodine. Thus, by carrying the method of computing costs a step further, all manufacturing costs charged against potash may be made to disappear.

The great initial purity of kelp brines and the ease with which all impurities are removed from the potash salts resulting from their evaporation make kelp a peculiarly favorable raw material for the manufacture of a chemical grade of potassium chloride. Only slight modifications in the process adopted for the manufacture of potash of fertilizer grade render it of a purity which will satisfy the most exacting demands. The cheapest source of American potash for fertilizer purposes, it may as easily become an equally cheap source of a chemical grade of potash.

Rapid Determination of Potash in Acid-Insoluble Silicates

By Manuel M. Green

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THE DETERMINATION of potash in an acid-insoluble silicate by decomposition of the sample with sulfuric and hydrofluoric acids, and precipitation of the potassium as cobaltinitrite after a basic acetate separation[2] requires about as much time as the regular J. Lawrence Smith method, and leaves much to be desired.

It is, of course, true that, by following a definite procedure using definite amounts of reagents and making certain corrections, there may be developed some methods which are accurate within certain limits. But in cases where potash is not being determined continually, such means are not satisfactory, and this method has therefore been developed.

BASIS OF THE METHOD

The strong dehydrating power of concentrated perchloric acid is well known, as is also the fact that the alkaline earth perchlorates are soluble in alcohol. Furthermore, according to the cobaltinitrite method[3] if the potash is determined as perchlorate, the cobalt is not removed but is dissolved out as perchlorate by the alcohol. This latter fact suggested the possibility of all metals except potassium forming alcohol-soluble perchlorates, and this assumption was made in working out the method.

METHOD

As finally worked out, the method is as follows:

Weigh out into a platinum crucible 0.15 to 0.35 g. of the sample, add 1.5 cc. of 2 *N* perchloric acid, then 3 to 4 cc. of 48 per cent hydrofluoric acid, and evaporate to fumes of perchloric acid. Cool, add water to fill crucible two-thirds full, heat to boiling, filter, and wash thoroughly with hot water, catching filtrate and washings in a platinum dish. Evaporate to perchloric acid fumes, cool, add 25 cc. of 97 per cent alcohol. Break up residue with a stirring rod, filter on an untared Gooch (which has previously been washed with a one per cent solution of perchloric acid in 97 per cent alcohol), and wash thoroughly with perchloric acid-alcohol wash water. (It is necessary that the residue be broken up as much as possible, and that the residue be fine and crystalline before filtering, as otherwise the following procedure will have to be repeated.) Transfer the asbestos mat by means of a stirring rod to a filter and wash the crucible with hot water, allowing the washings to fall on the filter containing the mat. Wash the mat and filter thoroughly with hot water, catching the filtrate in a platinum dish. (By this washing most of the iron and aluminium salts seem to be decomposed, leaving them as insoluble basic salts on the filter paper. Omission of this washing and subsequent evaporation gives results several per cent too high.) Add 0.5 to 1.0 cc. of 2 *N* perchloric acid, evaporate to fumes, cool, add 25 cc. of 97 per cent alcohol, break up

[1] Received August 28, 1922.
[2] Hillebrand, "Analysis of Silicate and Carbonate Rocks," *U. S. Geol. Survey, Bull.* 700, 210.
[3] *Ibid.*, 216.

the residue with a stirring rod, and filter the potassium perchlorate on a tared Gooch, which has previously been moistened with perchloric acid-alcohol wash water, wash with perchloric acid-alcohol wash water, and dry at 110° C. to constant weight. Weigh as potassium perchlorate. Time, 2 to 3 hrs. (If previous to this evaporation the product was not quite crystalline, the potassium perchlorate should be redissolved and the evaporation with perchloric acid repeated. If precipitate is pure potassium perchlorate, the weight then obtained will check with previous weight by ± 0.0003 g.) To correct for sulfate, the precipitate should be redissolved in hot water as described above and a drop of barium chloride solution added. If sufficient precipitate is obtained, it should be filtered off and the evaporation with perchloric acid repeated. Generally, however, this correction is unnecessary.

Using this procedure, eight samples of silicates were analyzed (in triplicate) with the following results.

No.	G. Sample Taken	G. KClO₄ Obtained	Per cent K₂O Found	Average of Detns.	Per cent[1] K₂O by J. L. Smith Method
	0.3075	0.1003	11.09		
1	0.3027	0.0986	11.08	11.11	11.25
	0.1221	0.0402	11.17		
	0.1499	0.0547	12.40		
2	0.2596	0.0938	12.28	12.38	12.32
	0.2745	0.1007	12.47		
	0.1614	0.0298	6.28		
3	0.1617	0.0308	6.48	6.33	6.43
	0.1605	0.0294	6.23		
	0.1709	0.0625	12.44		
4	0.1707	0.0613	12.21	12.37	12.32
	0.2745	0.1007	12.47		
	0.1601	0.0594	12.61		
	0.1457	0.0535	12.48	12.63	12.65
	0.2360	0.0890	12.81		
	0.2359	0.0872	12.56		
6	0.2005	0.0755	12.79	12.68	12.78
	0.1576	0.0589	12.70		
	0.1573	0.0465	10.02		
7	0.1885	0.0548	9.88	9.91	9.89[2]
	0.1853	0.0536	9.83		
	0.2284	0.0124	1.85		
8	0.3589	0.0192	1.82	1.83	1.89[2]
	0.1941	0.0104	1.82		

[1] Values obtained by U. S. Geological Survey.
[2] Value obtained by U. S. Geological Survey for No. 7 was 8.99 per cent, for No. 8 was 0.90 per cent, but check analysis by the author (J. L. Smith method) gave values indicated.

CONCLUSION

While it would be necessary to investigate this method more carefully if it were desired to use it for work requiring accuracy to more than ± 0.2 per cent, the method as given is as accurate as is desired for commercial work, and removes the determination of potassium in silicates from the list of analyses requiring a long and tiresome procedure for their completion.

ACKNOWLEDGMENT

Phosphoric Acid in Cane Juices[1]

By Herbert Walker

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The direct determination of plant-food ingredients in cane juices is suggested as a logical and easily applicable means of getting an approximate idea of the fertilizer requirements of cane soils. A large number of P_2O_5 determinations in crusher juices indicated that this element was fairly constant for a given field and, in general, for a given elevation, although marked differences existed between canes grown at different elevations, the lower fields producing juice containing the most P_2O_5. As a preliminary standard 0.020 per cent P_2O_5 (g. per 100 cc. crusher juice) is suggested. Fields averaging above this figure probably contain sufficient available P_2O_5 for maximum cane yields; a lower figure calls for field experiments. Where juices run less than 0.010 per cent, some phosphate should be applied as a precaution, even in the absence of experimental proof that it is needed. Similar work with potash is planned.

WHILE it is generally recognized that carefully controlled field experiments afford the only reliable means of knowing the fertilizer requirements of a cane soil, quicker methods of getting this information are much to be desired. Soil analyses alone, except in the few cases of extreme deficiency of some element, are not of much value; the plant food may be there, but for some unknown reason—be it chemical, physical, or biological—may not be available to the plant. Soil chemists are still trying to devise methods of extraction which shall imitate plant-root action and yield a solution containing the available plant food in soil.

A so-called "physiological" method of soil analysis has been suggested from time to time by various investigators, but does not seem to have been tried out to any great extent. According to this method, the amount of plant food available in a soil is indicated (relatively) by ash analyses of crops grown in it. The difficulty in getting representative samples and reducing them to ash for analysis is probably one reason why this method, which otherwise appears very practicable, has not been more extensively worked out. This difficulty was partially overcome by Burgess,[2] who compared the analyses of final molasses from a large number of plantations and pointed out the fact that "there exists a definite relationship between the percentage of potash present in the soils of a given region and that found in the final molasses from that section."

The relationship between low potash content of molasses and the need of potash fertilization has been partially confirmed. The greater majority of field tests made throughout the Islands have shown little or no increased yield of sugar from the application of potash fertilizers. The few soils which have responded are from those districts whose final molasses runs much lower than the average in potash.

A serious drawback to the use of molasses analyses for other than very general conclusions is the difficulty of determining from what particular field a sample of molasses has been derived. The average output of a plantation might show it to be, on the whole, well supplied with potash, even though certain fields were very deficient. Also, potash is the only element determinable by this method, since most of the nitrogen and phosphoric acid is eliminated in the process of manufacture.

A procedure that would appear to have most of the advantages and few of the disadvantages of plant ash or molasses ash analyses is the direct determination of plant-food ingredients in the cane juice. Samples can readily be obtained from the crusher or first mill during the grinding season without in any way disturbing factory or laboratory routine—nearly all factories make a practice of taking

separate samples of juice from each field for Brix and polarization tests, and portions of these can be set aside for plant-food analyses. A crusher-juice sample from a few cars of cane covers considerable field area and should be fully as representative as a composite soil sample from the same location. Theoretically, this method, once properly correlated with fertilizer experiments in the field, seems very logical.

Instead of trying to imitate nature by extracting soil in the laboratory with weak acids supposed to approximate the action of plant roots, we let the cane prepare its own "soil solution" and submit it to us ready-made for analysis. That the relative amount of plant food actually taken up is in some degree a measure of its availability seems a reasonable assumption.

The establishment of a numerical relationship between percentages of mineral constituents in cane juice and the fertilizer requirements of a field has yet to be worked out. It may or may not be possible. We have laid out several "plant-food" experiments in some of the higher fields which we suspect may be deficient in phosphoric acid, and these, when harvested in 1924, should give us a fair idea as to whether or not they need phosphoric acid or potash fertilization.

G. R. Stewart of the Hawaiian Sugar Planters' Association Experiment Station has just completed a preliminary soil survey from which we have available for comparison a considerable number of analyses of soils from typical fields throughout the plantation. During the last two months of the 1922 grinding season, we determined phosphoric acid in the crusher juice from each field harvested. Some 70 analyses were made, covering 28 different fields. The analytical work was done by George B. Glick, chief chemist of this factory, using a method adopted by W. R. McAllep for phosphoric acid determinations in connection with clarification experiments.

VOLUMETRIC P_2O_5 DETERMINATION IN CANE JUICE[3]

SOLUTION—(*a*) 10 per cent NH_4OH.
(*b*) Acetic acid.
(*c*) 10 per cent sodium acetate.
Dissolve 100 g. sodium acetate in water, add 50 cc. glacial acetic acid and make up to 1 liter.
(*d*) Standard uranium solution. (1 cc. = 0.005 g. P_2O_5.)
This may be either acetate or nitrate. Thirty-five g. per liter is the approximate amount using either salt. If nitrate is used add 50 cc. glacial acetic acid or a corresponding amount of weaker acid per liter. Excessive exposure to light reduces this solution.
Standardize against tribasic calcium phosphate.
INDICATOR—Powdered crystals of potassium ferrocyanide.
PROCEDURE—To 100 cc. of juice add 1 cc. of NH_4OH solution, acidify with acetic acid, and add 10 cc. of the sodium acetate solution. Titrate with the standard uranium solution using powdered potassium ferrocyanide on a drop reaction plate as an

[3] *See* Sutton's "Volumetric Analysis."

indicator. The solution will usually settle sufficiently to pipet off a small portion of clear liquid for the end-point determination.

Nearly all the uranium solution should be added in the cold and the titration finished in the hot solution (90° to 100° C.).

The method usually gives duplicate results on the same juice which vary not more than 0.002 per cent P_2O_5.

After the juices from a few fields had been analyzed, it became evident, first, that different samples from the same field usually showed very little difference in phosphoric acid, and, second, that there was a very decided difference between juices from different parts of the plantation. When possible, at least three crusher-juice samples, taken on different days, were analyzed from each field.

A few examples of analyses from Wahikuli section will illustrate the variations in amount of phosphoric acid found in different fields and in different samples from the same field.

Field	I8L	H8P	E5P
Approximate elevation, feet	50	200–300	800–900
Grams P_2O_5 per 100 cc. crusher juice	{ 0.062	0.023	0.015
	0.060	0.025	0.012
	0.067	0.023	0.013
Average	0.063	0.024	0.013

These figures are fairly typical of the plantation as a whole. The juices from fields nearest sea level are rather high in phosphoric acid, those from the central portion up to about 500 ft. elevation are moderately well supplied, while the highest areas are lowest in phosphate. This tendency has been so uniform that in the case of the fields thus far examined it would be possible, with the aid of a contour map, to predict roughly the amount of phosphoric acid to be expected in the juice from any field. Exceptions to this rule may be found in some of the red soils at the north end of the plantation. Most of the cane from these fields had been harvested before phosphoric acid determinations were started, but the samples we were able to get ran rather low in phosphoric acid, although from a moderate elevation.

In the following table are included those fields from which we now have both juice and soil analyses, arranged in the order of decreasing P_2O_5 content of the juice:

Comparison of Phosphoric Acid in Cane Juices and in Soils

Field	Elevation in Ft.	P_2O_5 in Juice	Soln. 1 Per cent Citric Acid	Soln. Conc. HCl	Soln. Conc. HNO₃	Total by Fusion	Variety	Tons per Acre
I5L	25–150	0.048	0.0115	0.15	0.17	0.35	Str. Mex. D 1135	45.11
O1L	25–50	0.048	0.0482	0.10	0.28	0.72	H109	44.82
C8L	100–300	0.034	0.0067	0.10	0.12	0.32	Str. Mex. H109	37.59
I4L	25–200	0.033	0.0054	0.12	0.13	0.31	Str. Mex.	36.13
B3P	300–500	0.032	0.0058	0.16	0.20	0.43	H109	63.93
LB1L	100–350	0.026	0.0048	0.08	0.15	0.26	Str. Mex.	50.23
H8P	200–300	0.024	0.0036	0.11	0.14	0.27	H109	43.47
B9P	400–900	0.020	0.0040	0.11	0.12	0.32	H109	54.70
G4P	400–500	0.014	0.0033	0.06	0.12	0.28	H109	54.37
F6P	700–900	0.013	0.0031	0.08	0.13	0.33	Str. Mex.	55.83
E5P	800–900	0.013	0.0018	0.10	0.14	0.24	Str. Mex.	72.42
Standard	.....	0.020	0.0040	..	..	....	....	...

Note header column: "P_2O_5 in Soil" spans the Per cent Citric Acid, Soln. Conc. HCl, Soln. Conc. HNO₃, Total by Fusion columns; "Cane" spans Variety and Tons per Acre.

Discussion of Results

It will be noted that in a general way the P_2O_5 in the juice is proportional to that dissolved from the soil by a 1 per cent solution of citric acid. The "standard" of 0.004 per cent for "available" or citric-acid-soluble P_2O_5 in the soil is considered to be about the dividing line between Hawaiian soils which do and those which do not respond to phosphate fertilizers. The standard of 0.020 per cent P_2O_5 in crusher juice is purely tentative and subject to revision. There are some indications that even the poorest fields on this plantation may have enough available phosphoric acid for their immediate needs. Field E5, with only 0.013 per cent P_2O_5 in its juice, produced the highest yield of cane of all those tested, and a juice so rich (20.39° Brix and 90.44 per cent purity) that it yielded over 10 tons of sugar per acre. Until we can prove whether it might not have done even better with more phosphate—it received 70 lbs. P_2O_5 per acre—it might be dangerous to

conclude that all soils capable of yielding 0.013 per cent P_2O_5 to the juices of cane growing in them contain a sufficient supply of available phosphoric acid.

A comparison of P_2O_5 percentages and cane yields in the different fields is of no value except to show that phosphoric acid is not our chief limiting factor in any case. The variations in yield caused by quantity and quality of irrigation water available are so great as to entirely obscure any possible effect of phosphate.

Fertilizer experiments in Field B6 at about 400 ft. elevation harvested in 1921 indicated little or no gain from phosphates. We have not been able to test juices from this particular plot, but neighboring fields harvested this year had about 0.025 per cent P_2O_5 in crusher juice. Considering this, and also the excellent yields obtained with less than 0.015 per cent P_2O_5 in juice, 0.020 per cent appears to be a fairly safe preliminary standard.

The objection sometimes raised against the possibility of establishing standards from cane-ash analyses, that the variety of cane may have as great an effect on the salts taken up as the soil itself, does not apply to juice analyses, as far as we now know. We have been unable to detect any consistent difference in the amount of P_2O_5 taken up between Lahaina, H109, Striped Mexican, and D1135, nor between plant and ratoon canes.

It is quite possible, however, that cane juices will always contain a certain minimum amount of P_2O_5 and that its lack in the soil will be followed by less cane yields rather than by a further diminution of P_2O_5 in the juice. A field test made by the Experiment Station at Oahu Sugar Company yielded a large increase in sugar by the application of 90 lbs. P_2O_5 per acre to a soil containing 0.16 per cent total HCl-soluble P_2O_5, of which 0.0024 per cent was soluble in 1 per cent citric acid. Juices from the plots receiving no phosphoric acid contained 0.008 per cent P_2O_5; those from plots receiving 90 lbs. phosphoric acid per acre had 0.010 per cent P_2O_5.

While we may never be able to conclude definitely from a juice analysis alone that a field needs phosphate fertilizer, a relatively high figure for P_2O_5 in the juice very probably will indicate that such fertilization is *not* needed, and thus by elimination help to locate field experiments where they are most necessary.

An interesting correlation between field and factory work is worthy of note in this connection. McAllep and Bomonti,[4] in their studies on clarification of cane juices, found that the completeness with which a cane juice may be clarified depends very largely on the amount of phosphoric acid it contains, and placed the approximate limit below which clear, settled juices are not apt to be obtainable at 0.030 per cent P_2O_5. According to this the first aid to determine which fields need phosphates would be a consultation with the sugar boiler. Those fields which consistently yield well-settled, brilliant, clarified juice may be dismissed at once as not in need of phosphoric acid, and more consideration may be given to fields whose juices clarify less readily.

Further Work Suggested

As a basis for future work along this line the writer submits the following:

Soils yielding cane with a phosphoric acid content of more than 0.020 per cent in its juice probably contain enough available phosphoric acid and are not in immediate need of phosphate fertilizers.

Where the juice contains less than 0.020 per cent P_2O_5, phosphates *may* be advantageous. Field experiments should be made to determine this point.

Where the juice contains less than 0.010 per cent P_2O_5, the soil will probably respond to phosphate fertilizers, and their moderate use should be continued even though no immediate gains are shown by field trials.

⁴ *Hawaiian Planters' Record*, **26**, 122.

Plastometer Tests on Alkaline Thin-Boiling Cornstarches[1]

By C. E. G. Porst and M. Moskowitz

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W ITH VISCOUS liquids the flow through capillary tubes is proportional to the pressure, and if the correction for kinetic energy and for the resistance outside of the tube is neglected, the flow through a given capillary is expressed by Poiseuille's formula:

$$n = \frac{\pi g r^4 \, pt}{8vl}$$

where n = viscosity in c. g. s. units, poises.
g = acceleration of gravity = 981 cm. per sec.[2]
r = radius of the capillary in cm.
p = pressure in g./sq. cm.
t = time of flow in sec.
v = volume of flow in cc.
l = length of capillary in cm.

The expression for the fluidity is $\frac{l}{n} = \frac{8l}{\pi g r^4} \frac{v}{pt}$. Since $\frac{8l}{\pi g r^4}$ is a constant for a given capillary depending upon its dimensions its value, K, can be substituted in the fluidity equation, which then becomes

$$\frac{l}{n} = K \frac{v}{pt}$$

In the equation above it can be seen that the radius is raised to the fourth power so that any error introduced by measurement produces a much larger error in K. It is, therefore, best to standardize the capillary with a liquid of known viscosity, such as standardized castor oil.

With plastic substances the flow through capillary tubes is not directly proportional to the pressure or shearing force, and does not vary directly as the pressure until a certain pressure has been exceeded. With such substances the terms rigidity and mobility are used instead of viscosity and fluidity. In the Bingham-Green instrument the pressure is varied and the flow in cc. per sec. is obtained. This is plotted against the total head in g. per sq. cm. To interpret this curve various attempts have been made to express the mobility, etc., in mathematical form.[3,4,6,5,7]

Bingham and Green[5] obtain a hyperbolic equation:

$$P^2 = AW^2 + B$$

from which they obtain the equation of a line through any part P, W on the hyperbola, parallel to the asymptote. The intercept of the asymptote with the pressure axis is taken as the yield value f.

Green[6] finds that for pastes the hyperbolic equation is no longer tenable, and Bingham suggests that the "yield shear

This paper is a continuation of the application of the Bingham-Green plastometer to the study of the paste characteristics of cornstarches,[2,3] particularly thin-boiling starches treated with varying amounts of alkali.

Addition of alkali in processing thin-boiling starches gives firmer pastes until the starch is nearly neutral. This corresponds to a pH of 6.2 to 6.3 in the paste or about 7.4 of the starch. Further increase of alkalinity causes the starch paste to be weaker, of smoother consistency, better spreading powers, and changes the paste from opaque to translucent. Plastometer tests are given and the logarithmic equations for flow derived which take into account not only the straight part of the curve, but the flow at lower pressures as well. Best conditions for heating up starch pastes have been found to be 95° C. The results on tests of thick-boiling cornstarches are summarized.

value" f be calculated from the intercept of the asymptote of the curve with the pressure axis.

Bingham[8] derives the relationship for mobility

$$\frac{8l}{\pi R^4 g} \frac{V/t}{(P-f)}$$

The lower portion of the graph is curved toward the left and is attributed to seepage. It has, therefore, been the custom to reject the lower portion and only consider the flow where the relationship is linear.

Herschel and Bergquist derive the same equation as was obtained by Bingham from Poiseuille's formula. The mobility is expressed as $\frac{l}{R} = \frac{KQ}{P-f}$, in which Q = cc./sec.

Buckingham[7] claims that Bingham has overlooked the condition when the shearing force F is equal to or less than the constant yield value f and, taking into account Green's hypothesis of viscous slip, he derives an equation having three unknowns:

$$\frac{V}{t} = \frac{R^4}{8l}\left(P - \frac{4}{3}p - \frac{p^4}{3p^3}\right) + \frac{\pi R^3 \epsilon \phi P}{2l}$$

where by definition $p = \frac{2lf}{R}$.

ϵ is the thickness of lubricating layer of liquid between the plastic material and the wall, and ϕ the fluidity. From this equation Buckingham concludes that the value of mobility and yield shear value cannot be determined from the straight part of the curve alone, and that to reduce the importance of slip it is necessary to use, not smaller, but larger capillaries. The simplification of this equation is still a problem.

In lieu of a more satisfactory equation the straight part of the curve will still have to be used for yield and mobility determinations. However, as a matter of interest, the authors have determined the equations for the flow of the sixty determinations included in this report.

Apparatus and Method of Procedure

The apparatus and method of procedure were essentially the same as that described in the articles by Herschel and Bergquist, and by the authors. It was found that more consistent results were obtained when the pastes were heated for one-half hour at 95° C. instead of 85° C. The results allowed closer duplication, and although the pastes were firmer the results were more reliable, so in testing about fifty thick-boiling starches the conclusions drawn from the plastometer tests were in agreement with the results obtained by paste makers using some of these starches. It was also found that

[1] Presented before the Division of Sugar Chemistry at the 63d Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.
[2] Herschel and Bergquist, This Journal, 13 (1921), 703.
[3] Porst and Moskowitz, Ibid., 14 (1922), 49.
[4] E. C. Bingham, Bur. Standards, Sci. Paper 278.
[5] Bingham and Green, Proc. Am. Soc. Test. Materials, 19 (1919), II, 641.
[6] H. Green, Ibid., 20 (1920), II, 451.
[7] E. Buckingham, Ibid., 21 (1921), II, 1150.

[8] Proc. Am. Soc. Test. Materials, 20 (1920), II, 486.

the temperature at which the paste is allowed to set is very important, and therefore the pastes were kept at 25° C. (± 1°) in order to obtain consistent results.

x = 0.002 Per cent Acidity
-o- = 0.023 Per cent Alkalinity
φ = 0.192 Per cent Alkalinity

Cc/Sec.

G./Sq. Cm.

FIG. 1—7 PER CENT PASTES OF 8 FLUIDITY STARCH

Capillary 6, one of the capillaries used by the authors for their previous tests, was used for all the determinations, because its dimensions were such that accurate flow determinations could be made in 2 min. for concentrations of starch pastes as used in practice. Its dimensions were:

Length Cm.	DIAMETER, CM.		Calculated Constant K (from Dimensions)	Determined Constant[1]
	Minor Axis	Major Axis	Calculated	
2.62	0.146	0.152	0.149	221.4	256.5

[1] Constant determined by castor oil used throughout for calculating mobilities.

Paste concentrations that were tested were such as to be fairly firm after setting. With thick-boiling starches heated to 95° C., this concentration is 7 per cent dry substance. The plastometer container was filled with the paste by carefully adding very thin horizontal layers of the paste by means of a spatula. The time of flow for each pressure increment was about 2 min., and instead of measuring the time between drops, definite intervals were taken. The last adhering drop from the end of the capillary was removed by means of the weighing bottle cover. For each determination 10 to 20 points were determined. If there is an air opening in the body of the paste spattering results and a larger flow is obtained, owing to the high velocity of the air going through the capillary and carrying the paste with it. Then, too, a lump of starch may become partly wedged in the capillary opening, decreasing the flow. This effect may remain during the determination of two or three points of the curve. Such an error is difficult to detect during the experiment, especially if the flow is but slightly decreased. It is for this reason that the points obtained must be carefully considered when the curve is drawn.

For this experiment thin-boiling cornstarches were prepared by treatment with different amounts of dilute alkali. The fluidities given in the table were determined by the present method for classifying commercial thin-boiling starches.[9]

The starches tested have fluidities of 8, 18, 22.5, 46, 52, 55, and 58, as determined by the C. P. R.[10] method. One liter of starch suspension containing 400 g. of starch was treated with a definite amount of caustic. After standing for several hours the starch suspension was filtered, the starch slowly dried (3 to 4 days) in a low-temperature oven.

[9] H. Buel, 8th Internat. Cong. of Applied Chem., 13 (1912), 63.
[10] Corn Products Refining Company.

The dried starch was tested for alkalinity and its pH determined colorimetrically as outlined by Clarke in "The Determination of Hydrogen-Ion Concentration."

Besides plotting the results on ordinary cross-section paper (Figs. 1 to 4, inclusive), each of the tests was plotted on the logarithmic paper. The logarithmic curves show that the values of the lower pressures bear a functional relationship to those at the higher pressures, and although all the points of the curve do not fall into a straight line, they form a curve which becomes tangent to the axis of flow at a definite pressure—i. e., they have a vertical tangent. Graphically, this pressure could be determined by extending the curve until it becomes tangent to the pressure axis. This pressure has been determined in almost all of the cases to within limits of 10 g. per sq. cm.

For curves going through the origin of the form $y = kx^b$, logarithmic plotting gives a straight line—$\log y = \log k + b \log x$, or

$$b = \frac{\log y - \log k}{\log x}$$

and if logarithmic paper is used b is the slope and k the y intercept (when $y = 1$). They can all be obtained by direct measurements. If, however, the logarithmic curve does not result in a straight line but still gives a curve, then the form of the equation $(y - B) = k(x - A)^n$ may be assumed. This curve has a vertical tangent if $n < 1$ and the horizontal tangent if $n > 1$. If the first graph plotted on logarithmic paper shows such a vertical or horizontal tangent, that point (A, B) may be selected as a new origin. The value of $x_1 = x - A$ and $y_1 = y - B$ should be used and the values of y_1 and x_1 plotted. The values of A and B are found from the first curve in x and y, and the value of k and n are found from the curve in y_1 and x_1—that is, after shifting the origin.

With the 60 curves plotted, only 5 did not need shifting of the axis to bring the upper and lower points into a straight line, the other 55 having vertical tangents at a certain pressure and approaching zero flow. It was, therefore, only necessary to shift the origin along the pressure axis. For each case three values were taken for the pressure at intervals of 5 g. per sq. cm. from the pressure determined graphically,

x = 22 Fluidity-Acidity .07 Per cent
-o- = 22 Fluidity-Alkalinity .04 Per cent
φ = 18 Fluidity-Alkalinity .017 Per cent
△ = 18 Fluidity-Alkalinity .084 Per cent

Cc/Sec.

G./Sq. Cm.

FIG. 2—8 PER CENT PASTES

and the curve taken that gave the most points in a straight line. The broken lines represent the results of the first plotting, the full lines the curves resulting after shifting the origin along the pressure axis. The curve for 9 per cent—55 fluidity, alkalinity 0.024 per cent may be used as an example. After the origin has been shifted 90 g. per sq. cm., all the

points are practically in a straight line. The intercept is 1.3×10^{-4} and the slope 1.17. The equation, therefore, is (cc. per sec.) $= 1.3 \times 10^{-4} (P - 90)^{1.17}$. By the usual practice the pressure is gradually raised from the point where there is no flow until flow just occurs. It has been found that the pressure
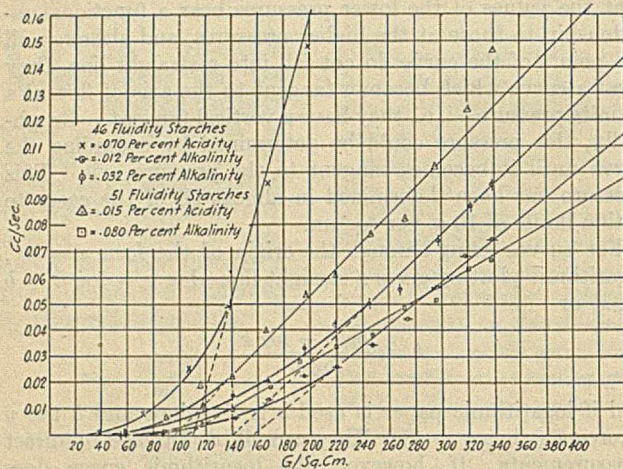
FIG. 3—9 PER CENT PASTES

determined by logarithmic plotting (the pressure at which flow starts) is close to the pressure found by experiments. Table I gives the data obtained.

DISCUSSION OF RESULTS WITH THIN-BOILING STARCHES

The physical characteristics of the starch pastes were altered by treatment with alkali. Up to a certain point the starch becomes firmer and beyond that increased alkalinity caused the paste to be more elastic, smoother, of better spreading power, and more translucent.

The pH of the pastes is in all cases lower than of the starch itself. The fluidity determined by the C. P. R. method decreases with increased alkalinity. By plastometer tests the paste with lowest mobility and highest yield should be firmest. The yield and mob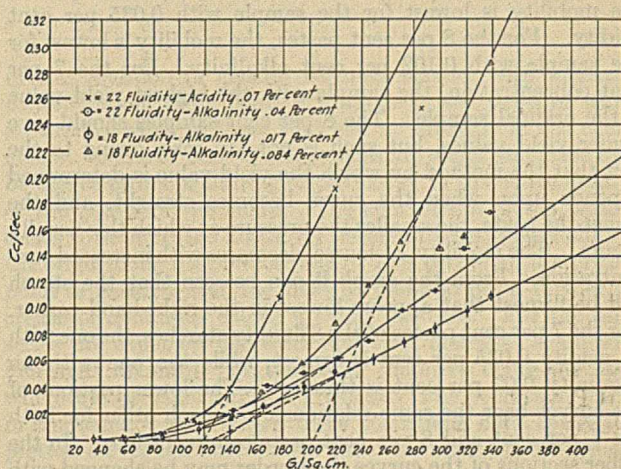ility values are not followed very easily. In the 8 fluidity series for the 7 per cent pastes, the mobility is lowest for the sample with 0.035 per cent acidity. For the 8 per cent pastes, the mobility is lowest for the sample with 0.102 per cent alkalinity. For the 7 per cent concentration, the sample with the highest yield value is the original sample. The 8 per cent samples should give higher yield values, but such is not the case, owing to the fact that the method by which the yield value is determined depends upon when the curve becomes straight, and the firmer the paste, the smaller the pressure at which this usually occurs. The mobility, of course, decreases with increased concentration. From the graph it can be seen that the starch will be firmest that appears lowest in the right-hand corner. For the 7 per cent pastes of the 8 fluidity starches, the one with an acidity 0.035 per cent is firmest, while the one with an alkalinity 0.02 per cent is thinnest. The lower portions of the curves bear the same relationship to each other for both the 7 per cent and 8 per cent paste concentrations. In the upper sections of the curves their order may be changed with the concentration. The curves for the 8 per cent concentrations straighten out below 0.03 per cent, while for the 7 per cent concentration the straightening out occurs at a flow of about 0.14 to 0.16 cc. per sec., which is relatively high.

Pastes usually become thinner with increased alkalinity, after the critical point is reached. This is true when the starch is very slightly acid or just slightly alkaline to phenolphthalein. In almost all cases the untreated starch is thinner than

the starch of even highest alkalinity. In general, the yield value of the untreated starch is lowest and the mobility is highest. The discrepancy in the relationship between yield values and increased concentration seems to be general and the explanation is that with increased concentration there are fewer points on the curved part of the graph and the straightening out occurs at lower pressures, so that the yield values as now determined are consequently smaller in value. For all the starches the mobility decreases very rapidly with increase of paste concentration. The mobilities in general for a given concentration decrease with increased alkalinity until a certain critical point is reached, after which increased alkalinity of the starch causes an increase in the mobility. This critical point is not identical for all of the starches—for instance, for the 22.5 fluidity starch, the critical point is reached at an acidity 0.003 per cent; for the 18 fluidity starch at an alkalinity of 0.017 per cent; for the 46 fluidity at an acidity of 0.006 per cent. For the 52 fluidity starch the mobility is lowest at an alkalinity of 0.08 per cent; for the 58 fluidity at an alkalinity of 0.04 per cent; and for the 55 fluidity at an acidity of 0.017 per cent. From these results it appears that between the acidity of 0.01 per cent and an alkalinity of 0.02 per cent, the critical point occurs and the paste is firmest and of lowest mobility. It also appears that where the pH of the paste is about 6.2 to 6.3 the paste is firmest. This corresponds to a pH of about 7.4 of the starch itself. The reason for the discrepancy of firmness with titration alkalinity for different series of starches may be the fact that the alkalinities of the starches are reduced during drying by the absorption of carbon dioxide from the atmosphere, which, although it may lower its titration alkalinity, does not affect the paste characteristics to the same extent, and since the starches were not all made up at the same time, such variations may be ascribed to this effect.

The authors believe that the equations of flow per second expressed as a function of the pressure have some advantage in the comparisons of the pastes. Although the equations do not allow separation into their component parts to indicate
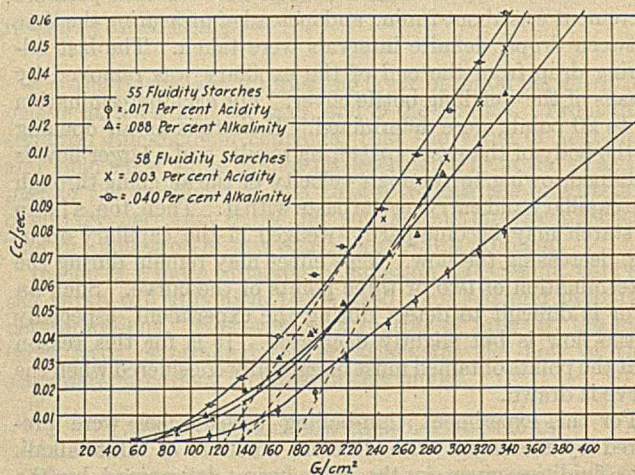
FIG. 4—9 PER CENT PASTES

slippage, etc., they show that for starches a consideration of the entire flow pressure curve is of interest and that the upper portion alone is not the only important part of the curve. There are three constants in the equation, two of which are more or less closely related to each other. The exponent of the equation depends upon the rate of flow, for it is obvious that where the increase of flow per second is comparatively large for a slight increase of pressure the

TABLE I—PLASTOMETER TEST USING CAPILLARY No. 6

Fluidity of Starch Original	Treated	Alkalinity Per cent	Acidity Per cent	Colorimetric Detn. pH of Starch	pH of Paste	D.S.[1] of Paste Tested Per cent	Yield Value G./Sq. Cm.	Dynes/Sq. Cm.	Mobility	Rigidity[2]	Constants of Equation for the Flow through Capillary in (Cc./Sec.)	Exponents
	7.8	...	0.002	7.2	4.5	7	216	212,000	0.312	3.2	$= 8.5\times10^{-7}$ (P-35)	2.12
	6.4	...	0.035	6.6	6.2		170	167,000	0.181	5.5	$= 8.7\times10^{-6}$ (P-90)	1.71
	6.4	0.023	...	8.4	6.4		167	164,000	0.251	4.0	$= 2.6\times10^{-6}$ (P-35)	1.94
	5.9	0.102	...	9.6	9.0		200	196,000	0.514	1.9	$= 4.7\times10^{-6}$ (P-0)	2.70
7.8	5.8	0.192	...	9.8	9.6		182	178,000	0.373	2.7	$= 2.3\times10^{-6}$ (P-0)	2.83
	7.8	...	0.002	7.2	4.5	8	180	176,000	0.0866	11.5	$= 6.2\times10^{-7}$ (P-85)	2.08
	6.4	...	0.035	6.6	6.2		202	196,000	0.101	9.9	$= 7.4\times10^{-6}$ (P-140)	1.70
	6.4	0.023	...	8.4	6.4		192	188,000	0.128	7.8	$= 7.0\times10^{-8}$ (P-35)	2.43
	5.9	0.102	...	9.6	9.0		133	130,000	0.0780	12.8	$= 1.2\times10^{-5}$ (P-60)	1.52
	5.8	0.192	...	9.8	9.6		155	152,000	0.101	8.8	$= 1.0\times10^{-6}$ (P-35)	1.98
	22.5	...	0.070			8	121	118,000	0.494	2.0	$= 3.0\times10^{-8}$ (P-28)	2.97
	12.5	...	0.017	6.9	5.2		124	122,000	0.162	6.2	$= 7.7\times10^{-8}$ (P-69)	1.33
	16.0	0.003	...	8.2	6.7		120	118,000	0.119	8.4	$= 2.4\times10^{-5}$ (P-60)	1.43
	9.0	0.020	...	8.6	6.5		184	180,000	0.893	1.1	$= 3.8\times10^{-6}$ (P-10)	2.46
22.5	16.0	0.040	...	9.2	8.0		134	131,000	0.180	5.5	$= 5.0\times10^{-6}$ (P-33)	1.83
	22.5	...	0.070	...		9	139	136,000	0.195	5.1	$= 3.7\times10^{-7}$ (P-35)	2.77
	12.5	...	0.017	6.9	5.2		195	191,000	0.0853	11.7	$= 4.5\times10^{-7}$ (P-100)	2.14
	16.0	0.003	...	8.2	6.7		152	149,000	0.0734	13.6	$= 5.3\times10^{-5}$ (P-125)	1.30
	9.0	0.020	...	8.6	6.5		156	153,000	0.0950	10.5	$= 6.4\times10^{-6}$ (P-80)	1.68
	16.0	0.040	...	9.2	8.0		159	156,000	0.110	9.1	$= 2.0\times10^{-5}$ (P-95)	1.61
	18.3	...	0.039	5.2	4.8	8	...					
	16.0	0.017	...	9.2	6.2		126	123,000	0.129	7.8	$= 1.22\times10^{-4}$ (P-70)	1.24
	19.1	0.048	...	9.4	6.6		205	201,000	0.546	1.8	$= 3.0\times10^{-8}$ (P-0)	2.75
	18.5	0.084	...	9.8	7.4		205	201,000	0.546	1.8	$= 4.7\times10^{-8}$ (P-0)	2.70
18.3	17.2	0.154	...	Above 9.8	9.4		176	172,000	0.613	1.6	$= 1.25\times10^{-7}$ (P-0)	2.58
	18.3	...	0.039	5.2	4.8		...					
	16.0	0.017	...	9.2	6.2	9	177	173,000	0.0742	13.5	$= 1.05\times10^{-5}$ (P-80)	1.94
	19.1	0.048	...	9.4	6.6		130	127,000	0.0860	11.6	$= 1.75\times10^{-5}$ (P-68)	1.50
	18.5	0.084	...	9.8	7.4		147	144,000	0.0658	15.2	$= 1.15\times10^{-5}$ (P-85)	1.52
	17.2	0.154	...	Above 9.8	9.4		128	125,000	0.123	8.1	$= 1.70\times10^{-6}$ (P-25)	1.44
	46.0	...	0.070			9	111	109,000	0.451	2.2	$= 9.2\times10^{-7}$ (P-20)	2.32
	32.0	...	0.006	7.4	6.3		154	151,000	0.110	9.1	$= 9.5\times10^{-7}$ (P-50)	2.02
	43.0	0.012	...	8.4	6.4		156	153,000	0.103	9.7	$= 2.7\times10^{-6}$ (P-60)	1.82
	41.5	0.032	...	9.0	6.6		140	137,000	0.122	8.2	$= 5.0\times10^{-6}$ (P-24)	1.72
46.0	40.0	0.047	...	9.0	6.8		142	139,000	0.109	9.2	$= 2.5\times10^{-6}$ (P-26)	1.81
	46.0	...	0.070	...		10	173	169,000	0.123	8.1	$= 9.2\times10^{-7}$ (P-70)	2.02
	32.0	...	0.006	7.4	6.3		216	212,000	0.0672	14.9	$= 2.4\times10^{-5}$ (P-180)	1.43
	43.0	0.012	...	8.4	6.4		166	163,000	0.0789	12.7	$= 4.8\times10^{-5}$ (P-135)	1.32
	41.5	0.032	...	9.0	6.6		182	178,000	0.105	9.5	$= 2.5\times10^{-6}$ (P-65)	1.80
	40.0	0.047	...	9.0	6.8		160	157,000	0.0734	13.6	$= 1.42\times10^{-4}$ (P-155)	1.07
	51.5	...	0.060	4.8	4.4		...					
	52.0	...	0.015	7.6	6.0	9	96	94,000	0.131	7.6	$= 6.8\times10^{-5}$ (P-50)	1.34
	49.5	0.012	...	9.2	6.8		199	195,000	0.366	2.7	$= 1.4\times10^{-7}$ (P-10)	2.49
	46.0	0.067	...	9.8	7.8		134	131,000	0.103	9.7	$= 1.45\times10^{-6}$ (P-30)	1.92
51.5	52.0	0.080	...	Above 9.8	9.2		105	103,000	0.0750	13.3	$= 2.5\times10^{-4}$ (P-100)	1.04
	52.0	...	0.015	7.6	6.0	10	158	155,000	0.0928	9.3	$= 1.95\times10^{-6}$ (P-65)	1.57
	49.5	0.012	...	9.2	6.8		143	140,000	0.0639	15.6	$= 1.5\times10^{-6}$ (P-90)	1.43
	46.0	0.067	...	9.8	7.8		132	129,000	0.0618	16.2	$= 3.7\times10^{-5}$ (P-85)	1.32
	52.0	0.080	...	Above 9.8	9.2		131	128,000	0.0649	15.4	$= 5.2\times10^{-5}$ (P-95)	1.27
	57.5	...	0.080			11	185	181,000	0.725	1.4	$= 6.7\times10^{-8}$ (P-11)	2.75
	47.0	...	0.003	8.0	6.6	9	181	177,000	0.238	4.2	$= 3.1\times10^{-6}$ (P-55)	1.91
57.5	47.5	0.04	...	8.4	8.0		127	124,000	0.190	5.3	$= 4.0\times10^{-6}$ (P-65)	1.49
	47.0	...	0.003	8.0	6.6	10	162	159,000	0.106	9.4	$= 5.5\times10^{-7}$ (P-60)	2.19
	47.5	0.04	...	8.4	8.0		181	177,000	0.100	10.0	$= 8.0\times10^{-7}$ (P-60)	2.00
	54.8	...	0.058	4.8	4.6		...					
	44.9	...	0.017	7.4	7.4	9	138	135,000	0.102	9.8	$= 6.0\times10^{-5}$ (P-100)	1.31
	51.2	0.024	...	9.2	7.0		119	117,000	0.105	9.5	$= 2.45\times10^{-4}$ (P-90)	1.17
	47.7	0.080	...	9.4	7.0		170	166,000	0.204	4.9	$= 1.0\times10^{-5}$ (P-60)	1.71
54.8	55.8	0.088	...	9.8	9.2		141	138,000	0.162	6.2	$= 3.2\times10^{-5}$ (P-65)	1.49
	44.9	...	0.017	7.4	6.4	10	192	188,000	0.0726	13.8	$= 1.9\times10^{-7}$ (P-85)	2.24
	51.2	0.024	...	9.2	7.0		181	177,000	0.104	9.6	$= 4.3\times10^{-6}$ (P-100)	1.53
	47.7	0.080	...	9.4	7.0		146	143,000	0.0772	13.0	$= 1.25\times10^{-5}$ (P-75)	1.53
	55.8	0.088	...	9.8	9.2		129	126,000	0.0764	13.1	$= 1.30\times10^{-4}$ (P-105)	1.14

[1] D. S. = dry substance.

[2] Rigidity $= \dfrac{1}{\text{Mobility}}$

logarithmic curve will be steep and the slope, therefore, large, giving a high value for the exponent. This same condition will give a lower intercept of the axis of flow, when $P = 1$, so that the coefficient of the equation will also be smaller. The pressure at which flow starts, or the origin of the curve, is the third constant depending on the quality and concentration of the paste. The larger this pressure is the firmer will be the paste if other conditions are equal. The value of the coefficient and the exponent depends to a small extent upon the shifting of the axis; the value of the exponent will vary about 0.050 to 0.10 for 5 g. per sq. cm. shifting, and the coefficient will change only several units in the significant figures for a variation of 5 g. per sq. cm. Increase of concentration increases the pressure at which flow starts or the third constant. From the data obtained with these starches, the relationship seems more constant than by a comparison of the yield value and mobility alone, and is in accordance with the observations of the paste.

Increased concentration gives an increased pressure at which flow starts, with two exceptions. Only in seven cases the coefficient of the equation does not become smaller with increased concentration, and in one of these cases remains identical at the two concentrations. The exponent of the equation in general becomes smaller with increased concentration, there being exceptions in ten cases of which six are the same as those that had no decrease in the coefficients. Some of these discrepancies are small and some may be due to errors in shifting of the axis or in the determination of the points of the curve. The comparison of the various series with increased alkalinity necessitated a greater shift to the origin along the pressure axis. This is true until a critical point is reached near the neutral point where a further increase of alkalinity causes a rapid decrease. For the same series the exponent decreases and then increases again with increased alkalinity in the same manner, being the least where the pressure value is greatest. The coefficient varies in the same way. Where these conditions hold, the curves plotted on regular coördinates show the starch to be firmest.

SUMMARY OF TESTS OF THICK-BOILING STARCHES

Summarizing numerous tests on thick-boiling starches the following general conclusions were drawn:

From chemical data alone there seems to be no definite relationship between the paste characteristics and the soluble and the protein content. Previously a starch was judged

Table II—Typical Data

7 Per cent—8 Fluidity Starch

No.	Acidity—0.002 Per cent Total Head G./Sq. Cm.²	Cc./Sec.	Acidity—0.035 Per cent Total Head G./Sq. Cm.²	Cc./Sec.	Alkalinity—0.023 Per cent Total Head G./Sq. Cm.²	Cc./Sec.	Alkalinity—0.102 Per cent Total Head G./Sq. Cm.²	Cc./Sec.	Alkalinity—0.192 Per cent Total Head G./Sq. Cm.²	Cc./Sec.
1	58.4	0.00066	63.7	.....	63.4	0.00165	60.1	0.00367	62.1	0.00148
2	88.2	0.00263	93.7	0.000078	89.9	0.00532	87.5	0.00918	86.3	0.00842
3	122.7	0.01010	119.4	0.00283	118.8	0.0154	106.6	0.01542	107.6	0.01515
4	146.2	0.01062	148.7	0.00807	146.1	0.0250	128.4	0.0242	126.3	0.0206
5	162.5	0.0258	169.0	0.0149	165.0	0.0335	147.3	0.0285	147.0	0.0310
6	188.3	0.0353	190.6	0.0250	186.4	0.0437	165.3	0.0360	165.3	0.0398
7	211.6	0.0465	206.1	0.0321	212.2	0.0657	190.2	0.0483	187.2	0.0486
8	233.2	0.0646	219.6	0.0364	231.0	0.0698	209.1	0.0646	213.7	0.0580
9	251.6	0.0678	236.9	0.0468	250.3	0.0834	230.8	0.0807	233.9	0.0768
10	270.6	0.0917	252.4	0.0557	267.9	0.0983	250.1	0.1130	251.9	0.1008
11	296.6	0.0985	268.8	0.0685	284.7	0.1053	273.1	0.1453	274.1	0.1250
12	313.4	0.1018	284.3	0.0706	299.3	0.1198	292.4	0.1833	295.4	0.1690
13	329.8	0.1380	300.0	0.0774	313.5	0.1203	313.3	0.2102	312.1	0.1885
14	341.3	0.1510	313.4	0.0857	330.7	0.1598	339.1	0.2804	329.9	0.2144
15	355.2	0.1695	329.1	0.1068	341.9	0.1558	364.1	0.3366	342.6	0.2340
16	366.1	0.1585	340.5	0.1022	365.3	0.1935			363.5	0.3176
17			361.3	0.1350						

8 Per cent—8 Fluidity Starch

No.	Acidity—0.002 Per cent Total Head G./Sq. Cm.²	Cc./Sec.	Acidity—0.035 Per cent Total Head G./Sq. Cm.²	Cc./Sec.	Alkalinity—0.023 Per cent Total Head G./Sq. Cm.²	Cc./Sec.	Alkalinity—0.102 Per cent Total Head G./Sq. Cm.²	Cc./Sec.	Alkalinity—0.192 Per cent Total Head G./Sq. Cm.²	Cc./Sec.
1	69.5	.....	73.2	.....	63.0	0.000165	66.3	0.000975	63.0	0.00046
2	97.7	0.000565	90.5	.....	91.0	0.00111	87.3	0.001725	91.0	0.00251
3	120.5	0.00092	118.4	.....	118.0	0.00313	110.4	0.00432	110.2	0.00328
4	143.3	0.00236	146.2	0.000032	147.6	0.00456	129.5	0.00600	130.1	0.00575
5	167.4	0.00560	169.0	0.00210	173.0	0.01082	149.3	0.01070	150.6	0.00968
6	189.1	0.01130	191.0	0.00307	193.3	0.01387	168.5	0.01533	169.8	0.050
7	213.1	0.01421	209.3	0.00926	213.9	0.01835	192.0	0.01940	194.2	0.0211
8	232.3	0.0203	224.7	0.00982	231.4	0.0246	210.9	0.02364	210.4	0.0245
9	255.8	0.0256	237.6	0.01438	253.2	0.03420	236.3	0.0300	234.1	0.0309
10	268.6	0.0281	251.7	0.0208	268.7	0.03620	253.2	0.0353	253.0	0.0430
11	283.8	0.0347	269.3	0.0258	282.6	0.04520	272.9	0.0436	274.4	0.0480
12	301.1	0.0407	285.5	0.0226	297.4	0.05450	283.4	0.0444	295.6	0.0582
13	312.8	0.0532	299.4	0.0412	317.2	0.05420	313.9	0.0504	313.6	0.0652
14	329.5	0.0633	313.1	0.0386	329.3	0.06180	333.5	0.0588	328.2	0.0681
15	340.1	0.0650	322.9	0.0473	342.9	0.07550	363.1	0.0662	342.7	0.0740
16	354.8	0.0573	335.1	0.0530	364.9	0.09070	....	.....	367.4	0.0835
17	363.6	0.0678	343.2	0.0456	....	....	....	....	....	.....
18	.....	.....	355.3	0.0500	....	....	....	....	....	.....
19	.....	.....	365.5	0.0596	......	....	....	....	....	.....

by degree of refining noted from its soluble and protein content. It has been found that only for a given sample of starch will the reduction of protein or solubles give a paste of slightly better characteristics, but when comparing different samples such a relationship is not apparent. Powdering a starch and putting through silks produces a better starch from a pearl starch, in some cases more than in others, due to the extra sifting from impurities it receives, but where a starch has very good characteristics in the pearl form powdering will not have as much effect. Nor can powdering bring an inferior pearl starch up to maximum paste characteristics. Washing will only improve a starch to a certain extent if it is inferior at the start, but once it has been thinned down in some part of the process extra refining cannot bring it back to normal. For a 7 per cent concentration of thick-boiling starch heated to 95° C. in making up the paste, the mobility of 0.055 to 0.060 is obtained for good grades of starch, with a yield value of 250 to 300 g. per sq. cm. Where the mobility rises to 0.075 the starch begins giving pastes that are inferior in paste characteristics. For thick-boiling starches firmness is desired, and the firmer it is the better it is considered, and the lower the starch appears in the flow per second—pressure diagram, the better the starch. With thin-boiling starches firmness is not the desirable characteristic, but the ability to use the starch in higher concentrations and of different paste characteristics.

Paper Industries Exposition

Quite recently, when the executive committee of the American Paper and Pulp Association decided that the time was propitious for the holding of an exposition of the paper industries, and that they would place their moral support with an organization to conduct it, the corner-stone was laid in the foundation for the Paper Industries Exposition, which will be conducted at the Grand Central Palace, New York, during the week of April 9, 1923, by the International Exposition Co., with Charles F. Roth and Fred W. Payne as managers. This exposition will be held during the same week as the meeting of the American Paper and Pulp Association, the National Paper Trade Association, and other associations of the paper industry which meet at the same period.

The hours for the exposition will be daily from noon to 10:30 P.M.

The management states that the exposition will tell the complete story of paper, starting from the forest and emphasizing the care in forest use to prevent waste, to encourage reforestation of cut-over lands to insure a supply of paper raw material for the future, the handling of the raw materials entering into paper and what they are, through the machinery with auxiliary apparatus and instruments with which the finished paper is made and the various products therefrom. Among the latter will be shown the newest products of the paper-maker and converter. The exposition will conduct an educational campaign; there is provision made in its program for the showing of motion pictures of the industry, and it is expected to have a program of experts to discuss paper-making phases to schools and colleges, the students from the technical schools being admitted at certain definite periods during the week for the purpose of hearing the speakers and after the address or lecture to view the exhibits.

Though this exposition will be the first of its kind, its success is assured by the interest already shown by manufacturers who have asked for space. The success of the project can be further estimated by the successful exhibitions of paper-making machinery, equipment, and supplies, which the management of the exposition has already given in the eminently successful expositions of the chemical industries, which they have conducted for many years and in which for several years they have had a special section for the paper industry. Likewise, in that exposition they have had for the past few years a section of containers where fiber boxes, cartons, barrels, bags, and numerous other containers of paper have been successfully shown and where exhibitors have found the exposition an excellent business medium.

A strong committee has been organized for the paper industries exposition comprising organized and unorganized groups of paper manufacturers, the trade publications, educational institutions, engineers, and manufacturers of paper machinery, wires, felts, etc. The chairman of this committee is Hugh P. Baker, secretary of the American Paper and Pulp Association.

Notes on the Determination of Phosphorus

By G. E. F. Lundell and J. I. Hoffman

BUREAU OF STANDARDS, WASHINGTON, D. C.

(Concluded)

B. EXPERIMENTAL

I. TESTS OF THE ALKALIMETRIC METHOD FOR THE DETERMINATION OF PHOSPHORUS

THE EXPERIMENTS listed in Table II were carried out in order to indicate the performance of the alkalimolybdate method at different temperatures, and in the presence of various interfering elements. In every case synthetic solutions were prepared by dissolving 1 g. of electrolytic iron, adding phosphorus and adulterants in the amount shown, and then proceeding as in the alkalimetric method given under Methods of Analysis.

The most important point brought out by the data in Table II is that nonattention to the temperature of precipitation leads to more serious error in most cases than does the presence of moderate amounts of the common interfering elements. It is also seen that the method is less reliable for very small amounts of phosphorus.

TABLE II—THE DETERMINATION OF PHOSPHORUS BY THE ALKALIMETRIC METHOD

Temperature °C.	Phosphorus Added Per cent	Found Per cent	Adulterants Added Per cent	Remarks
40	0.272	0.274		
40	0.272	0.273		
60	0.272	0.282	None	
75	0.118	0.133		
20	0.272	0.273		Precipitated after addition of FeSO₄ and SO₂, and with 10 min. shaking
40	0.272	0.276	0.10 Ti	Precipitates contained titanium and filtrates contained phosphorus
60	0.272	0.276	0.10 Ti	
20	0.293	0.291	0.10 Ti	Precipitated after addition of FeSO₄ and SO₂, and with 10 min. shaking
20	0.015	0.013		Incomplete precipitation of phosphorus
40	0.272	0.267		
40	0.272	0.287	0.045 As	
40	0.272	0.274		
60	0.272	0.304		
20	0.293	0.301	0.023 As	Precipitated after addition of FeSO₄ and SO₂, and with 10 min. shaking
20	0.015	0.021	0.035 As	
40	0.272	0.271	0.3 V	Precipitates were orange colored and contained vanadium, filtrates contained phosphorus
60	0.272	0.276	0.3 V	
40	0.272	0.265	0.50 Zr	Filtrates contained phosphorus and precipitates contained zirconium
40	0.272	0.220	2.00 Zr	
40	0.118	0.118	0.50 W	Precipitates contained no tungsten and filtrates no phosphorus
40	0.118	0.118	1.00 W	
40	0.272	0.285	0.10 Ti	Precipitates contained titanium and filtrates contained phosphorus
60	0.272	0.289	0.045 As	
20	0.293	0.300	0.10 Ti	Precipitated after addition of FeSO₄ and SO₂, and with 10 min. shaking
20	0.015	0.020	0.03 As	
40	0.272	0.257	0.10 Ti	Precipitates contained titanium and vanadium, filtrates contained phosphorus
60	0.272	0.284	0.30 V	
60	0.272	0.275		
20	0.293	0.280		Precipitated after addition of FeSO₄ and SO₂, and with 10 min. shaking
40	0.272	0.257		
40	0.272	0.273	0.045 As	
60	0.272	0.278	0.030 V	
60	0.272	0.302		
40	0.272	0.284	0.10 Ti	
60	0.272	0.276	0.05 As, 0.30 V	
20	0.272	0.272		Precipitated after addition of FeSO₄ and SO₂, and with 10 min. shaking
20	0.272	0.276		
40	0.297	0.308	5 g. NaNO₃	Precipitated in a solution free from iron
40	0.297	0.320	5 g. NaNO₃	

Table III is interesting in that it gives a direct comparison between the performance of the alkalimetric and reduction methods with phosphomolybdate precipitates obtained under varying conditions. In every case synthetic solutions were prepared by dissolving 1 g. of electrolytic iron, adding phosphorus in the amounts shown, and then proceeding as in the alkalimetric method given under Methods of Analysis. The titrated solution was filtered after the addition of an excess of alkali, fumed with nitric and sulfuric acids, and oxidized with permanganic acid. The solution was then reduced in a Jones reductor, the solution caught in a solution of ferric sulfate and phosphoric acid, and titrated with a permanganate solution which had been standardized against sodium oxalate.

The chief point of interest in Table III is that the nitric acid content of the phosphomolybdate is apparently more variable than the molybdic acid content, and that consequently the reduction method is slightly more reliable with solutions containing no interfering elements. The advantage, however, does not overweigh its added inconvenience, and probably vanishes with phosphomolybdate obtained in the presence of such reducible substances as titanium, arsenic, and vanadium.

TABLE III—COMPARISON OF ALKALIMETRIC AND REDUCTION METHODS

Phosphorus Present Per cent	Per cent Phosphorus Obtained by Alkalimetric Method	Per cent Phosphorus Obtained by Reduction and KMnO₄ Titration	Temperature of Precipitation, °C.	HNO₃ Present Per cent by Volume	MoO₃ Present Per cent	NH₄NO₃ Present Per cent
0.293	0.296	0.293	20			
0.029	0.032	0.031	20			
0.293	0.299	0.298	40			
0.029	0.033	0.032	40	11	1.5ᵃ	11
0.293	0.311	0.301	80			
0.029	0.035	0.034	80			
0.293	0.314	0.299	40			
0.029	0.048	0.031	40			
0.293	0.307	0.298	80			
0.029	0.039	0.032	80	28	1.5	11
0.293	0.314	0.296	40c			
0.293	0.327	0.300	80c			
0.293	0.297	0.297	40			
0.029	0.039	0.034	40			
0.293	0.303	0.302	80			
0.029	0.042	0.035	80	26	3.7ᵇ	13
0.293	0.321	0.305	40c			
0.293	0.304	...	80c			
0.293	0.289	0.289	40	5	1.5	1.4
0.029	0.029	0.028	40			
0.293	0.297	0.294	40			
0.029	0.032	0.031	40	11	1.5	17

a = 40 cc. and b = 100 cc. of molybdate reagent.

[1] Phosphomolybdates were precipitated and analyzed as in the alkalimetric method given under Methods of Analysis, except that a final volume of 180 cc. was held in all cases and the total precipitation period was 10 min. except in those experiments marked (c) where the precipitation was started at the temperature indicated, the solution then allowed to cool and stand over night.

II. METHODS OF ANALYSIS

Two methods are desirable for the determination of phosphorus in metallurgical products—one, an accurate method for use in such work as primary standardization or umpire analyses; the other, a more rapid routine method which will yield values sufficiently accurate for the work in hand. Two such methods, which have been found acceptable at the Bureau of Standards for the analysis of iron, steel, alloy steel, and bronze, are accordingly given. Both require preliminary direct precipitation of phosphorus as phosphomolybdate, which is no novelty except in the case of bronze and of material containing appreciable amounts of such elements as titanium.

A favorite procedure with material containing titanium is that of Pattinson,[1] in which the phosphorus is first separated by adding an aluminium salt, precipitating with ammonium hydroxide in a suitable solution, igniting the precipitate, and separating the phosphorus by fusion with sodium carbonate and extraction with water. In the method to be described carbonate fusions and extractions are used only when ab-

[1] J. Soc. Chem. Ind., 14 (1895), 443, 1022. F. Ibbotson, "Chemical Analysis of Steel Works Materials," 1920 ed., Longmans, Green & Co., p. 62.

solutely necessary, and then with only a portion of the phosphorus involved in the test.

The direct precipitation of phosphorus in bronze is not often recommended. No difficulty whatever has been experienced at this Bureau in applying direct precipitation to such bronzes as will dissolve to a clear solution in the amounts of mixed concentrated nitric and hydrochloric acids given in the method below; in fact, better recovery of phosphorus has been so obtained than in the widely used Oettel method,[2] where deposition of the phosphorus depends on the tin-phosphorus ratio and is by no means certain even though the ratio be as high as 20 : 1. The experiments in Table IV are inserted here to illustrate these points.

TABLE IV—THE DIRECT PRECIPITATION OF PHOSPHORUS IN BRONZE

| | Composition of Bronze | | | | | Per cent Phosphorus | Percentage of Phosphorus | |
Expt.	Cu	Sn	Sb	Pb	Fe, Zn, Ni not Considered As	Present	Gravimetric Method	Alkalimetric Method
1	88	8	0.16	1.5	None	0.586[1]	0.588	....
2	88	8	0.16	1.5	None	0.020[1]	0.021	....
3	88	8	0.16	1.5	None	0.147[1]	....	0.157
4	95.8	3.78	..	..	Not detd.	0.208[2]	0.212	0.211
5	95.5	4.00	...	....	Not detd.	0.36[2]	0.365	0.370

[1] This value represents the amount of phosphorus actually added to the phosphorus-free alloy.
[2] This value was obtained by a modification of Oettel's method.

In the determination of phosphorus by Oettel's method in Expts. 4 and 5, small amounts of phosphorus escaped precipitation with the *m*-stannic acid; in both cases recoveries were made by direct precipitation with molybdate reagent and added to the final solutions. Slight amounts of phosphorus escaped precipitation by the short precipitation by the alkalimetric method, and no attempt was made to correct for these; no phosphorus was found in the molybdate filtrate after the longer precipitation period by the gravimetric method.

1—GRAVIMETRIC METHOD (FOR STANDARDIZATION)—*a. Preliminary Solution of the Material.* (1) *Iron.* Dissolve 1 to 3 g. of the sample in a covered casserole in 30 cc. of dilute nitric acid (1:1). When solution is complete add 10 cc. of dilute hydrochloric acid (1:1), evaporate to dryness, and bake for 15 to 20 min. on the hot plate. Cool, drench the residue with concentrated hydrochloric acid, dilute to 50 cc. with hot water, and warm until the salts are in solution. Filter without delay, wash with dilute hydrochloric acid (5:95), and evaporate the filtrate to sirupy consistency. In the meantime place the paper containing graphite and silica in a platinum crucible, burn off the carbon, cool, and add 5 to 10 drops of concentrated hydrochloric acid and 1 to 2 cc. of hydrofluoric acid. Evaporate just to dryness, take up any residue in 5 cc. of concentrated hydrochloric acid, and add the solution to the main solution which is being evaporated. When the solution is of sirupy consistency, transfer it to a 300-cc. Erlenmeyer flask by alternate washing with dilute nitric acid (1:1) and hot water, using not more than 30 cc. of the former and 70 cc. of the latter. Heat to boiling, digest for 10 min., and precipitate as in (*b*) below.

(2) *Plain Carbon Steel.* Dissolve 1 to 3 g. of the sample in a 300-cc. Erlenmeyer flask in 30 cc. of dilute nitric acid (1:1). When solution is complete, boil and slowly add a saturated solution of potassium permanganate until oxides of manganese are precipitated. Clear the solution by the slow addition of a solution of ferrous sulfate (10 to 20 per cent and free from phosphorus), boil, digest for 10 min., and precipitate as in (*b*) below.

(3) *Alloy Steel.* The only steels which require special treatment are those which leave a residue at any time during the treatment given in (2)—such as certain chrome steels, steel containing a high percentage of silicon, titanium, or zirconium, and tungsten steel.

The preliminary solution of chrome steel should be as in plain carbon steel except that the nitric acid treatment must be continued until all carbides are in solution, a few drops of sulfuric acid being added if necessary.

With steel containing a high percentage of silicon, the preliminary solution is carried on as with irons in (1).

Steels containing much titanium or zirconium are apt to cause difficulties, owing to the separation of titanium or zirconium phosphates. In case these are in evidence after the final 10-min. digestion in (2), the solution should be diluted with hot water, digested for a longer period, filtered, and the residue washed, ignited, fused with sodium carbonate, and the water extract of the melt added to the main solution.

Tungsten steel does not dissolve in nitric acid, and is treated as follows:

Dissolve 1 to 3 g. of the sample in a porcelain dish provided with a cover glass, with 20 cc. of nitric acid (sp. gr. 1.42), and 60 cc. of hydrochloric acid (sp. gr. 1.19). Heat gently until the sample is decomposed and then evaporate to dryness. Remove the cover glass and bake until the acid is completely expelled. Cool, add 30 cc. of hydrochloric acid (sp. gr. 1.19), and warm until the soluble salts are dissolved. Dilute to 100 cc., filter, wash with dilute hydrochloric acid (1:10), and evaporate the filtrate to sirupy consistency. In the meantime dissolve the tungstic acid on the paper in hot, dilute ammonium hydroxide, washing the paper first with hot, dilute ammonium hydroxide, then with hot, dilute hydrochloric acid. Render the solution faintly acid, add 1 g. of alum, and then ammonium hydroxide in slight excess. Boil for 3 min., filter, wash slightly with hot water containing a little ammonium chloride, and discard the filtrate. Dissolve the precipitate in hot, dilute hydrochloric acid, add the solution to the main solution which is being evaporated, and proceed as with iron in (1).

(4) *Bronze.* Dissolve 1 to 3 g. of the sample in a 300-cc. Erlenmeyer flask in a mixture of 15 cc. of concentrated nitric acid and 5 cc. of concentrated hydrochloric acid.[3] When solution is complete, add 15 cc. of hot water, digest at 80° to 90° C. for 10 min., dilute to 50 cc., and precipitate as in (*b*) below.

b. Precipitation with Molybdate Reagent. Treat the hot solution obtained as above with 100 cc. of molybdate reagent, shake for 10 min. and allow to stand for 4 to 6 hrs. or preferably over night. If an appreciable amount of vanadium is present, this precipitation should be carried out in a solution which has been cooled to 20° C. and treated with 2 to 3 cc. of ferrous sulfate solution (10 to 20 per cent and phosphorus-free) and several drops of sulfurous acid.

Filter on a paper of close texture, keeping as much of the precipitate in the flask as possible, and wash the flask and the precipitate with not more than 50 cc. of cold, dilute nitric acid (1:99). Set the filtrate and washings aside after thorough mixing and see whether further separation of phosphomolybdate occurs. Dissolve the precipitate on the filter in 20 cc. of dilute ammonium hydroxide (1:1) to which have been added 2 g. of citric acid, catch the solution in the original flask containing the bulk of the yellow precipitate, and finally wash the filter several times with dilute hydrochloric acid (5:95). If the ammoniacal solution of the phosphomolybdate is not clear at this point, heat it to boiling, filter through the same paper, and wash the paper with hot water. In this case, and whenever appreciable amounts of such elements as titanium, zirconium, or tin are known to be present in the original material, preserve the paper and ignite it in a small platinum crucible with the paper reserved below.

c. Precipitation with Magnesia Mixture. Render the ammoniacal solution acid with hydrochloric acid, add 20 cc. of magnesia mixture and then ammonium hydroxide (sp. gr. 0.90) slowly until a crystalline precipitate appears, and then finally an excess of 3 to 5 per cent by volume. The volume of the solution at this point should not exceed 100 cc. Allow the solution to stand in a cool place for 4 to 6 hrs., or preferably over night.

Filter, keeping as much of the precipitate as possible in the flask, and wash the flask and the precipitate moderately with dilute ammonium hydroxide (1:20). Set the filtrate and washings aside after thorough mixing and see whether further precipitation occurs. Dissolve the precipitate on the filter in 25 cc. of dilute hydrochloric acid (1:1), catching the solution in the original flask containing the bulk of the precipitate. Wash the filter thoroughly with dilute hydrochloric acid (5:95). In case the original material contains appreciable amounts of the elements mentioned above (titanium, zirconium, or tin), add the paper to the one reserved above, ignite, fuse any residue with as little carbonate as possible (not over 0.5 g.), extract the

[2] *Chem.-Ztg.*, **20** (1896), 19; Treadwell and Hall, "Analytical Chemistry," Vol. II, 5th ed., J. Wiley & Sons, Inc., p. 238.

[3] Where the percentage of tin or antimony is so high as to be troublesome, the procedure suggested by W. B. Price of the Scovill Mfg. Co., and published in the *Proc. Am. Soc. Testing Materials*, **22** (1922) (not yet published), is desirable. This method calls for solution of the alloy in nitric acid, expulsion of the nitric acid by repeated evaporation with hydrochloric acid, separation of copper, tin, lead, and antimony by reduction with zinc, precipitation of phosphorus by the addition of ferric chloride and ammonia, and final determination of phosphorus by usual procedures.

cooled melt with hot water, filter, and add the water solution to the hydrochloric acid solution. Transfer the solution to a 200-cc. beaker. In case the amount of arsenic is known to be very small, add 0.5 to 1 g. of ammonium bromide and boil the hydrochloric acid solution to a volume of 5 to 10 cc. Where large amounts of arsenic were originally present, treat with hydrogen sulfide, digest, filter, and wash with acidulated hydrogen sulfide water. Boil to expel hydrogen sulfide and to reduce the volume to 50 to 75 cc. Add 0.1 to 0.2 g. of citric acid, 2 to 3 cc. of magnesia mixture, make ammoniacal as above, and allow to stand in a cool place for 4 to 24 hrs.

Filter, wash with dilute ammonium hydroxide (1: 20), and ignite the precipitate carefully and at as *low a temperature* as possible until the carbon has been destroyed and the residue is white. Finally, ignite at approximately 1000° C. to constant weight. Dissolve the ignited residue in 5 cc. of dilute nitric acid (1: 1) and 20 cc. of water. Filter, wash the residue with hot water, ignite, and weigh. Treat with a few drops of hydrofluoric acid, evaporate to dryness, ignite, and reweigh. Subtract any loss of weight from the original weight of the pyrophosphate, and calculate on the basis of this purified magnesium pyrophosphate.

Table V presents results which have been obtained by the use of the gravimetric method for the analysis of material containing varying amounts of such interfering elements as arsenic, titanium, vanadium, zirconium, and tin. As 0.1 mg. of $Mg_2P_2O_7$ represents 0.003 per cent of phosphorus on a 1-g. sample, and 0.001 per cent of phosphorus on a 3-g. sample, it is apparent that the method is accurate in the presence of titanium, zinc, arsenic, vanadium, lead, antimony, tin, and large amounts of iron and copper.

TABLE V—DETERMINATION OF PHOSPHORUS BY THE GRAVIMETRIC METHOD

MATERIAL	Weight Taken G.	Per cent Phosphorus Present or Added	Found	Ti	Zr	As	V
B. of S. Cast Iron No. 5d	2	0.230	0.229	0.077	...	0.03	0.02
B. of S. Cast Iron No. 7a	1	0.839	0.843	0.10	...	0.04	0.06
British Standard Iron B	3	0.026	0.027	0.108	...	0.03	...
Pure Iron	1	0.293	0.295	1.00	1.60	1.00	0.50
Pure Iron	3	0.020	0.021	1.00	1.60	1.00	0.50
B. of S Bessemer Steel No. 10c	3	0.105	0.105	0.66	0.50	0.01	Trace
B. of S. Cast Bronze No. 52	1	0.586	0.588	...	...	...	...
B. of S. Cast Bronze No. 52	3	0.020	0.021	...	...	...	...
Bronze (95.8 Cu, 3.78 Sn)	1	0.208	0.212	...	...	...	...
Bronze (95.5 Cu, 4.00 Sn)	1	0.360[1]	0.365	...	...	...	...

[1] Percentage obtained by Oettel's method.

2—ALKALIMETRIC METHOD (FOR ROUTINE DETERMINATIONS)— *a. Plain Carbon Steel.* Dissolve 0.50 to 2 g. of the sample in a 300-cc. Erlenmeyer flask in 100 cc. of dilute nitric acid (sp. gr. 1.135). When solution is complete, boil and slowly add a saturated solution of potassium permanganate until oxides of manganese are precipitated. Clear the solution by the slow addition of a solution of ferrous sulfate (10 to 20 per cent and free from phosphorus), and boil to expel oxides of nitrogen. Cool

and add to the cold solution 40 cc. of ammonium hydroxide (sp. gr. 0.96), 40 cc. of ammonium molybdate solution, and shake for 5 min. (If the operations are correctly performed, the solution will be acid at this point and of a temperature quite close to 40° C., owing to the heat of neutralization.) Allow to settle for 5 to 15 min., filter, and wash the flask and precipitate with not more than 50 cc. of cold dilute nitric acid (1: 99) and then 10 times with a 1 per cent solution of potassium nitrate. Return the precipitate and paper to the original flask, add a measured excess of a 0.1 N sodium hydroxide solution free from carbonate and 25 cc. of freshly distilled water. Shake until the precipitate has dissolved, dilute to 100 to 200 cc. with cold, freshly distilled water, add 3 drops of a 0.2 per cent solution of phenolphthalein, and discharge the pink color with standard acid. Finish the titration by adding standard alkali to the reappearance of the pink color. In the experiments given in Table VI, the alkali solution was standardized by means of the Bureau of Standards standard benzoic acid, Sample No. 39b, by the method described by Morey[4] and the ratio of sodium hydroxide to phosphorus taken as 23 : 1. This method of standardization serves to give a basis for comparing values, and is desirable in coöperative analysis; for routine analyses in works' laboratories, or for analyses of special materials, it is preferable to standardize the solution by the method chosen against like material whose phosphorus value has been obtained by weighing as magnesium pyrophosphate as in the gravimetric method.

b. Cast Iron. The only modification consists in filtering off the graphite and silica after the clearing of the solution with ferrous sulfate.

c. Alloy Steel. Modifications are required with vanadium or tungsten steels. With the former, the sole change consists in cooling the solution to 20° C. after the preliminary treatments, reducing vanadium by the addition of a little ferrous sulfate and sulfurous acid and then shaking and digesting for a slightly longer period (30 min.) after adding the molybdate reagent. With tungsten steel the preliminary attack is as in the gravimetric method, the tungstic acid and its small phosphorus content being disregarded, and the hydrochloric acid filtrate being neutralized with ammonium hydroxide, then made acid with nitric acid and treated as in (a) above.

d. Bronze. Phosphorus is precipitated as phosphomolybdate as in the gravimetric method, filtered after 30 min. digestion, and then washed free from tin by means of dilute nitric acid solution (1.5 per cent by volume) before the final washing with 1 per cent potassium nitrate. This is necessary to prevent hydrolysis of the stannic salts present. With bronzes, it is also much more desirable to standardize the alkali solution by direct titration.

Table VI presents values obtained by the use of the alkalimetric method for the analysis of material containing the same interfering elements as were listed in Table V.

It is seen that the method yields, under severe conditions, values which are sufficiently accurate for technical purposes, provided attention is paid to the temperature at which the phosphomolybdate is precipitated. It is to be borne in mind, however, that the apparently good values obtained in some cases are the result of compensating errors.

[4] Bur. Standards, Sci. Paper 183; J. Am. Chem. Soc., 34 (1912), 1027.

TABLE VI—DETERMINATION OF PHOSPHORUS BY THE ALKALIMETRIC METHOD
(All results calculated on a 23NaOH: 1P ratio)

MATERIAL	Weight Taken G.	Temperature of Precipitation—° C.	Per cent Phosphorus Present or Added	Found	Ti	As	V	Zr	REMARKS
B. of S. Cast Iron No. 5d	2	40	0.230	0.231	0.077	0.03	0.02	...	
	2	60	0.230	0.250	0.077	0.03	0.02	...	
	2	20	0.230	0.237	0.077	0.03	0.02	...	V reduced by FeSO₄-SO₂
B. of S. Cast Iron No. 7a	1	40	0.839	0.838	0.10	0.04	0.06	...	
	1	50	0.839	0.850	0.10	0.04	0.06	...	
	1	60	0.839	0.877	0.10	0.04	0.06	...	
	1	20	0.839	0.846	0.10	0.04	0.06	...	V reduced by FeSO₄-SO₂
British Standard Iron B	3	40	0.026	0.024	0.108	0.03	...	...	
	3	60	0.026	0.029	0.108	0.03	...	...	
	3	20	0.026	0.025	0.108	0.03	...	...	With FeSO₄-SO₂ treatment
B. of S. Steel B. O. H. No. 13b	2	40	0.026	0.026	...	...	...	...	
B. of S. Steel A. O. H. No. 20b	2	40	0.063	0.064	...	0.01	0.01	...	
B. of S. Steel Bessemer No. 10c	1	40	0.106	0.107	...	0.01	<0.01	...	
B. of S. Steel Bessemer No. 22a	2	40	0.119	0.118	...	...	<0.005	...	
	2	75	0.119	0.133	...	...	<0.005	...	
Zirconium Steel	1	40	0.272	0.265	...	...	...	0.50	
	1	40	0.272	0.220	...	...	...	2.00	
B. of S. Cast Bronze No. 52	2	40	0.147	0.157	...	...	...	...	Preliminary washing with 1.5 per cent HNO₃
Bronze (95.8 Cu, 3.78 Sn)	1	40	0.212	0.211	...	...	...	...	Preliminary washing with 1.5 per cent HNO₃
Bronze (95.5 Cu, 4.00 Sn)	1	40	0.365	0.370	...	...	...	...	Preliminary washing with 1.5 per cent HNO₃

Measurements on the Gases Evolved from Glasses of Known Chemical Composition[1]

By J. E. Harris and E. E. Schumacher

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The gases evolved by glasses when heated have been measured and analyzed. Seven different samples representing four distinct types of glass have been experimented with. Six of these samples of glass have been carefully analyzed and definite relations found between the gases evolved and the chemical composition of the glass. It has been found that a glass relatively free from absorbed gases can be produced by using special precautions in manufacture.

THIS investigation of the gases evolved by certain glasses when heated was undertaken with a view to securing a glass which, after an initial period of heating, should cease to give off appreciable quantities of gas. The use of such a gas-free glass would obviously be desirable in the experimental investigation of vacuum tubes, in which the filament and other parts within the tube may be affected adversely by gases evolved from the heated glass during manufacture of the tube.

The work of Guichard,[11,*] Langmuir,[19] Sherwood,[30] Washburn,[37] and others has established the following points with respect to the gases evolved by the glass when heated. The gases may be held as an adsorbed film or dissolved throughout the glass; the adsorbed gases are evolved readily at temperatures less than 300° C., whereas the dissolved gas, although it begins to come out of the surface layers at 200° C., comes out slowly, by reason of the slowness of diffusion through the glass, even at much higher temperatures. Consequently, the total gas evolved at each of a series of temperatures is a maximum somewhere between 200° and 400° C.; this decreases to a minimum, and rises again at temperatures approaching the softening range of the glass.

The main gases held by the glass are carbon dioxide (from the carbonates and possibly from the furnace gases), water (from the materials and the furnace gases), with smaller quantities of sulfur dioxide, oxygen, and nitrogen. The amounts of the gases may correspond to a real equilibrium under the condition of melting; but more usually the viscosity of the melt has been such as to prevent the gases present in solution from escaping completely during the melting. Commercial glasses consequently retain some gas, which escapes slowly when the glass is reheated.

In most of the investigations published in the past, the gases have been divided into three fractions: (1) condensable above −78° C., (2) condensable between −78° and −190° C., (3) not condensable at −190° C. These fractions represent with fair accuracy (1) water vapor, (2) carbon dioxide, (3) the permanent gases—oxygen, nitrogen, hydrogen. In general, water vapor is the most abundant, followed by carbon dioxide; but, owing to lack of the necessary data, it is not possible to correlate these findings with the composition of the glass, still less with the mode of its melting.

APPARATUS AND METHOD

The apparatus used for determining the gases evolved from the glass on being heated is shown in Fig. 1.

The water vapor was removed by surrounding the condensation trap with a mixture of frozen and liquid acetone contained in a Dewar vessel, this mixture being obtained by adding liquid air to acetone until its freezing point, −95° C., was reached. The carbon dioxide was removed similarly by

means of liquid air. Readings were taken on the McLeod gage: (1) with no condensing agent, this giving the pressure of the total gas evolved, (2) with frozen acetone as condensing agent, this giving the pressure of gases less the water vapor, and (3) with liquid air as condensing material, corresponding to the pressure of the permanent gases. From the several pressures thus obtained the respective volumes could readily be calculated.

For the purpose of determining the amount of gases given up by the various types of glass, the glass was first cleaned with chromic acid, and washed thoroughly with water. It was then placed in the sample container—made of the same glass as that being tested—and the pump operated for several hours in order to dry the sample thoroughly. The pump—a mercury vapor pump in conjunction with two oil pumps—was operated until the pressure within the apparatus after being trapped off from the pump remained constant at about 1×10^{-6} mm. for a period of at least 2 hrs. The glass was then heated to a temperature as close to the softening range as it was possible to go without causing the container to collapse; it was kept at this temperature until the gas pressure became constant, when the volumes of the gases were determined in the manner outlined above. The period required for completely driving off the gases ranged from 65 to 80 hrs.

TYPES OF GLASS USED

The types of glass worked with, together with their chemical compositions, are given in Table I.

TABLE I—CHEMICAL ANALYSIS OF THE GLASSES USED

	1	2	3	4	5	6
SiO₂	69.93	69.40	64.64	61.50	72.05	65.47
Al₂O₃	1.54	0.78	0.20	0.57	2.21	2.99
Fe₂O₃	0.19	0.14	0.04	0.11	0.05	0.51
PbO	1.44	Trace	21.66	22.55	6.11	20.20
CaO	3.17	5.15	0.02	0.21	0.06	0.22
MgO	0.03	4.09	0.02	0.36	0.09	0.13
Na₂O	21.02	16.67	9.10	8.14	4.23	6.40
K₂O	0.10	0.20	3.20	3.76	1.12	3.59
P₂O₅	0.08	0.16	0.75	0.34	Trace	Trace
Sb₂O₃	0.05	0.10	....	Trace	....	....
MnO₂	0.09	0.19	....	0.19	0.01	0.073
F₂	....	....	Trace	....	Trace	....
B₂O₃	2.36[1]	3.12[1]	0.37[1]	2.27[1]	14.07[1]	....
SO₃	....	....	....	....	....	0.013
BaO	....	....	....	....	....	Trace

[1] By difference.

It will be observed that Nos. 1 and 2 are soda-lime glasses, Nos. 3, 4, and 6 are soda-lead glasses, and No. 5 is a borosilicate of lead and soda.

EXPERIMENTAL RESULTS

The results of the determinations are shown in Table II. If we may assume that the low-melting glasses (1–4) worked with in this investigation received approximately the same heat treatment during their manufacture, then the data presented in Table II indicate that there is a definite relation between the gas evolved and the chemical composition

TABLE II—GASES EVOLVED FROM GLASS OF KNOWN CHEMICAL COMPOSITION DURING HEAT TREATMENT IN VACUO

Sample	Per cent Alkali in Glass	Vol. of Sample Cc.	Surface Area Sq. Cm.²	Temp. to Which Glass Was Heated °C.		Total Gas Vol. Cc.	Comp. of Gas Per cent	Vol. in Cc. per Sq. Cm. × 10⁴	Vol. per Cc. Glass × 10⁴
1	21.12	37.2	580	400	H_2O	2.70	88.5	46.6	726
					CO_2	0.32	10.5	5.5	86
					P. G.	0.03	·1.0	0.5	8
					Total	3.05	..	52.6	820
2	16.87	31.9	540	400	H_2O	1.62	92.6	30.0	508
					CO_2	0.11	6.3	2.0	34
					P. G.	0.02	1.1	0.4	6
					Total	1.75	..	32.4	548
3	12.30	26.5	565	400	H_2O	1.34	96.4	23.7	506
					CO_2	0.03	2.2	0.5	11
					P. G.	0.02	1.4	0.4	8
					Total	1.39	..	24.6	525
4	11.90	24.1	540	400	H_2O	1.37	97.2	25.4	568
					CO_2	0.02	1.4	0.4	8
					P. G.	0.02	1.4	0.4	8
					Total	1.41	..	26.2	584
5	5.35	25.2	469	500	H_2O	0.03	33.3	0.6	12
					CO_2	0.04	44.5	0.9	16
					P. G.	0.02	22.2	0.4	8
					Total	0.09	..	1.9	36
6	9.99	15.6	292	400	H_2O	0.03	49.6	1.0	19
					CO_2	0.03	49.6	1.0	19
					P. G.	0.0005	0.8	0.02	0.3
					Total	0.0605	..	2.02	38.3

NOTE: P. G. = Permanent Gases.

of the glass. The amount of gas given up per square centimeter of glass surface is found to be closely parallel to the alkali content except in the case of glass No. 6. This parallelism holds more closely for the amount of water vapor than it does for the other gases, although the relation does hold to a less striking extent for carbon dioxide. In a paper by Niggli[24] that treats of the phenomena of equilibrium between R_2O, SiO_2, and CO_2 (R_2O = Na_2O, K_2O, Li_2O), in melts at temperatures of 900° to 1000° C. under a pressure of one atmosphere CO_2, it is interesting to note that the results obtained show the amount of CO_2 in the melt, when equilibrium is reached, to decrease as the composition of the melt becomes less alkaline. The amount of permanent gases evolved is roughly the same for the various types of glass. The reason for glass No. 6 falling out of line with the other glasses will be discussed later. The authors, after making inquiries at several glass-manufacturing concerns, feel that the statement can be made with a fair degree of justice that ordinary commercial glasses of like composition

FIG. 1

usually received approximately the same heat treatment in their manufacture. Preservation of melting pots, saving in fuel, etc., make it very essential for the glass manufacturer to know the lowest temperature that can be used with the assurance of producing good glass. In all the glass factories where we made inquiries, we found that this minimum temperature was about constant in cases where glasses having about the same melting points were being made. In these factories we were also told that the furnaces were usually

held as near this minimum temperature as possible throughout the entire melting process.

Glass No. 1 undoubtedly received a higher heat treatment in the melting process, because of its higher melting point and greater viscosity, than did the other glasses that were tested. The data given in Table II show that this glass gave off very little gas when subjected to heat treatment *in vacuo*. The high heat treatment that this glass received in its manufacture is probably responsible in part for this small evolution of gas, but its low alkali content is probably equally responsible. It will be noted when reference is made to Table II that this glass was heated to 500° C., whereas the other glasses were only subjected to a heat treatment of 400° C.

EVOLUTION OF ADSORBED AND ABSORBED GAS

To determine the relations of adsorbed gases to absorbed gases in the six samples of glass, the pressures of the gases evolved were determined at intervals of 100° C. from 100° C. to the softening point of the glass. In addition to the six samples of glass, a run was taken on Pyrex glass which will be indicated in the experiment as No. 7. No analysis was made of this glass, but it is known to be a borosilicate glass practically free from alkali and heavy metals. From the pressures of the gases obtained, the distribution of gas evolution over the various intervals was determined. Expressed in terms of percentage of the total gas evolved over the entire range, these results are shown graphically in Fig. 2.

It will be noted first of all that these curves, with the exception of No. 6, are in general similar to those obtained by Sherwood[30] in that they show both maximum and minimum points. Glass No. 6 was found in this experiment as in the preceding one to behave quite differently from Nos. 3 and 4, although chemically it is very similar. The explanation for this difference will appear later. The curves show very clearly the distinction between the adsorbed and absorbed gases. It is seen that the adsorbed gases for the lime and lead glasses are practically all given up at a temperature of 200° C., while 300° C. is required in the cases of the borosilicate glasses. The absorbed gases begin to come off at the softening points of the various glasses, 400° C. for the lead and lime glasses, and 600° C. for the borosilicate glasses. The steeper slopes of the curves 1 and 2 above 300° C., as compared to 3 and 4, are undoubtedly due to the fact that these glasses (lime glasses) become fluid more rapidly than do the lead glasses, and therefore give up their dissolved gases at a more rapidly increasing rate than do the others. In this connection it should be stated that the amount of ab-

sorbed gases found in the above experiments represents only that portion of the dissolved gases which lies nearest the surface of the glass. Owing to the great viscosity of the glass at the temperatures used, the rate of diffusion of the gas would be altogether too slow to permit any considerable portion to reach the surface.

FIG. 2

Some data that were taken in some of the experiments carried on in the investigation of the adsorbed gases are interesting in that they seem to throw considerable light on the question of the manner in which these gases are held to glass. Warburg and Ihmori[36] have maintained that the gases are held by chemical forces (primary valence forces), while other writers have maintained that the gases are held primarily by physical forces (secondary valence forces). The measurements of Warburg and Ihmori were made with water vapor, and, while no analyses of the glasses were made, it was found that only those glasses that contained alkali were capable of taking up water vapor.

Glass Nos. 1, 2, 3, 4, 5, and 6 were experimented with in this connection. The glasses were heated to a temperature high enough to drive off all the adsorbed gases, as indicated by the curves in Fig. 1 (200° for Nos. 1, 2, 3, and 4, and 300° for No. 5) and the amount of carbon dioxide and permanent gases determined. The results are shown in Table III.

TABLE III—SHOWING THE RELATION EXISTING BETWEEN ADSORBED CARBON DIOXIDE AND PERCENTAGE ALKALI IN THE GLASS

Glass No.	Vol. of Adsorbed CO_2 in Cc. $\times 10^5$ per Sq. Cm.	Vol. of Adsorbed Permanent Gas in Cc. $\times 10^5$ per Sq. Cm.	Per cent $Na_2O + K_2O$ in Glass
1	19.3	1.300	21.12
2	10.4	1.800	16.87
3	7.5	2.650	12.30
4	7.5	2.350	11.90
5	4.5	0.480	5.35
6	6.5	0.009	9.99

These data show in a remarkable way the relation existing between the adsorbed carbon dioxide and the alkali content of the glass. This experiment indicates that adsorbed carbon dioxide may be held by primary valence forces. Many other glasses must be tested, however, before such a statement can be accepted as a fact. Nevertheless, it seems very plausible to believe that carbon dioxide is taken up by a film of sodium hydroxide which has been formed by the slow hydrolysis of the glass.

This coincides with the view of Krause,[17] who found, in the case of a single glass which was high in soda, that no carbon dioxide is adsorbed when glass and gas are both carefully dried, and also that no carbon dioxide is adsorbed by the glass if it has been washed with boiling water to remove the film of alkali on the surface. The foregoing results do not necessarily indicate, however, that all gas held on the surface of the glass is held by primary valence forces. Indeed, a determination that was made of the permanent gases given up by the glass up to 200° C. indicates that these gases are held to the glass primarily by secondary valence forces. Table III shows that, while appreciable quantities of these gases were evolved, no correlation existed between these quantities and the chemical composition of the glass. A similar determination was not made for water vapor because the capacity of the McLeod gage used in the experiment was too small to take care of the large quantities of water vapor evolved; if a determination had been made in this connection, it seems highly probable that a definite relationship, existing between the adsorbed water vapor and the alkali content of the glass, would have been noted.

MANUFACTURE OF RELATIVELY GAS-FREE GLASS

In our first experiment we melted some ordinary commercial glass in vacuo. The temperature within the vacuum furnace was kept considerably above the melting point of the glass under examination, and was held there for a period of about one hour. For a portion of this time huge quantities of gas were evolved. After this evolution subsided the furnace was cooled to room temperature and the melt was removed. Some of the glass obtained from this melt was later reheated in vacuo at various temperatures up to 500° C. At the lower temperatures, from 20° to 200° C., a measurable amount of gas was evolved, but above 200° C. there was practically no gaseous evolution. The results obtained from this and other similarly conducted experiments make it seem probable that a vacuum furnace process for the manufacture of certain kinds of glass is possible. The expense incurred, however, in the manufacture of gas-free glass by this method would undoubtedly always prohibit its general use in the industries. After realizing that, owing to the difficulties of making it, a gas-free glass could be used only in a very limited field, we sought next to determine if it would not be possible to modify the ordinary standard procedure now pursued in glass-making in such a way as to make a relatively gas-free glass.

At our request, one of the large manufacturers agreed to undertake some experiments to produce glass that would be more nearly gas-free than that obtainable on the market.

In one of the most successful experiments and the only one that will be recorded here, materials that would produce a low melting-point glass were subjected to a heat treatment of between 1500° and 1600° C. for a period of one hour. For a chemical analysis of the glass produced and for its behavior upon being heated in vacuo, see Tables I and II—No. 6.

Attention has been called to the fact that this glass behaved quite differently in the above experiments from the other glasses of the same type, in two particulars: (1) The total amount of gas given up by the glass is very much less.

than for the other glasses of like composition. (2) Of the gas given up by this glass, 90 per cent is given up at 200° C., indicating that this proportion of the gas is adsorbed gas. We may conclude, then, that the special treatment of this glass in its manufacture was very efficient so far as the removal of the absorbed or dissolved gas was concerned. It could not, however, prevent the adsorption of gases by the glass on standing. The adsorbed gases, however, are rather unimportant from the standpoint of vacuum-tube work since such gases can be fairly readily removed by a preliminary heating.

Summary of Results

The results of our investigation may be summarized as follows:

1—Glasses whose compositions run high in alkali give off more gas during their heat treatment than do those of lower alkali content.

2—A definite relation appears to exist between the amount of water vapor held by a glass and its alkali content.

3—A relation, although not as pronounced as that mentioned above, appears to exist between the amount of carbon dioxide held by a glass and its alkali content.

4—Adsorbed carbon dioxide seems to be held to glass primarily by primary valence forces.

5—Adsorbed permanent gases seem to be held to glass primarily by secondary valence forces.

6—Glass relatively free from absorbed gas can be produced by means of heating the glass during its melting process to a sufficiently high temperature.

Acknowledgment

The authors wish to express their thanks to Dr. J. Johnston, to whom they are especially indebted for assistance and advice.

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Local Section Officers

Southeast Texas

The following officers of the Southeast Texas Section of the American Chemical Society have been elected for the year 1923:

President: L. S. Bushnell.
Vice President: W. A. Slater.
Secretary: P. S. Tilson.
Treasurer: L. B. Howell.
Councilor: F. M. Seibert.

Wisconsin

At the December meeting of the Wisconsin Section of the Society, the following officers were elected for the year 1923:

Chairman: J. H. Mathews.
Vice Chairman: A. J. Marschall.
Secretary-Treasurer: F. Daniels.
Councilors: L. F. Hawley and V. Lenher.
Wisconsin Editor of the Chemical Bulletin: H. A. Schuette.

Delaware

The officers for 1923 of the Delaware Section of the American Chemical Society are as follows:

Chairman: F. C. Zeisberg.
Vice Chairman: J. F. Garrett.
Secretary: J. W. Stillman.
Treasurer: J. L. Bennett.
Councilors: C. L. Reese and C. M. Stine.

Northeastern

The officers of the Northeastern Section of the American Chemical Society for the year 1923 are as follows:

Chairman: G. J. Esselen.
Secretary: E. B. Millard.
Treasurer: R. S. Williams.

At the last meeting of the section resolutions were adopted in appreciation of Herman C. Lythgoe, who has served the section as treasurer for the past eighteen years.

Sulfur-Terpene Substitution Compounds[1]

By William Beach Pratt

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T HE TERM "OIL" indicates substances differing widely in composition and properties. We have the fixed oils, which are generally glycerides of stearic, palmitic, and oleic acids; also the essential oils, consisting wholly or in part of hydrocarbons or mixtures of hydrocarbons with compounds of carbon, hydrogen, and oxygen. Broadly, the term is used to include also such as are known as mineral oils, which are petroleum hydrocarbons, coal-tar hydrocarbons, and various compounds of these series.

It will only be possible to mention sulfur products of some of these oils in a general survey of the subject. It is the large division of the essential oils, known as the terpenes, to which our work has been directed and with which we have had experience in commercial application.

The particular terpene always associated with sulfur, and on which one of the largest industries of our country has been established, has a well-recognized reaction with sulfur. Nevertheless, little is understood as to the real chemistry of vulcanization in the rubber industry.

It is really remarkable in view of the commercial value in relation to the combining of sulfur with this terpene, rubber, that for so many years the other terpenes had not been investigated in regard to such reaction.

CONNECTION WITH VULCANIZATION

About twelve years ago the interest of our laboratory was directed to this work through the rapidly increasing demand for vulcanizing rubber to fabrics. Attempts had been made under pressure, *in vacuo*, and by every conceivable mechanical device, to more perfectly incorporate rubber-benzene solutions with cotton fabric, in order to give a better bonding with rubber compounds. The colloidal structure of the rubber and the impossibility of securing a penetration even between the fibers of the thread, led to this definite problem— the possibility of constructing a sulfur-terpene compound, noncolloidal in character, which would be absorbed by the cotton fiber, so that when a rubber compound was placed in contact with the fabric, reaction would occur between the intimately associated sulfur terpene of the fabric and the rubber mass, thereby effecting a union more permanent in relation to the necessary endurance test of commercial use and application.

There has been little published in the literature concerning the combination of sulfur and the liquid terpenes. Because of our work on the vulcanizing of rubber, we drew the conclusion that high temperature and high pressure were essential factors to such reaction. In 1915 we had a bomb constructed in order to carry out a reaction between sulfur and the liquid terpenes at a pressure of 1200 lbs., and carried on experiments for many months with varying pressures and temperatures. We found that, although little had been presented for publication, many of those connected with the technical work of the rubber industry had made similar attempts.

This subject, as originally designated for discussion in the following paper, presents a broad field and one which has been so little discussed in the literature that it will be necessary to confine this presentation to that class of oils and their sulfur compounds which have been the subject of research work and its relation to commercial application, as directed by our laboratory.

After several years of work the direction of research indicated the use of a simple reflux condenser and the ultimate process and product are now patented.[2]

We had found that the sulfur-terpene product obtained corresponded almost exactly with our ideas of what we were originally working to secure. The especial value was found to be in the treatment of fabric for the manufacture of automobile tires and other rubber articles. Being noncolloidal its solutions penetrated the fibers as we had anticipated, so that they became impregnated with this product and were so strengthened that American peeler cotton thus treated became comparable to the more expensive untreated Sea Island or Egyptian cottons.

The solution of the sulfur-terpene compounds is styled "toron," and the fabric, after impregnation with it, "toron-treated fabric." Experience has shown that rubber may be calendered to toron-treated fabric with much greater ease than to the original gray goods, and that the operation is attended with a complete absence of the skips or blisters which occur in ordinary practice with gray goods. This is due to the fact that the treatment with toron conditions the gray goods so that the surface of the fabric is everywhere uniformly prone to adhesion to and incorporation with the rubber. As a consequence "spreading" becomes unnecessary, and thus the time and expense attending this operation are eliminated. Moreover, the "friction," which is the term used in the rubber industry to connote the resistance of the rubber to separation from the fabric, is markedly greater for the toron-treated gray goods than for the same gray goods untreated. Various other advantages in use, such as protection of the tire fabric from contact with air, moisture, and molds, follow such impregnation. But the full effects of these are now the subject of searching investigations.

The fundamental sulfur-terpene compounds themselves have especially engaged the attention of the author, and it is the purpose of this paper to present the more important results so far obtained in the investigation of the products resulting from the reaction of sulfur and turpentine.

DESCRIPTION OF PRODUCT

The sulfur-terpene product prepared in the manner described in the first patent of the series referred to above, from sulfur and American oil of turpentine, which consists largely of α-pinene, varies physically from a dark liquid or semisolid viscous mass to a black, hard, brittle mass which breaks with conchoidal fracture and presents a vitreous luster on the surfaces of fracture, and in many respects resembles the mineral rubbers. The character of the product obtained depends on the proportions of reacting materials, the temperature, duration of the process, and other conditions of formation.

These products are insoluble in water, but are very soluble in chloroform, carbon disulfide, benzene, toluene, and xylene. The "semisolid" products are also almost entirely soluble in most of the other common organic solvents, but they are

TABLE I—PRODUCT A

	WEIGHT G.	DESCRIPTION	Index of Refraction at 18° C.	Composition Per cent C	H	S
Fraction 1, up to 155° C.	1.8	Light yellow liquid, smelled of turpentine mixed with sulfur compound	1.4694	85.55	10.93	3.52
Fraction 2, 180°–214° C.	2.2	Red liquid, disagreeable odor, faint turpentine odor	1.5587	68.61	8.35	23.04
Residue	20.0	Hard, brittle mass	......	51.62	4.60	43.78
Loss	7.0					

TABLE II—PRODUCT B

	WEIGHT G.	DESCRIPTION	Index of Refraction at 18° C.	Composition Per cent C	H	S
Fraction	2.0	Similar to Fraction 1 of Product A	1.4784	84.51	10.68	4.81
Residue	46.0	Stiff, viscous mass	......	55.22	5.57	39.21

very difficultly soluble in ethyl and methyl alcohol. The "hard" products are as a rule considerably less soluble than the others.

Solutions of these sulfur-terpene compounds pass readily through parchment and according to this test are to be regarded as noncolloidal. This conclusion as to the noncolloidal nature of the sulfur-terpene compounds is confirmed by determinations of the depression of the freezing point of pure benzene by several of these compounds.

The sulfur content of the various products varies with the proportions of sulfur and turpentine in the reacting mixture, as well as with the course of the reaction in their formation. Products containing as high as 50 per cent sulfur have been obtained.

Analysis of sulfur-terpene compounds prepared from turpentine which contained less than 0.50 per cent of oxygen has demonstrated the absence of oxygen as a constituent of these compounds, and it has been shown further that the passage of air through the sulfur-turpentine mixture during reaction does not result in the introduction of oxygen as a constituent of the final sulfur-terpene product.

The reaction between sulfur and turpentine is accompanied by the evolution of hydrogen sulfide, and this fact may be taken as proof that the reaction is in part at least one of substitution. But the proportions of carbon, hydrogen, and sulfur in the resultant product, as shown by analysis, are not in harmony with an assumption of substitution alone. Rather, the evidence favors strongly also a simple addition of sulfur to the terpene molecule. Moreover, the results of determinations of apparent molecular weights by the freezing-point method seem to require a further assumption of a reaction involving the condensation of two or more molecules of sulfur-terpene compounds.

Interesting experiments were made to determine the effect of air agitation during reaction. The results show that the passage of air through the reacting sulfur and turpentine did not affect the introduction of oxygen as a constituent of the final product, but it did apparently cause a reduction in the sulfur content of the product.

DISTILLATION OF THE SULFUR-TERPENE PRODUCTS IN PARTIAL VACUUM

PRODUCT A (without air treatment)—A sample (31 g.) of A was subjected to fractional distillation under a pressure lying between a maximum and minimum of $2^3/_8$ and $1^7/_{16}$ in., respectively.

The distillates were condensed in receivers cooled to about −10° C. The temperature of the heating bath of oil was raised slowly to 155° C. At this temperature there was a decided break in the distillation, and the succeeding fraction did not distil until a temperature of 180° C. was reached. The operation was continued up to a maximum of 214° C. The distillation at the higher temperatures was no doubt accompanied by considerable decomposition, as evidenced by the very disagreeable odor of escaping gases or vapors and by the deficiency in weight of the total fractions.

The results are shown in Table I.

It thus appears that the sulfur-terpene product A contained about 6 per cent of unattacked turpentine which could be removed by distillation. By making due allowance for the effect of Fraction 1 on the original analysis of Product A, by calculation we obtain the corrected analysis of the sulfur-terpene product A: C, 49.16; H, 5.57; S, 45.27 per cent.

If we assume that this substance is a pure, individual compound which is, however, unlikely, and that it contains the same number of carbon atoms as the original terpene from which it was derived, or a multiple of the same, we may write its empirical formula most closely in accord with analysis as $C_{20}H_{27}S_7$.

PRODUCT B—The maximum temperature of the bath during the distillation of a sample of B (48 g.) was 156° C., and the contents of the distilling flask reached a maximum of 130° C. The pressure varied from $1^1/_4$ to $1^1/_{16}$ in. Only one fraction was removed.

There was no evidence of any decomposition during the distillation.

From this analysis the empirical formula $C_{20}H_{24}S_5$ may be derived.

COMPOSITION OF A TYPICAL "HARD" SULFUR-TERPENE COMPOUND

This compound was prepared from equal parts by weight of ordinary turpentine and sulfur. The operation was conducted at a comparatively low temperature for approximately 90 hrs., after which time the reaction was completed at about 170° C. At the end of the operation, at 170° C., the product was so stiff that it could no longer be stirred, and it showed no tendency to flow. On cooling it became a hard, brittle mass, which for convenience of reference we shall designate as "C."

ANALYSIS OF C

	Per cent
Carbon	46.14
Hydrogen	4.33
Sulfur	47.80
Oxygen (by difference)	1.73

The small proportion of oxygen was very probably derived from the oxygen of the crude turpentine used. Reducing this

TABLE III

SUBSTANCE	FORMULA	Composition Per cent C	H	S	O	Weight of Sample G.	Weight of Solvent G.	Undercooling (Mean of 2 Observations) ° C.	Depression F. P. (Mean of 2 Observations) ° C.	Depression of F. P. by 1 G. Sub. in 100 G. Solvent ° C.	Apparent Molecular Weight
B₁ (before distillation)		56.80	5.82	37.50	....	0.4604	26.4954	0.323	0.257	0.1474	339.3 } 344.4
	$C_{20}H_{24}S_5$					1.1830	26.8366	0.613	0.635	0.1430	349.5
B₂ (after distillation)		55.22	5.57	39.21	....	0.4176	20.4902	0.191	0.277	0.1356	368.7 } 375.3
						0.2300	23.0264	0.47	0.1315	0.1310	381.8
C	$C_{20}H_{24}S_1$	46.14	4.33	47.80	1.73	0.3980	19.2274	0.125	0.223	0.1075	464.8 } 457.3
						0.2414	20.0012	0.21	0.1345	0.1112	449.8

analysis to an oxygen-free basis, we have: C, 46.96; H, 4.41; S, 48.63 per cent.

This composition corresponds very closely to that of a compound of empirical formula $C_{10}H_{12}S_4$ or $C_{20}H_{24}S_8$.

Depression of the Freezing Point by Solutions of Sulfur-Terpene Compounds

These determinations were made in the usual manner for molecular-weight determinations by the freezing-point method, with the Beckmann apparatus, using pure benzene as solvent. The substances examined and the results are shown (Table III).

The results of these determinations show that the depression of the freezing point of benzene by the sulfur-terpene compounds is proportional to concentration; and, furthermore, the values obtained by calculation of molecular weights from the freezing-point data are of such magnitude as one should expect in the case of noncolloidal substances.

The molecular weight as determined for B_2 (375) is somewhat lower than that required for a compound $C_{20}H_{24}S_5$ (424). This is true also in the case of C, where the determined value is 457 as against 520 required for $C_{20}H_{24}S_8$. But only an approximation to agreement was to be expected, as in neither case was the substance supposed to be a single pure compound. However, in both instances, the results indicate condensation of terpene molecules along with the introduction of sulfur.

Discussion

It must be recognized that the reactions between sulfur and turpentine may be and most likely are very complicated, and that the resultant sulfur-terpene products are in consequence very probably mixtures of considerable complexity. For this reason any attempt at the present stage of our investigation to represent by equations and formulas the course of reactions and the constitution of the sulfur-terpene products can be only speculative. If we were dealing here with a pure terpene, the problem would be in large measure simplified. However, since the turpentine employed consists largely of α-pinene, we may assume the reactions in the main to be those between pinene and sulfur, and on this assumption several interesting possibilities are at once suggested. We may consider one such possibility.

As previously stated, the results of our experiments show not only substitution and simple addition in the terpene molecule, but also some kind of condensation of molecules. Assuming the Baeyer picean-ring representation of the constitution of α-pinene,[3] we should expect the addition of one atom of sulfur at the position of the double bond. The possibility of the addition of a second sulfur atom is suggested by the ready intramolecular rearrangement of the pinene molecule so commonly observed, wherein dipentene, containing two double bonds, is derived from pinene.[4]
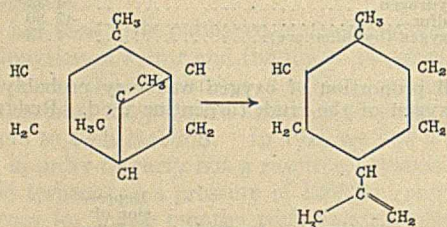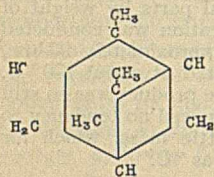
Assuming, therefore, the addition of two atoms of sulfur to one molecule of pinene, we may express this action in two stages:

[3] *Ber.*, **29** (1896), 2779.
[4] Wallach, "Terpene und Campher," **1914**, 15.
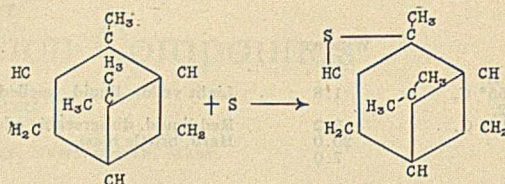
The addition of the second atom of sulfur may be represented as accompanied by molecular rearrangement as follows:
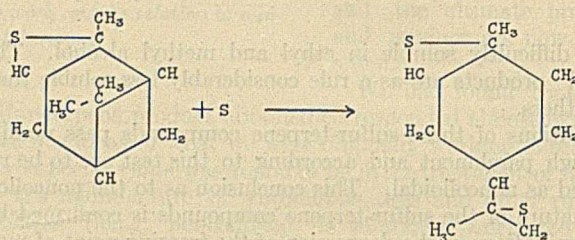
The formation of a compound of the composition $C_{20}H_{26}S_7$ from the above $C_{10}H_{16}S_2$ by substitution of sulfur might then be represented in the following manner:
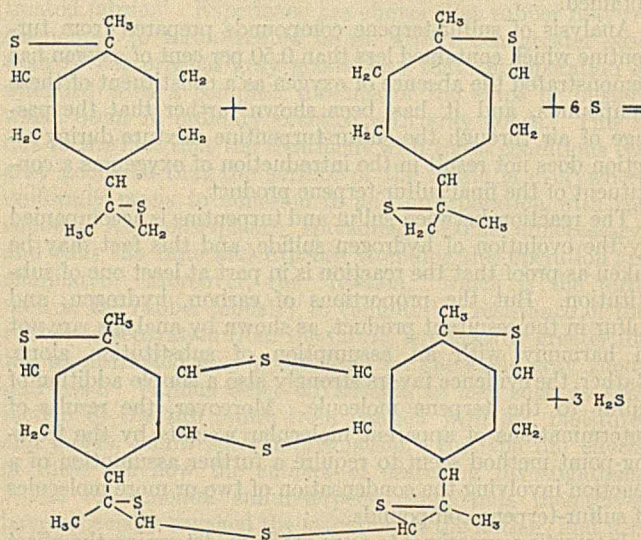
Some such explanation as this may be applicable to the formation and structure of the sulfur-terpene product A, described above, and having the composition represented by the empirical formula $C_{20}H_{27}S_7$, and with such modifications as may be required in each case, to the other products.

The Action of Sulfur on Organic Compounds. Some Typical Examples

One of the oldest examples of the action of sulfur on organic substances is the well-known method of preparing hydrogen sulfide by the fusion of paraffin with sulfur, which appears to involve the formation of more condensed hydrocarbon molecules from which hydrogen has been partially removed in combination with sulfur.[5] And in the field of the dyes[6]

[5] Clarke, "Data of Geochemistry," *U. S. Geol Survey, Bull.* **330** (1908), 627, footnote.
[6] Lange, "Die Schwefelfarbstoffe, ihre Herstellung und Verwendung;" Nietzki, "Chemie der Organischen Farbstoffe;" Cain and Thrope, "The Synthetic Dyestuffs, etc.;" Wahl and Atack, "The Manufacture of Organic Dyestuffs."

we have that large class of substances known as the sulfur dyes, many of which are the result of the direct action of sulfur. The reactions involved in the formation of these dyes are doubtless in most cases quite complex, but in numerous instances they are well established as consisting essentially in the addition or substitution of sulfur, usually accompanied by the evolution of hydrogen sulfide, and the conjugation of two or more molecules through sulfur. Furthermore, the role of sulfur in the formation of natural and artificial asphalts[7] is very generally recognized as an important one and as involving the condensation and polymerization of organic materials to form products which may or may not contain sulfur as a constituent. For instance, according to Winkler[8] artificial coal-tar asphalt can be greatly improved by heating with about 5 per cent of sulfur until the evolution of hydrogen sulfide ceases, whereby a molecular condensation takes place, with removal of hydrogen and the formation of a more difficultly fusible residue. Very similar products are the well-known wood cement of Häusler[9] prepared from coal tar, pitch and sulfur, and the sulfur-tar or benzasphalt,[10] made by boiling two parts of sulfur in three parts of coal tar.

Many other such examples of the action of sulfur on organic compounds are to be found in the literature, and we give below a bibliography which we believe is representative of the literature regarding those compounds whose reaction with elementary sulfur has been investigated.

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[7] Köhler, "Die Chemie und Technologie der Natürlichen und Künstlichen Asphalte," 1913.
[8] *Chem. Zentr.*, **29** (1858), 337.
[9] See Nöthling, "Der Asphalte," 192.
[10] *Wagner's Jahresber.*, 1860, 554.

A Rapid Method for the Determination of Salt in Oleomargarine and Butter[1]

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The following method for the determination of salt in oleomargarine and butter has been used in making hundreds of determinations and has been proved to be rapid and accurate.

A 3-g. sample is weighed out on a torsion balance sensitive to 10 mg. For this purpose a small, narrow copper funnel has been found most useful. Its dimensions are 2 in. long, tapering from $^3/_4$ in. at the large end to $^3/_8$ in. at the small end. It is easily made by cutting a sector out of No. 22 gage sheet copper with tin shears. If the edges are smoothed with a file the piece is easily rolled into a neat funnel. When weighing, it is supported on a tripod made by twisting up No. 18 copper wire.

After weighing the sample, the funnel and tripod are transferred to the neck of a 300-cc. Erlenmeyer flask. The top of the funnel, which projects about one-third of its height above the mouth of the flask, is gently warmed with a small Bunsen flame. The fat melts and runs into the flask. The funnel is then rinsed down with 15 cc. of chloroform in such a way as to remove the film of fat, and the flask is gently rotated until solution is complete. The funnel is then washed down by playing a stream of hot water upon it from a wash bottle. Not more than 50 cc. of water should be used.

Five or six drops of 10 per cent potassium chromate indicator are added and the salt titration conducted by running in 0.1 N silver nitrate solution. The flask should be rotated constantly during the titration. Duplicate determinations should check within 0.1 cc., and 0.1 cc. should be deducted for the end-point. A complete determination, including weighing, may be made in 5 or 6 min.

A blank should be run on the chloroform, using 50 cc. of water and 5 drops of chromate indicator. Occasionally, old samples of chloroform develop phosgene and hydrochloric acid, so that if more than 0.1 cc. of silver nitrate solution is required to give a strong end-point, the chloroform should be shaken in a separatory funnel with dilute sodium hydroxide and filtered through a dry, folded filter.

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Titration Curves for Some Common Acids and Bases as Determined by the Hydrogen Electrode[1]

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It has been suggested that a complete set of electrometric titration curves for the various acids and bases be made available through the adoption of a standard method of procedure. A set of electrometric titration curves in which the same standard procedure was employed throughout has been given for hydrochloric acid, sulfuric acid, o-phosphoric acid, primary calcium phosphate, and citric acid, with sodium hydroxide and sodium carbonate. Owing to the differences in chemical reaction in some cases as well as differences in the salt content of the solution, reversing the order of titration does not result in titration curves that are mirror images of each other.

SINCE the work of Hildebrand[2] and others, the methods, theory, and apparatus for hydrogen-electrode titrations have been advanced to a considerable extent. Coupled with this progress has been a gradually increasing demand on the part of theoretical investigators, instructors in chemistry, analysts, and practical technicians, for complete titration curves of each of the different acids and bases. In order for such curves to be of the maximum value all titrations should be carried out under the same conditions of volume, temperature, etc. Furthermore, the procedure should be such that it conforms to correct analytical practice, the results of which will give the analyst a complete description of every stage of the operations he so often performs. It will aid him in selecting the proper indicators and intelligently judging end-points.

During the course of some researches in this laboratory it became necessary to titrate several acids and bases with the hydrogen electrode. Realizing that a great many other investigators must be doing the same thing for other acids and bases, we are publishing our methods and results in detail, with the hope that some standard may be adopted wherever possible, and that ultimately a complete set of titration curves for all acids and bases will be available in such shape that they may be compared directly one with the other.

PROCEDURE

The procedure that we have adopted and that is proposed for general adoption is as follows:

VOLUME OF SOLUTIONS USED—Make up the volume of the solution to be titrated to 200 cc. and titrate with a reagent of such strength that 30 to 40 cc. are required for complete neutralization. Use a 50-cc. buret. The remaining 10 to 20 cc. are used to finish the curve. This procedure is general quantitative analytical practice.

TYPE OF CELL—The titration cell should be of the closed type. This is absolutely necessary; otherwise, owing to the length of time required for titrations, the various changes in the composition of the air of the laboratory will affect the solution undergoing titration and the result will be worthless. The authors found it impossible to duplicate titration curves in an open cell. Various types of titration cells have been described in the literature and many of them have been made available by the instrument makers. An exceedingly simple and efficient cell, used by the authors, is shown in Fig. 1. The solution to be titrated is contained in a 300-cc. flask or beaker. A close-fitting, 4-hole stopper carries the salt bridge, hydrogen electrode, buret, and stirrer. A small test tube is cut off at the bottom and a 2-hole stopper carries the hydrogen electrode and hydrogen gas intake. The tube is adjusted so that the open end dips beneath the surface of the solution in the flask. The electrode is then adjusted so that it projects beneath the tube just far enough to still make a contact with the solution when a bubble of gas is escaping from the tube, thus giving all the advantages of a rocking electrode with none of its disadvantages.

HYDROGEN ELECTRODES—The authors used a platinum rod coated with platinum black. This gives reliable service over a long period of time if it is carefully handled. The platinum electrode required from 3 to 5 min. between additions of the titrating reagent to come to equilibrium. The electrodes were cleaned after each titration by immersing in sulfuric acid-dichromate solution and washing in distilled water, after which they were boiled three times in fresh portions of distilled water.

STIRRING—Efficient stirring is absolutely necessary to attain equilibrium quickly. The authors encountered difficulty in using a mechanical stirrer operated by an electric motor. Stray currents caused such a variation in the observed voltages of the cell that the mechanical stirrer had to be abandoned in favor of a hand-operated one.

CALOMEL ELECTRODES—The saturated potassium chloride-calomel electrodes and the saturated potassium chloride salt
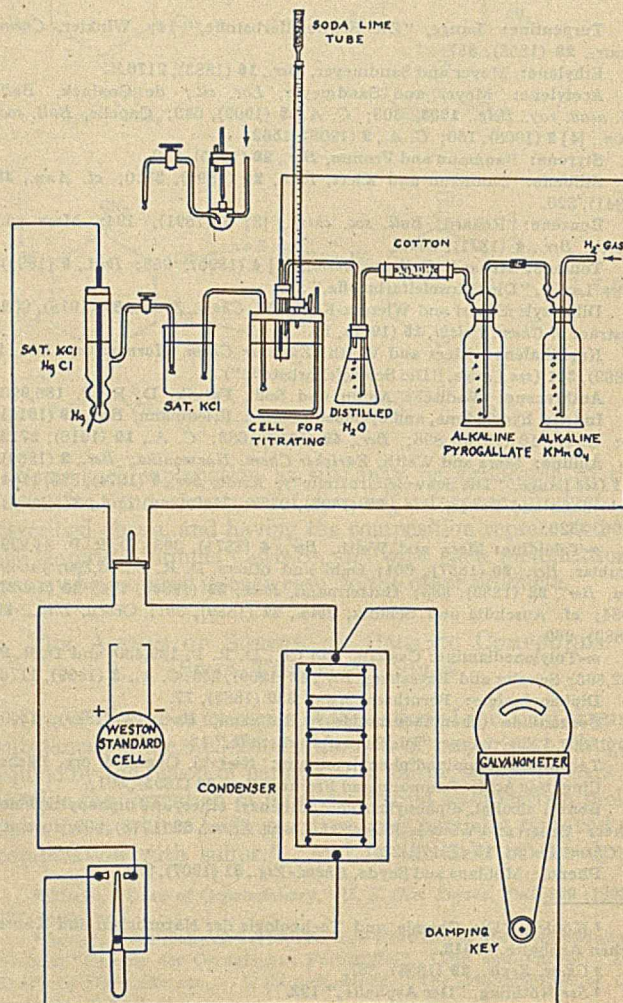
FIG. 1

[2] *J. Am. Chem. Soc.*, **35** (1913), 847.

bridge have been demonstrated by Fales and Mudge[3] to be the most reliable. They give constant results over long periods of time. Fales and Vosburgh[4] have shown that the contact potential differences between saturated potassium chloride and molar hydrochloric acid is zero, and in many other combinations it is at a minimum. Accordingly, the saturated potassium chloride-calomel electrode and saturated potassium chloride salt bridge were used, wooden pegs being employed to reduce diffusion. This gave results constant to 0.2 millivolt, care being taken not to have the plugs tight enough to affect the voltage of the cell.[4] The mercury used was purified by distilling under reduced pressure.[5] The calomel was prepared by the electrolytic method of Ellis.[6] The potassium chloride was purified by twice recrystallizing from distilled water Baker's analyzed potassium chloride and then fusing in platinum.
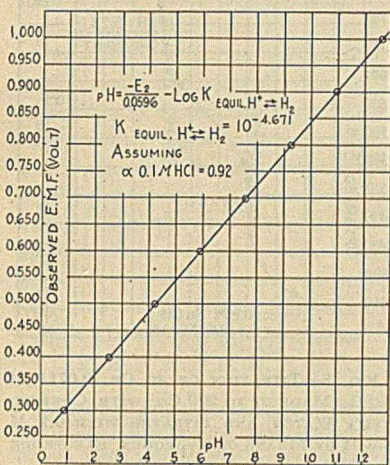
FIG. 2—OBSERVED E. M. F. $\sim$ pH AS DETERMINED BY THE SYSTEM:
Hg | HgCl·KCl (SATD.) | KCl(SATD.) | UNKNOWN SOLN. | H$_2$·Pt
E$_1$ E$_2$

$E_2 = E_1 -$ OBSERVED E. M. F.
$E_1 = 0.5266$ Volt, ASSUMING Hg | HgCl·01 M KCl at 25° C. = 0.5648 Volt

HYDROGEN—Compressed hydrogen was used, purified by passing it successively through alkaline potassium permanganate, alkaline pyrogallate, cotton wool, and finally through distilled water to saturate the gas with water and prevent removal of water from the titration cell.

CONDUCTIVITY WATER—The so-called "conductivity" water used in this work was prepared by distilling first from a sulfuric acid-dichromate solution and then from barium hydroxide. Only a part of the steam distilling over was condensed.

E. M. F. MEASURING INSTRUMENT—Owing to the nature of some of the work in this laboratory, certain cells of high internal resistance, solutions of low concentration of electrolytes, have to be measured. Accordingly, the apparatus described by Beans and Oakes[7] was installed and was used for this work. Any high-grade instrument accurate to 0.1 millivolt is satisfactory for titration work. The method of calculating results is shown in Fig. 2, which includes a graph for rapid conversions of observed e. m. f. readings in volts directly into pH values. (See Lewis, Brighton and Sebastian,[8] Lamb and Larson,[9] Fales and Vosburgh,[4] Fales and Mudge.[3])

FIG. 3—TITRATION OF 30 Cc. 0.1 M HCl WITH 0.1 M NaOH BY MEANS OF HYDROGEN ELECTRODE AT 25° C. END-POINT FROM CURVE 30.0 Cc. 0.1 M HCl $\rightleftharpoons$ 29.86 Cc. 0.1 M NaOH FROM TITRATION (USING PHENOLPHTHALEIN) 30.0 Cc. 0.1 M HCl $\rightleftharpoons$ 29.99 Cc. 0.1 M NaOH

[3] J. Am. Chem. Soc., 42 (1920), 2434.
[4] Ibid., 40 (1917), 191.
[5] Hulett, Z. physik. Chem., 33 (1900), 611.
[6] J. Am. Chem. Soc., 38 (1916), 737.
[7] Ibid., 42 (1920), 2116.
[8] Ibid., 39 (1917), 2245.
[9] Ibid., 42 (1920), 229.

HYDROCHLORIC, SULFURIC, AND CITRIC ACIDS WITH SODIUM HYDROXIDE

The titration curves for these three acids are given in Figs. 3, 4, and 5, respectively. Both the dibasic sulfuric acid and the tribasic citric acid give curves similar to the monobasic hydrochloric acid in that there is only one inflection, but citric acid is much less active than either of the other two and its end-point is not nearly as sharp. While a choice of indicators changing over a wide range of pH is possible in titrating hydrochloric and sulfuric acids, great care must be exercised in selecting an indicator changing color at pH very close to 7.3 when titrating citric acid.

FIG. 4—TITRATION OF 29.8 Cc. 0.1 M H$_2$SO$_4$, MADE UP TO 200 Cc. WITH CONDUCTIVITY WATER, AND TITRATED WITH 0.2 M NaOH BY MEANS OF HYDROGEN ELECTRODE AT 25° C.

The electrometric titrations of hydrochloric and sulfuric acids check the indicator titrations very closely, as is seen from the figures. The citric acid was purified by repeated recrystallizations and dried at 103° C. Calculations on the basis of 1 molecule of water of crystallization show an error of 2.4 per cent in the electrometric titration. Considering the shape of the inflection of the curve for citric acid, this error is not excessive and is no greater than the error encountered using indicators.[10]

PRIMARY CALCIUM PHOSPHATE WITH SODIUM HYDROXIDE

Figs. 6 and 7 show the results of titrating commercial primary calcium phosphate, making up the solutions in boiled distilled water and again in conductivity water. Taking the middle point of the inflection in each curve, it is seen that the former requires 22.75 cc. of alkali corresponding to 89.25 per cent primary calcium phosphate in the sample, while the latter requires 22.00 cc., showing the sample to contain 86.80 per cent primary calcium phosphate. Gravimetric analysis of this sample showed it to contain 87.00 per cent primary calcium phosphate. Failure to completely

FIG. 5—TITRATION OF 0.2498 G. CITRIC ACID IN 200 Cc. CONDUCTIVITY WATER WITH 0.1 M NaOH BY MEANS OF HYDROGEN ELECTRODE AT 25° C.

FIG. 6—TITRATION OF 0.2983 G. Ca(H₂PO₄)₂ (COMMERCIAL) IN 200 Cc. BOILED DISTILLED WATER WITH 0.1 M NaOH BY MEANS OF HYDROGEN ELECTRODE AT 25° C.

FIG. 7—TITRATION OF 0.2965 G. Ca(H₂PO₄)₂ (COMMERCIAL) IN 200 Cc. CONDUCTIVITY WATER WITH 0.1 M NaOH BY MEANS OF HYDROGEN ELECTRODE AT 25° C.
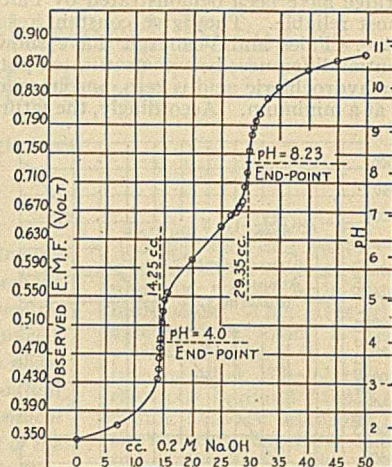
FIG. 8—TITRATION OF 40 Cc. 0.0711 M H₃PO₄, MADE UP TO 200 Cc. WITH CONDUCTIVITY WATER, AND TITRATED WITH 0.2 M NaOH BY MEANS OF HYDROGEN ELECTRODE AT 25° C.
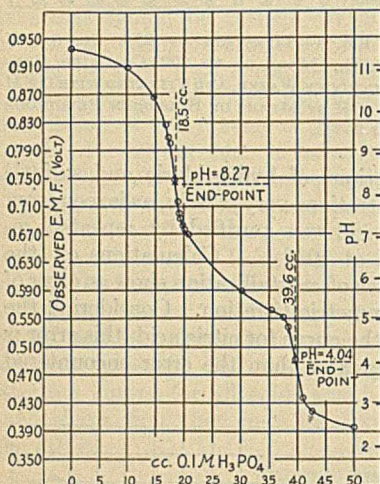
FIG. 9—TITRATION OF 40 Cc. 0.1 M NaOH, MADE UP TO 200 Cc. WITH CONDUCTIVITY WATER, AND TITRATED WITH 0.1 M H₃PO₄ BY MEANS OF HYDROGEN ELECTRODE AT 25° C.
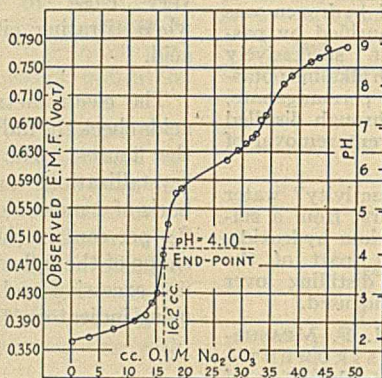
FIG. 10—TITRATION OF 40 Cc. 0.0888 M H₃PO₄, MADE UP TO 200 Cc. WITH CONDUCTIVITY WATER, AND TITRATED WITH 0.1 M Na₂CO₃ BY MEANS OF HYDROGEN ELECTRODE AT 25° C.
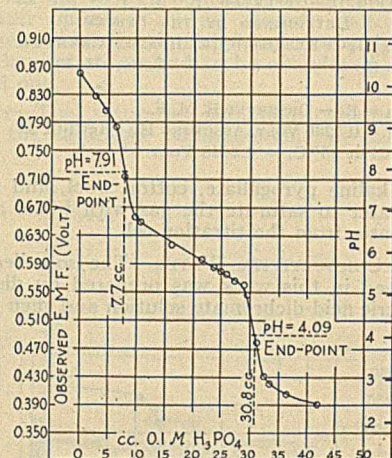
FIG. 11—TITRATION OF 0.1734 G. Na₂CO₃, IN 200 Cc. BOILED DISTILLED H₂O WITH 0.1 M H₃PO₄ BY MEANS OF HYDROGEN ELECTRODE AT 25° C.

remove carbon dioxide from the water before making up the solution resulted in a false titration curve (Fig. 6), with an error of over 2 per cent in the final results. The great difficulty experienced by analysts in titrating solutions of primary calcium phosphate is readily explained by the curve of Fig. 7. The indicators commonly employed for this work do not change at the correct pH and the inflection is not sharp enough for end-points. This coupled with the precipitation of secondary calcium phosphate makes the ordinary indicator titration of little value.

ORTHOPHOSPHORIC ACID WITH SODIUM HYDROXIDE

Orthophosphoric acid was prepared by refluxing phosphorus pentoxide several hours and allowing it to stand two days before standardizing. The results of titrating this acid with sodium hydroxide are shown in Fig. 8. The chief points of interest are that there is no third inflection due to the third hydrogen ion of the acid, and the second end-point requires more than twice as much acid as does the first. Several other titration curves were made on various

samples of phosphoric acid, and both these points were confirmed in every case.

In a titration of a portion of this same acid using color indicators the methyl-orange end-point required 14.20 cc. of alkali, thus checking very closely 14.25 cc. as determined electrometrically. The phenolphthalein end-point required 28.53 cc. alkali as against 29.35 cc. from the curve. It is evident, then, that through the influence of the third hydrogen ion of the acid the second inflection is inhibited at its start and prolonged at the end, thus raising the whole section of the curve. Fortunately, phenolphthalein changes color at a point still on the steep part of the inflection and where exactly twice as much alkali is used up as for the first end-point.[11]

Reversing the operation and titrating sodium hydroxide with phosphoric acid does not give an exact mirror image of Fig. 8. Such a reverse curve is shown in Fig. 9. The

[11] The presence of primary phosphate would cause the second end-point to require more than twice as much alkali as the first, but every precaution was taken to eliminate this error. It is certain that Fig. 8 represents the facts for o-phosphoric acid.

end-points of the two inflections check those of Fig. 8, but the corresponding pH values at the extremities of the two curves are quite different and the shapes of the curves are different, owing to the different amounts of different salts present at any corresponding points in the two curves. As before, the end-point at pH 4.04 gives the correct analysis of the acid. In this particular instance it will be seen that for analytical purposes it makes little difference whether the acid is run into the alkali or the alkali into the acid. This is by no means always the case, as will be seen later.
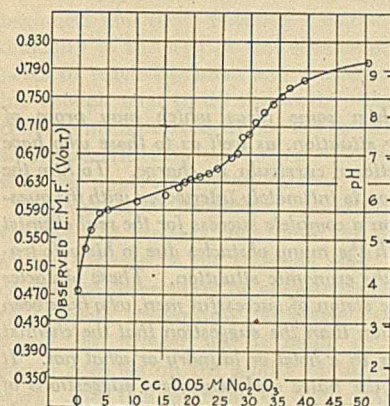
Fig. 12—Titration of 0.2963 G. Ca(H₂PO₄)₂ (Commercial) in 200 Cc. Boiled Distilled Water with 0.05 M Na₂CO₃ by Means of Hydrogen Electrode at 25° C.

Orthophosphoric Acid with Sodium Carbonate

When o-phosphoric acid is titrated with sodium carbonate, the first part of the curve is identical with the sodium hydroxide curve. As seen in Fig. 10, the end-point is practically identical with that of Fig. 8. The first end-point in Fig. 10 requiring 16.20 cc. of sodium carbonate was checked by a methyl-orange titration where the end-point for 40 cc. of the same acid required 16.21 cc. of the same carbonate solution. The second inflection of this curve is so flat that neither indicator nor electrometric titration can be relied upon for quantitative analytical purposes. Reversing the order of the titration gives results as plotted in Fig. 11. The upper portion of this curve is totally different from that of the preceding figure. The inflection is abrupt and the end-point sharply defined. In this case the order of titration makes a vast difference in the character of the curve. Three times as much phosphoric acid (30.80 cc.) are required to reach the first end-point (7.7 cc.). A study of the conditions necessary for equilibrium at these two points shows that the following equations represent the facts, and also shows why it requires three times as much acid to titrate from the first to the second end-point as to titrate to the first.
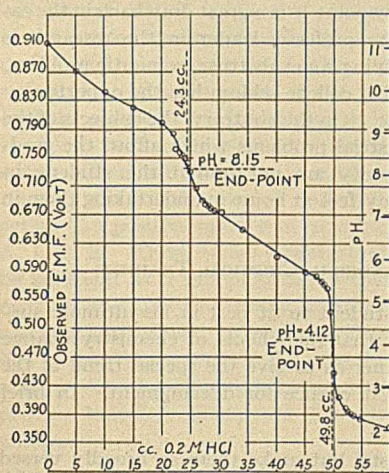
Fig. 13—Titration of 0.5365 G. Na₂CO₃ in 200 Cc. Boiled Distilled Water with 0.2 M HCl by Means of Hydrogen Electrode at 25° C.

First end-point:

$$2Na_2CO_3 + H_3PO_4 = 2NaHCO_3 + Na_2HPO_4.$$

Second end-point: $2NaHCO_3 + Na_2HPO_4 + 3H_3PO_4 = 4NaH_2PO_4 + 2H_2O + 2CO_2.$
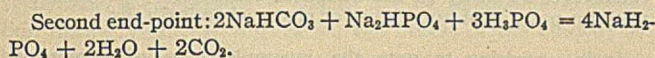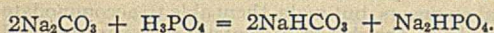
These equations were checked by an indicator titration of sodium carbonate with o-phosphoric acid in which the titrating flask was part of a carbon dioxide absorption train. Air was drawn through this absorption train, first passing it through a solution of sodium hydroxide and then through conductivity water. It then bubbled through the solution in the titrating flask and finally through a clear solution of limewater. In making the titration, two indicators from the Clark and Lubs series[12] were used. Thymol blue changes from blue to yellow at pH 8.0. The titration was first carried to this point and then bromphenol blue was added, giving the solution a blue color again. The bromphenol blue changes from blue to yellow at pH 3.8 upon continuing the titration. The o-phosphoric acid was added in small portions and time allowed after each addition for a complete change of air in the titrating flask. In this way the point where carbon dioxide was first liberated was noted by the limewater becoming slightly cloudy. This point was found to be just past the first end-point, thus checking the first equation in regard to the liberation of carbon dioxide. After adding bromphenol blue the titration was continued and carbon dioxide was liberated. The relation between the two end-points was found by the color changes to be exactly the same as indicated by the equations and by Fig. 11.
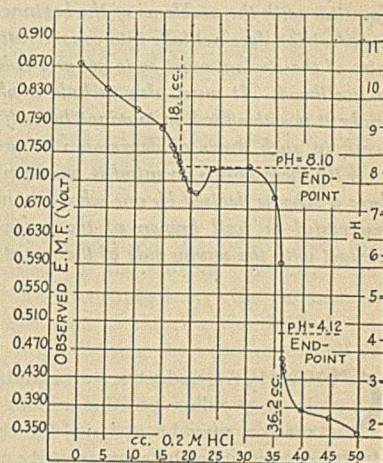
Fig. 14—Titration of 0.3876 G. Na₂CO₃ in 200 Cc. Boiled Distilled H₂O with 0.2 M HCl by Means of Hydrogen Electrode at 25° C.

Primary Calcium Phosphate with Sodium Carbonate

When a solution of primary calcium phosphate is titrated with sodium carbonate, the same type of curve is obtained as for the second portion of Fig. 10. The inflection is less abrupt as shown in Fig. 12, and the end-point can only be guessed.

Sodium Carbonate and Hydrochloric Acid

The sodium carbonate titration is particularly interesting because of its application to standardizing solutions. By titrating the solution rapidly the curve represented in Fig. 13 is obtained. The first inflection is not very abrupt and judgment of the end-point is therefore correspondingly inaccurate. The second inflection point is abrupt and steep, with the end-point well defined. The titration required about 4 hrs. for its completion. Fig. 14 represents the results of a duplicate titration, except that after the first end-point was passed the solution was allowed to stand for some time with the hydrogen bubbling through it to remove the liberated carbon dioxide. This brought the curve back up to the true end-point at pH 8.10, and of course gave a different shape to the second inflection. The second end-point was chosen at a point requiring just twice as much acid as the first. The pH 4.12 of this point, it will be noted, is the same as for the corresponding point in Fig. 13. These two curves show the nature of the end-points under different circumstances. The advantage of the methyl-orange over the phenolphthalein titration is obvious.

12 Clark, "Determination of Hydrogen Ions."

The Chemist's Education[1]

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Improvement in the method of education of chemists has been much discussed by individuals, organizations, and publications in the chemical field, and is necessarily of the highest import to the student undertaking the study as a life work. Various committees and commissions have been appointed by the different organizations to study existing methods with a view to improvement, but with little real success. The work of these organizations has been greatly handicapped by the fact that those contributing opinions have been men of assured standing, who are perhaps less intimately familiar with the problems of the beginner than they realize. Their broad vision does not take into consideration the fact that the primary aim of the student must be to get and hold a job which will yield him a livelihood. It must also include a phase of training which will make it possible for him to adapt himself to other lines of chemical work in such times of depression as are common in the industry.

With these points in mind it has been thought of value to present here a scheme devised by one who does not count himself among the successful or well known of the profession, but whose intimate contact with the seamy side of the recent period of economic reverse

in the industry has given him some ideas which may prove of value to others in a similar situation, as well as to those who have the designing of our educational curricula in charge. To him the question of chemical education is intimately interwoven with the question of making the profession a complete success for the real chemist by thrusting out of his path the many obstacles due to historic tradition and the vagaries of the economic situation. These obstacles are believed to be outside the vision of successful men, who have been able to offer no better solution than the suggestion that the chemist of the future start his career in a hotel or laundry or what not. It is not proposed to criticize the naive and benevolent suggestions of these gentlemen, although it may be noted that they have strangely avoided trying their own solutions. It is proposed to present a criticism of existing methods of education and what seems to be a logical solution, to the end that the profession may attain to its most rapid growth and that the success of the graduating student may be assured. To the writer it is axiomatic that one completing successfully the required years of chemical study has the same right to success as has a tailor or a typesetter.

CHEMICAL industries are, and probably always will be, in a peculiar position among human activities. Two reasons may be assigned for this—the profits of the industry do not have the same security as those of other industries, and the public at large lacks a sympathetic understanding of the processes involved. Strong international competition, unavoidable hazards in operation, and the constant friction between the industry and the public on account of nuisance proceedings, as well as the possibility of development of new products which make previous undertakings immediately obsolete, militate against the financial security of chemical operations in a way entirely different from other industries. The lack of understanding of chemical processes on the part of the layman is a serious drawback to both the industry and the profession on account of the well-known tendency of people generally to regard as suspicious those things which they cannot understand, a fact which is especially unfortunate to the young chemist should he attempt to enter a consulting business. The businesses of lawyers, physicians, architects, mechanical engineers, and other professionals are sufficiently well understood by the layman to warrant his confidence, but it is seldom that the possibility of the service of a chemist is either understood or appreciated. This lack of public appreciation makes it necessary for ninety per cent or more of chemists and chemical engineers to find employment in industrial plants, when comparatively few of them as now educated are fitted for such work.

The disaccord between the personality of the chemist and the industrial world, although having some inherent causes, is largely developed by the plan of chemical education. Educational methods have been organically progressing since the Middle Ages, and might go on in the same way were it not for their relation to industrial life, which has developed quite differently. It is quite in accord with the requirements of chemical education that a young chemist should absorb in almost the same measure the laws and methods of inorganic, analytical, organic, physical, and applied chemistry. From the viewpoint of industrial applicability it would be far better to develop one of these lines

strongly in each man at the expense of the others. As it now stands, the most benevolent industrial employer is at a distinct loss to ascertain which of his young applicants will be good in a vacant position. The traditional degrees of bachelor, master, and doctor tell him nothing of this. It is becoming necessary to turn out analysts, research workers, production men, construction men, and so on, rather than "chemists" as the term is now broadly applied.

The old idea of having every chemical student devote a year to research under some well-known teacher was, and for that matter still is, of great benefit in the advancement of science; but from the student's viewpoint it is a great drawback in the career of the graduate. The professor-leader in the research is most often engaged in studying some abstruse, romantic problem, but the student after leaving college seldom has the opportunity to choose such lines of work. On the contrary, the subjects of the majority of chemical industrial problems which afford the graduate the greatest opportunity are not taught the student in such a manner that he may feel at home in undertaking them in the plant.

Suggested Changes in Chemical Training

In order to adapt the student to fit best in his ultimate surroundings, it is suggested that the schools of chemistry change their plans in such a manner as to give the special trend of the student's mind the greatest chance for development. In brief the suggested plan is:

Train analytical chemists, but make them so broadly versed that they can accommodate themselves in a short time and with great ease to the laboratory of any plant—be it coal-tar distillery, acid plant, dyestuff plant, or aluminium smelter.

Train research chemists, but acquaint them as well with the experimental juggling with different organic groups as with electric furnaces or low-temperature work.

Train chemical engineers, but make them able to accommodate themselves as easily to the design of centrifugal separators and vacuum pans as of autoclaves or electrochemical cells.

It is surprising to note the incompleteness of suggestions offered heretofore on this subject. It might be thought that

the subject were of far less importance than the description of some synthesis or the building of a new chemical laboratory, to judge from the amount of space given it in our literature. Emphasis has been placed on the selection of teachers, especially for beginners and those finishing a course of study. The practical difficulty in the way of this scheme of providing two sets of experts to teach freshmen and seniors, respectively, is in obtaining enough men to do the work. The further suggestion that the intermediate students be left to less experienced men is open to severe criticism, for certainly no single phase of the science is of less importance than another.

Equipment for teaching is also of primary importance to both teacher and student, but often its importance is emphasized at the expense of the teaching staff. A school with the best equipment improperly or unsystematically used can never hope to compete successfully with one even very poorly equipped where the utmost use is made of the apparatus available. Much depends on the ability of the teachers as organizers of work, and the selection of men could well be based more on this requirement than is done at present.

Although the combination of a good teacher and a good scientist assisted by a wealth of equipment is worth at least fifty per cent of the total needed for turning out good chemists, a combination of much equipment with a poor teacher is, on the contrary, a negative magnitude. In such a case the costly equipment gives the school a face quite out of harmony with its internal content.

After proposing in a general way that chemical schools should turn out chemists with a profound theoretical and experimental knowledge in the different branches of chemistry, but specialized only along one or another trend of work—analysts, research men, construction men, production men, organizers—we will try to show how the whole system of chemical education must be reformed to get the best results in this direction.

Limitation of the Number of Chemical Schools

It will hurt the pride of some small colleges or their subsidizers, but we think it an axiom that there is no reason for chemical departments in the majority of the small universities. These institutions cannot afford equipment in any sufficient or efficient degree, and their graduates, unless they all are geniuses, will always remain below the average. This would not be so bad if not for the fact that the low-grade chemist will always underbid the high-grade one, when doing practical work. A necessity for the limitation of the number of chemical schools (not the number of students, however) is unassailable. The only trouble is in its accomplishment, but this difficulty can be overcome. Chemical education is going to be standardized, if not through the interference of the written law, then through the action of a positive opinion of such bodies as the A. C. S. or the A. I. C. E. These bodies might decide what curriculum would be sufficient as a minimum for a chemical school, what equipment is absolutely necessary for efficient teaching, and how the teaching staff should be formed. This opinion, which we would like to call "the unwritten law of rationality," would easily eliminate a lot of inferior schools or make them merge together to provide better facilities and join the ranks of standardized schools.

The First Year

The first year in the chemical school should be devoted, not so much to making the students absorb some minimum of knowledge as to the study by the teachers of the student's trend and abilities. Nowadays, when everybody tries to ascertain the fitness of applicants for vacant positions by means of some unsystematic questionnaire, it should not be impossible to ascertain during a year of observation the fitness of the student to become a chemist. Of course, the program must be made to fit this purpose. In this direction we propose the following:

Program of the First Year in Chemistry

(Knowledge of trigonometry, of the essential features of analytical geometry, and of differential calculus must be acquired either in the high school or in the summer session before entrance.)

(1) General chemistry—not simply inorganic chemistry with a little about the hydrocarbons, but a short, systematic review of chemistry in relation to the universe.

(2) General chemical and related experiments—not a simple accomplishment of a number of experimental inorganic problems, but diversified experimenting covering the use of the balance, the microscope, the electric furnace, the spectroscope, the electrolytic cell, the calorimeter, and other scientific and industrial apparatus.

(3) General chemical conferences. Reading selected articles from chemical books of the semipopular type; discussion of the material as read; discussion of the experimental work; free-hand drawing in connection with this work; cost calculations in connection with the results of some preparative work done in the laboratory or read from the books.

(4) The outline of the chemical industries and the chemical profession. A truthful statement of the situation in the chemical industries; the nuisance of waste gases and liquids; the fate and obstacles on the way of different inventions of the past, and so on.

(5) Chemical excursions. Visits to the mines, fields, packing houses, etc., as the sources of raw materials; visits to chemical factories; visits to the stockrooms of concerns dealing in chemical equipment both for the laboratory and industry.

(6) Shop work. A student of chemistry must be given ample opportunity to become well acquainted with the lathe and milling machine, carpentering and wood turning, molding and glass blowing. This work shall be strongly emphasized particularly in the summer session before the second year.

During this first year, the members of the faculty must ascertain individually the features of the student's personalities. Their judgment, corrected and controlled by the judgments of others, should provide a means of showing the student the best line for him to follow, of eliminating the incapables, and of strengthening such features as are too indefinitely developed in the student as he enters the school. The following features of the student's personalities should be studied: (1) memory, (2) swiftness of impression, (3) swiftness of action, (4) system of action and thought, (5) imagination, (6) intuition, (7) clearness of perception of space and time, (8) exactness and neatness of work, (9) patience, and (10) ability to defend a given opinion. On the basis of these observations the students could be classified definitely as: (1) no chemists at all, (2) chemical clerks and salesmen, (3) analytical chemists, (4) research men or experimenters, (5) construction men, (6) production men and organizers, and (7) chemical educators and popularizers of chemical science.

Subsequent Development

During the first year the teaching staff will have ample opportunity to discover a very large percentage of students, who, although clever enough to absorb some knowledge, or to do some experimental work, are quite unfit for the intensive pursuit of the chemical profession. Their minds may be very alert, but, nevertheless, not only the teachings of radionics and electronics, but even the questions of better means of material transport in the factory seem to them highly specialized and purely theoretical. These men are often far more sociable, far more the type of a good fellow or a mixer than the real chemist by God's blessing. If they are allowed or forced to remain in the university, they will be nothing less than a constant menace to all other representatives of the profession. They have always some intuitive assurance that they are bound to succeed, and have therefore a "sunny disposition," which is so pleasing to the business man. Of course, when such men occupy positions of analysts or draftsmen, or work in a plant, they hate their "narrow" field of work, and do everything to change to the sales or office forces. Here they succeed, but before they come to it their former positions remain long closed to the men who really fit into them. These men do not need a profound college education at all. Let them, if they be discovered in the freshman year, go their own ways and become straightaway chemical

clerks or chemical salesmen. They might as well leave the university after the first year and make good without a heavy loss of time to themselves and others.

Nevertheless, if they are considered still too young to go into practical life or have a desire to spend more time getting "college refinement," let them stay and take a special course, which may include:

(1) Advanced general chemistry.
(2) Natural history of the raw materials.
(3) Intensive study of descriptive applied chemistry.
(4) Advanced visits to chemical plants, and factories making chemical equipment.
(5) Statistics of the chemical industries and chemical imports and exports.
(6) Watching the work of the students going more deeply into chemical science.

The proposed sophomore course for the chemical clerks and salesmen is especially planned to let men of this type go without experimental or laboratory work. They cannot make good in it, and it is better to leave them without any temptation to take a position in the laboratory or the drawing room as a temporary job before going into their "real" business of making money. Instead of this, it is of benefit to require from them the spending of a certain time in watching the chemical work of the students of another type. Business men, even if they have a college chemical education behind them, are apt to look contemptuously upon the men who have to work for a small salary, making analyses or doing routine research work. Too often they do not even realize the strenuousness of the work of getting reliable results in testing a stuff or a process. This might be helped if they could see and note the patience, the experimental skill, and the ways of thinking of real chemists.

Education of the Production Chemist

The production chemist is next to the chemical salesman as far as the preponderance of business-man lines in his character is concerned. He also is very rarely interested in chemical problems of more general magnitude, although he takes seriously the intermediate problems, covering the utilitarian field of his special occupation. Much as sociability, eloquence, humor, and talkativeness are the main features of the good salesman, the production man must possess an inherent and strongly developed trait of leadership. He comes in contact with different people and has to get his plans to going nicely, no matter how short this contact be. The workingmen and foremen, the warehouse keepers and the superintendents must answer quickly to his orders, conforming more to his will than to his persuasions. Strong will, quickness of action, aggressiveness, and ability to make observations and have them ever ready in their memory, are the characteristics which lead to their promotion.

At the present time the largest part of any student body in a school of chemistry is striving to become production chemists. The prerequisites of will and leadership, together with a far larger opportunity to make a fortune either in the form of high bonuses or by becoming independent manufacturers, have a strong appeal to the student's soul and mind, but these characteristics of the production chemists, no matter how positive, cannot but be followed by others of a quite opposite character.

The production chemist must have an extensive knowledge of chemical industries and processes to be able to make a quick change from one to another, and, even more, to be able to see analogies and apply them to his work. He must have a good basic knowledge of chemistry to be able to make a deeper study into the subject he is interested in. He must know how to proceed to do analytical or experimental work in case of emergency, or when he wants to prove some of his ideas. He must be able to analyze graphically and numerically the run of his process. He must possess imagination and ability to represent on paper the scheme of apparatus or installation which he wants to put into action. All this can be accomplished if he has a special education, very different from the curricula of to-day. Chemists of this type should be put into practical life as soon as possible, a two-year special college course being quite sufficient.

Negative Features of the Production Chemist's Education—(1) The future production chemists should not be required to bother much with laboratory work or with theoretical organic or physical chemistry.

(2) The theoretical side of every course he is obliged to take, outside of that of applied chemistry, must be reduced to the minimum.

Positive Features of Production Chemist's Education—(1) He must get a very broad knowledge of the whole applied chemistry in its up-to-date character, and a very elaborate knowledge of about ten branches, taken in the most different lines of chemical industries.

(2) He must have an elaborate practical knowledge of chemical transportation and power machinery, and be able to locate troubles and direct the repairs, sometimes even doing the repairs himself.

The second and third (the last) years of the production chemist's course should include the following subjects:

Second Year

(1) Essentials of general chemistry.
(2) Selected examples of analytical and preparatory work.
(3) General applied chemistry.
(4) Accounting and bookkeeping.
(5) Visits to chemical plants with reports.
(6) Free-hand and instrumental copying of chemical schemes and apparatus.

Third Year

(1) Special study of selected industrial processes.
(2) Parallel study of physics and physical chemistry in a form applied to industry.
(3) Experimental work on selected topics.
(4) Conferences on chemical calculations and grapho-analytical discussion of chemical processes.
(5) Power, transportation, and chemical machinery.
(6) Practical work on dismantling and assembling of all three groups of machinery.
(7) Practical work on lead burning, autogenous and electric welding, and ironsmithing.

There could be added a special course in chemical economics and management of chemical plants; but since chemical economics is still to be created, and no standardized or generally acknowledged ideas about chemical management exist, such courses could not prove so highly useful as the courses in management of mechanical plants and structural work. Instead of leaving the student to study these subjects theoretically another year, he should be helped in getting a place in the practical industrial life, where he could get and develop such knowledge in the most efficient way.

The Education of the Analytical Chemist

During the first year a certain number of students will be found to have the ability to do exact chemical work under conditions enabling them to do it in quiet and clean surroundings far away from the noise of machinery. Such students show also the inherent trait of doing everything themselves, and of neither relying upon nor leading groups of men. These students will make reliable analytical chemists for either routine or research work. Such students should not be required to go through the very general curriculum of the usual chemical school. It is not to be denied that the majority of graduate chemists leave college with a disgust for unromantic analytical work, and that a large part of this majority are totally unable to do exact analytical work after graduation. If they learn to do it later, no thanks are due the chemical school from which they graduated, but to the imperative condition, "Do exact work or get out." Would it not be better if the minority of students, who really like such work and are fitted for it, were allowed to specialize and to

start their practical life along a line where no big salaries can be expected, at least without the competition of people of an unsuited type?

If so, then the whole program must be made to fit this purpose. Analytical chemistry must be made the central subject, all other being taught in connection with it, and as a help to it. Quite a number of analytical chemists could be graduated after the second year, if they want to do only routine work. The program of their education in the second year might be as follows:

(1) Advanced general chemistry.
(2) Analytical chemistry.
(3) Physical and physicochemical analytical methods.
(4) Laboratory work in analytical chemistry.
(5) Analytical calculations.
(6) A short course in the essentials of chemical industries.

After the completion of the second year, the men who lead in analytical work could continue by taking a course as follows:

(1) Selected chapters of physics and physical chemistry.
(2) Advanced organic chemistry.
(3) Special work in analytical chemistry.
(4) Special work in complex analyses and reagents.
(5) Special work in physical or physicochemical methods.
(6) Glass-blowing, lens work, etc.
(7) Design and construction of analytical apparatus.
(8) A descriptive and critical course in laboratory apparatus, machinery, and general arrangement of equipment.

OTHER TYPES OF STUDENTS

There remain still three groups of chemical men who should have specialized training in order to develop their inherent features to the utmost before they leave the chemical school. They are the research chemists, the chemical construction men, and the chemical engineers. It is the first and last groups to whom really are adapted, or at least are thought to be adapted, the curricula of the chemical and the chemical engineering schools.

The programs of the chemical schools, as planned by scientists for forming squads of followers and developers of science, cannot be criticized except in details. The truth is that the majority of the well-equipped and well-organized schools really are able to turn out enough people to develop science and its practical application. Nevertheless, we are at a loss to understand why their staffs insist upon the hopeless task of making every chemical worker, be he a future salesman, production man, or analyst, go through the same course in the same way. It would be far more rational to select the few real research chemists and give them real opportunities to start their practical life through a straight course of research work.

The educational programs in chemical engineering have not undergone such a process of organic development as the pure chemistry programs, and hence they are too diversified and artificial, and represent a mechanical mixture of a shortened program in chemistry, with some subjects in mechanical, civil, and electrical engineering. The proportions in this mixture always depend on the temporary facilities of the institutions to which these schools belong. As a matter of fact, the usual four-year courses in chemical engineering are not able to make a real engineer. The proportion of chemical subjects must remain large enough to give the engineer a good chemical education, and therefore the proportion of the other subjects becomes too small to give the student a real knowledge of mechanical and other matters. This is the reason why chemical engineers are mostly occupied in production, analytical, or sales work, which condition is quite irrational and works against the fundamental aim in training chemical engineers.

It must be acknowledged that chemical engineers cannot be trained in a four-year course. To be able to handle the requests made to them, chemical engineers should have at least the same chemical education as the research chemists, plus a large part of the education needed by mechanical and electrical engineers.

Therefore, a special six- or seven-year course will be inevitable in the future.

A rational four-year course might be very useful to build up a body of chemical construction men who could work in accord with research chemists and bring more positive results than does the coöperation of the chemist and the mechanical engineer, who are apt to speak different languages. During the second year such a course might well be identical with the course of the production chemists. In the third and fourth years the students specializing in construction might devote more time to drafting, mechanical and chemical calculations, and especially to work in different shops where parts of chemical apparatus are being made, finished, and assembled.

PROPOSED CHANGES IN GENERAL CURRICULA

At present there are three subjects which form a regular part of chemical education, but which are quite inadequately treated. They are mathematics, physics, and analytical chemistry.

Too often the teaching of mathematics to future chemists is done by representatives of pure mathematical science. These teachers, who are mostly too specialized to have a fundamental knowledge either of chemistry or of chemical industries, cannot do more than give the students a shortened course in mathematics devoid of any practical application. Such a formal course is too easy to forget, and therefore very few chemists apply mathematical thinking to their practical problems. To eliminate this situation two alternatives are possible. Either the student (preferably in the third or second year) should be required to become versed in the fundamentals of mathematical science through outside work and prove it by passing a special examination, or mathematics should be taught by an experienced chemical engineer who has specialized in the mathematical tackling of chemical and physical problems.

The same, but in a more definite manner, is true of the teaching of physics. Physics might be considered, and rightly so, as the fundamental science of the chemist and chemical engineer. Nevertheless, in the form in which it is taught to these students, it becomes something of an average between high-school physics and the physics for the physicist. It is no wonder that students of chemistry regard physics as quite an auxiliary science, and care neither for the theoretical development of their knowledge of it nor for the laboratory work. No professor of physics who is not an experienced chemical engineer (in our enlarged meaning of this word), or at least a well-educated chemist, should occupy the chair of physics in the chemical school. The course he teaches must be so constructed as to give the future chemical worker the maximum fitness to develop the physical features of a process or an apparatus. The laboratory work in physics should occupy a far greater place in the chemist's education.

The present system of teaching analytical chemistry, although of respectable origin and development, is impractical, particularly with respect to qualitative analysis. From the beginning of his analytical study the student should be taught the elegant, clean, and exact methods of *quantitative chemistry*, and he should learn qualitative methods of identifying the chemical elements and groups incidentally, and not as a special course of study. The student must be given a large opportunity to work in the direction of analytical speed and efficiency. Such old propositions as to leave a reaction to be completed "over night" should not be allowed either in the technical laboratory or in pure scientific research. The analytical chemist, armed with a knowledge of physicochemical laws, must be able to accelerate any reaction or mechanical process belonging to his work, so that it is complete in half an hour instead of sixteen hours.

INFLUENCES OF THE PROPOSED CHANGES

Many opinions were printed on the question of how the chemical school might help the chemical industries. The form of this

question is false. There is no doubt that any profits which industry got in the last twenty-five or thirty years were derived only from the knowledge and hard work of the chemists, and that the latter only developed those principles which were given to them by the chemical schools, no matter how high or low these schools stood in matters of teaching. The chief trouble lies in a quite different direction. It is the chemist who has been too much and too long handicapped by the unfitness of his education. It is he who can never say beforehand in which line of industry he will fit in the future and who never can be sure that his innate abilities for doing this or that kind of work will find suitable application.

The proposed changes will help right many unpleasant situations of the present time, and in these particular ways:

(1) The old degrees of bachelor, master, and doctor will cease to exist. At present they help only to mix all chemists to a quite indefinite mass.

(2) The same will happen to the indefinite terms of "chemist" and "chemical engineer." They will be changed and become imbued with a far more real meaning.

(3) A quite different type of spirit will find its logical expression and as such lead to the formation of chemical social bodies having identical interests and the same social standing. Societies of analytical chemists, of research chemists, of chemical engineers, etc., can develop strong social wills, and become quite able to insure for their members proper conditions of work and remuneration.

(4) Employers will know exactly where to find the special type of chemist suited for particular needs. They will not ask a man with engineering abilities to become an analytical chemist, and the analytical chemist will not have the temptation to go in the construction bureau or to become a salesman.

RESEARCH CHEMISTS AND CHEMICAL ENGINEERS

No matter how great the changes may be that are contemplated in the system of chemical education, there will always remain two groups of chemical workers who cannot under the present system be guaranteed against unemployment in times of financial stress. These groups will include those most valuable from the standpoint of humanity and the nation, the research workers and the chemical engineers. The suggestion that employers make special provisions to hold these men through times of depression is naive in the extreme and certainly has been made without consideration of present-day economic trends. Luckily enough these two groups are small and this makes the problem of their living less difficult. It is proposed that these two groups be considered from the time they enter training as a specialized corps working for the nation. Just in the same way as the nation supports the army and navy, it should support these men for the benefit of industry. Arrangements should be made that they be available to industry in case of need, but that during times of financial depression they may be considered as governmental employees and allowed to continue their work on problems of universal application.

Then remain still three groups of chemical men who should have specialized training in order to develop their inherent features to the utmost during their stay at the chemical school. They are the research chemist, the chemical instructor, and the chemical engineer.

The Importance of "Impurities"[1]

By Jerome Alexander

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C ONTINUALLY throughout human experience principles of great importance have lain unrevealed, because no one understood or even noticed some minute or seemingly unimportant impurity which was the key to the correct understanding of the situation and would have opened the door to a big advance in knowledge. The recent recognition of vitamins has rendered necessary a complete revision of our data on food values, but there is no reason why they could not have been discovered long ago, had some one only investigated, for example, just why cod-liver oil is valued so highly. The early British explorer Captain Speke reported a then curious superstition among the Congo natives, that the coming of the tsetse fly was associated with the incidence of sleeping sickness, but scientific men took no notice of a "native superstition." Now, however, we appreciate the role of the insect carriers of disease—the mosquito for malaria and yellow fever, the wood tick for Rocky Mountain or spotted fever, the rat flea for bubonic plague, etc. Other biological instances of the devious ways of nature are found in the fungus that causes the rust in wheat, which must spend part of its life in the barberry; in the fresh-water mussel which spends part of its life in the gills of certain fish; and in the curious life cycles of the trichina and the tapeworm.

IMPORTANCE OF MINUTE QUANTITIES OF "IMPURITIES"

In considering the question of impurities from the standpoint of the chemical engineer, we must in the first place stress the point that excessively minute quantities of substances may exert

effects of technical importance. Bredig reports that one part of platinum black will decompose one million parts of hydrogen peroxide, the manufacturers of which well know the stabilizing action of such substances as acetanilide commonly used in the commercial product. According to Brodie, one mol of molybdic acid in 33 million will exert an appreciable influence upon the reaction between hydrogen peroxide and hydriodic acid. The great power of the enzymes is well known—one part of invertase will hydrolyze 200,000 parts of sucrose, and one part of rennet will clot 400,000 parts of caseinogen—although enzymes are never of 100 per cent purity. In fact, their very impurities stabilize them. According to E. F. Armstrong, lactase may effect in one hour a change that would take $2 N$ HCl at 35° C. three weeks to accomplish.

Another point to remember is that minute traces may produce results quite contrary to those produced by larger amounts. This is commonly the case with antiseptics and has been illustrated with experiments on fertilizers containing borax. Biological reactions are especially delicate—witness the tremendous power of the bacterial toxins. According to Bertrand, one part of manganese in 10 million exercises a visibly beneficial effect on the growth of *Aspergillus niger*, although Raulins found that one part of silver nitrate in 1,600,000 parts stopped its growth, and an attempt to raise the fungus in a silver cup proved futile. Duclaux, commenting on this, remarked that "it is almost impossible to detect chemically any dissolution of silver into the liquid. But the fungus proves it by dying." In view of these facts we can understand the predilection of the old-fashioned housewife for copper or brass preserving kettles, especially as

we now know the fungicidal and chromostatic action of traces of copper; also the value of baked potatoes, which retain all their soluble salts.

Surprising results sometimes follow the presence or absence of traces. Prof. H. B. Baker[2] reports enormous increases in the boiling point of liquids that had been superdried by standing some years in the presence of phosphorus pentoxide. His results showed:

	Years Standing	Increase in Boiling Point
Bromine	8	55°
Mercury	9	62
Hexane	8 1/2	14
Benzol	8 1/2	26
Carbon disulfide	1	30
Carbon tetrachloride	9	34
Ethyl ether	9	48
Ethyl alcohol	9	60
Methyl alcohol	9	54
Propyl alcohol	9	39

Absolutely pure zinc sulfide does not give luminous paint, though it is not easy to determine the activating impurities. Iodoform owes its antiseptic value to the iodine it splits off, and if catalytic impurities are absent it may fail to work—too pure a drug is valueless. Minute amounts of iodine are essential in food if goiter is to be avoided. A continually renewed supply comes into the atmosphere from colloidal sea salt resulting from the ocean's spray.

Value of Detection

Impurities may be telltales. Thus the Germans, on analyzing the British "mustard gas" (diethyldichlorsulfide), learned from the impurities present just how it was made, and scrapped their inefficient method for that of Sir William Pope.

Extreme care is necessary in detecting impurities. The rare gases of the atmosphere had been isolated by Cavendish, and W. F. Hillebrand had isolated helium from cleavite; but Sir William Ramsay's genius for taking infinite pains, revealed argon, helium, neon, xenon, krypton, and niton.

Helpful and Troublesome Traces

Traces of substances may be beneficial or detrimental, and a few instances thus classified are as follows:

Helpful Traces—The resistance of the tungsten filament, according to W. C. Whitney, is increased by traces of rare metal oxides where larger quantities have failed. The value of traces of salts in water for brewing, baking, and other operations is beginning to be appreciated, and we hear now of these being added as "yeast foods" and in "Burtonizing" water. Sodium bromate is said to have reduced the yeast bill of one large baking company from $1,000,000 per year to $500,000 per year. While 0.216 per cent of arsenic reduces the conductivity of copper 39 per cent, pure copper rolls much less readily than that containing arsenic, and yields tubes that corrode ten times more rapidly. A little lead in brass makes it machine easily and prevents chattering. The reputation of Swedish iron is due to the impurities, mainly manganese, it contains. A little copper inhibits the corrosion of steel. Small quantities of barium (0.07 per cent) harden lead and make it ring like a bell. In many alloys small quantities of aluminium deoxidize the melt and prevent atmospheric corrosion of the casting. In the electrodeposition of metals, small quantities of "addition compounds," which are in many cases protective colloids, give a desirable cathodic deposit. The experience of Auer von Welsbach, who found the great effect produced by ceria in the thoria mantle—the optimum value being about 1 per cent—is well known. Thus, in a certain flame a pure thoria mantle gives 7 c. p., whereas the standard mantle with 1 per cent ceria gives 88 c. p. With 0.25 per cent ceria the luminosity sinks to 56 c. p., while with 5 per cent ceria it is only 44 c. p.

Goodyear had no trouble in vulcanizing his rubber, because of the various nitrogenous impurities present in the crude product

[2] *Trans. Chem. Soc.,* **21** (1868).

of his day. With the advent of modern pure plantation rubber it has become necessary to add various accelerators. Old patents show that celluloid dissolved in the "wood spirits" of that day, which contained ketones in considerable quantity, but refined methanol is not a solvent for it. Traces of lead tetraethyl will take the "gasoline knock" out of an internal-combustion engine, even 0.06 per cent being effective.

Troublesome Traces—The mercaptan intermediate in making sulfonal has an appalling odor, and as one four-millionth of a milligram is readily detected, it presents a technical problem quite on a par with "poison gas." In hydrogenation the catalyst is readily poisoned. Sabatier reported that traces of bromine in the air of the laboratory made it impossible to hydrogenate phenol that had stood there in an open flask; and thiophen prevents the hydrogenation of benzol to cyclohexane. This recalls Victor Meyer's experience. While attempting to exhibit to his class his color reaction for benzol, he happened to use an especially pure benzol and the reaction failed to materialize. The failure led to the discovery of thiophen as the unsuspected impurity that had been responsible for the reaction.

When mechanical presses were used to squeeze out the grape juice for sherry wine, instead of the old method of "treading the wine press" with the bare feet, the wine did not have the right flavor. The more efficient machine introduced some of the bitter substances next to the seeds.

In making dry batteries, traces of iron in the pyrolusite, or of copper in the ammonium chloride, are highly objectionable. One part of sulfur per million of coconut oil is said to create trouble in the soap-making process. In lead burning, traces of arsenic in the hydrogen used to make it impossible to secure a good joint. Attempts to make a good nickel steel were for years frustrated by impurities present in the commercial nickel of the day.

A manufacturer of brewing sugar came to see how his new product was working in a brewery and found the brew-master running an inky black liquid into the sewer. Being a chemist, the manufacturer immediately wired his analytical department that its product was full of iron, and in reply received a telegram saying that the batch complained of had only 0.002 per cent of iron. But that was enough to make plenty of ink with the hop tannins.

Even 0.1 per cent of pyridine in ammonium nitrate used for filling shells in 80:20 admixture with trinitrotoluene, produced enough gas to cause "spewing."

The contact mass used in making synthetic ammonia is very sensitive; sulfur dioxide poisons it, as do selenium, tellurium, phosphorus arsenic, boron, and to a lesser extent lead, bismuth, and tin. Iron containing even as little as 0.01 per cent of sulfur is quite useless for making the contact body. White leather cannot be produced in the presence of traces of iron or copper. Color lakes or dyeings are thrown off shade by traces of iron, but here one may make a virtue of necessity and produce a new shade by liberal use of the impurity.

Bismuth, cadmium, and antimony injuriously affect brass. Sulfates interfere with the electrolysis of magnesium chloride and the electrolyte production of sulfates. Iron, cobalt, and especially antimony seriously affect the electrolytic deposition of zinc.

In determining hydrogen-ion concentration traces of impurities may poison the platinum electrode and give incorrect results. Very pure hydrogen sulfide, carbon disulfide, and phenol are practically without odor.

Tellurium is difficult to handle because traces are absorbed and gradually eliminated, giving the worker a frightfully unpleasant aroma.

Instances of character similar to those given are undoubtedly familiar to all. It is essential, however, to bear in mind continually the fact that so-called negligible traces may make or mar a process or a product.

Some Cartoons of van't Hoff[1]

By Ralph H. McKee

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IN THE Dutch periodicals, particularly of the weekly type, it is customary to cartoon professorial and scientific men in the public eye equally with those prominent in political life.

Professor van't Hoff was a man of particular note and as well one whose name was connected with a number of items of "news" type. Accordingly, he was perhaps more often cartooned than other Dutch scientists.

I wish to discuss one series of five by the Dutch cartoonist Braahensiek, and a multiple cartoon whose authorship is obscure but which was gotten up at the suggestion of Prof. Ernst Cohen, van't Hoff's success or at the University of Utrecht.

The five cartoons by Braahensiek had as their occasion van't Hoff's leaving the University of Amsterdam and Holland to accept the new position created for him at the University of Berlin, at the then unprecedented yearly salary for a professor of chemistry, of 40,000 marks. The cartoons are based on the old fairy tale of the fisherman and his wife as given by Grimm. You will recall how the fisherman sought favors of the talking man-

fish he had befriended, a typical conversation being as follows:

> Fisherman: "O man of the sea!
> Come listen to me,
> For Alice, my wife,
> The plague of my life,
> Hath sent me to beg a boon of thee!"
>
> Fish: "Well, what does she want?"
>
> Fisherman: "Ah! My wife wants to be king."
>
> Fish: "Go home, she is king already."

The second series of van't Hoff cartoons had as its origin the twenty-five year celebration of the passing of the examination for the Ph.D. degree by van't Hoff. At noon of December 19, 1899, in Rotterdam, was the formal celebration with its proper speeches. In the evening at the Van der Velde restaurant the family of van't Hoff, together with a large group of more intimate friends, gathered to celebrate in a more informal way. Here there was shown the multiple cartoon due to Prof. Ernst Cohen, a favorite pupil of Professor van't Hoff.

Below the small pictures you will note a number of names. These are the signatures of those present at the celebration. After these had signed the original it was given to Mrs. van't Hoff. Those present received lithographed

PROF. VAN'T HOFF: "Fish, O Fish of the sea, Bring me an appointment as a professor."

FISH: "It is done!"   (1879)

PROF. VAN'T HOFF: 'Fish, O Fish of the sea, Bring me a new laboratory building."

FISH: "It is done!"   (1892)
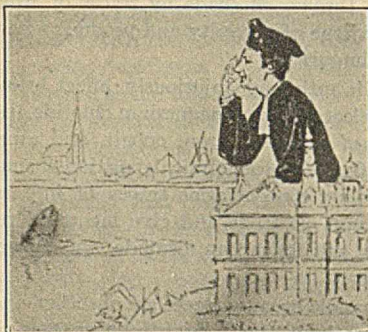
PROF. VAN'T HOFF: "Fish, O Fish of the sea, Make me a member of the Order of 'Nederlandschen Leeuw.'" (Order of Dutch "Immortals")

FISH: "It is done! Here is the insignia."   (1895)

PROF. VAN'T HOFF: "Fish, O Fish of the sea, -------"

FISH: "Have I not done enough? Adieu!"

reproductions such as the copy used by the present writer. Among the signatures more easily recognized are those of Cohen, Hoogewerff, Spring, Rooseboom, Bredig, Ostwald, van Laar, Meyerhoffer, Abegg, and Lorenz.

1—If work gave him much pleasure he would show more of it. (van't Hoff was not a hard worker in his university days.)

2—He is, let him have his pledge, in the Australian group the third. (van't Hoff and two other students, Janse and Roorda Smit, who planned to seek their fortune in Australia, often met on Saturday evenings at a certain restaurant to discuss their future doings.)

3—Activity and isomerism never leave his desk. Then he grasps his pen with eagerness and writes down "Tetrahedra." (A reference to his introduction of the concept of optical isomerism, 1874.)

4—Laboratory at Utrecht, Holland. (Professor Cohen succeeded him as head of this laboratory.)

5—Olympus here he mounts on this noble Pegasus. Herr Kolbe looks at him in astonishment, and then there comes an awful crash. ("Pegasus" is a reference to the fact that at the time van't Hoff's "Chemistry in Space" was published, van't Hoff was a professor in a veterinary college. Kolbe, then one of the leaders of the time, considered "Chemistry in Space" as foolishness.)

6—Old laboratory at Amsterdam. (This laboratory was outgrown and in 1892 van't Hoff moved to the new laboratory. See Item 10.)
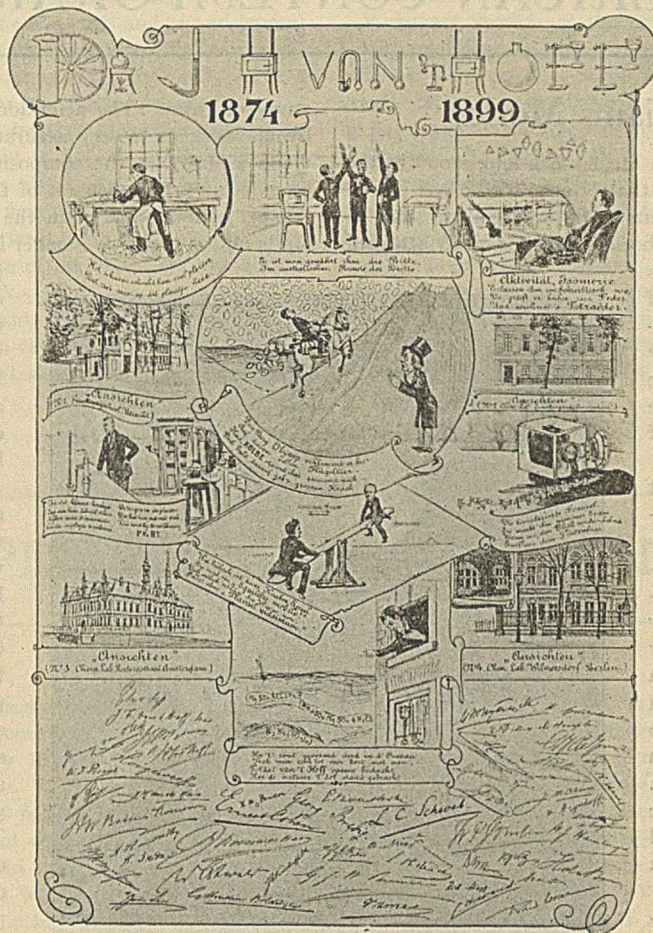
TWENTY-FIFTH ANNIVERSARY CARTOON

7—Often in his small corner he stands looking at his osmosis-meter with its enclosed membranes. The pressure in the plants did not leave him free until he explained $PV = RT$. ("Dilute solutions obey the gas laws.")

8—How pleasant is this youngster's game; they are in mobile equilibrium. But finally the seesaw goes down, even without "maximum work." (Berthelot held that the reaction evolving the maximum heat would be the reaction taking place. van't Hoff held that other factors were the determining factors.)

9—The complicated formula was no joke to him, even if it was dark to others as it flowed from his inkwell. (van't Hoff, like present-day physical chemists, was often given to using complicated mathematical formulas. His formula for osmotic pressure contained forty-one letters.)

10—New laboratory at Amsterdam. (The "Institute" built in 1892.)

11—As the ocean contents warmed, what happened was not clear, until van't Hoff opening his window found that Nature had brought him a gift. (A reference to van't Hoff's solution of the way in which the German potash beds had been formed.)

12—van't Hoff Laboratory, Berlin. (About 1897.)

Fuel Oil in Industry. By STEPHEN O. ANDROS, A.B., E.M. Second edition, 1922. Petroleum Extension University, Fort Wayne, Ind., 198 pp., 95 illustrations. Price, $3.75.

This volume has evidently been written with the idea of presenting the subject of fuel oil and its utilization in such a manner that the person having little or no training in engineering, mathematics, or chemistry can grasp the subject without difficulty. It is unfortunate that this method of presentation has not been followed as consistently as it might have been. This has been due, for the most part, to the fact that many articles relating to fuel oil have been inserted in the book, word for word, without undergoing the necessary simplifying translation. As an example of this, the first part of the book explains what the symbols for hydrogen and carbon are and how these elements unite with oxygen in definite proportions, while later on the chapter on colloidal fuel is full of words such as "colloid," "Brownian movement," "fixateur," and "peptization," accompanied by little or no explanation.

The proofreading of the book has not been done as well as it should have been. Most of the errors are not serious, but it is certainly misleading when the columns for "Saybolt Time" and "Redwood Time" are reversed in the reference table for conversion of viscometer readings, and when a table on boiler efficiencies mentions ten per cent excess oil supply, when *air* supply is meant.

The subject matter of the book has been arranged in a logical and convenient form. The first half of the book deals with the principles of oil combustion, the physical and chemical properties of fuel oil, the storage and distribution of the oil, and the furnaces and burners used for combustion. The second half takes up the specific industrial uses for fuel oil.

The chapter on fuel-oil burners is particularly complete, and the description of the various types is very clear. The later chapters on industrial uses give general descriptions of the various industries as well as the more specific application of fuel oil to those industries.

The book is well illustrated, well bound, and is printed on a good grade of paper.

Despite the obvious defects which have been mentioned, this book should be useful to those seeking a general description of fuel oil and its uses in our industries.

ALFRED R. POWELL

New buildings and laboratories, constituting a department for chemical instruction which in size and equipment is second only to that of the largest American institutions, have been opened by the Technical College of Stockholm. The dedication ceremony was performed by the King of Sweden in the presence of a large assembly of prominent educators and men of affairs. The chemical department includes four laboratories devoted to research, and instruction in organic, inorganic, and technical chemistry, and electrochemical processes.

AMERICAN CONTEMPORARIES

Edward Williams Morley

The name of Edward Williams Morley has long stood in the annals of American chemistry as that of a man who has placed the science of exact measurements both in chemistry and in physics on a plane which has not been excelled or rarely attained by any of the other investigators of the world. Fortunate indeed for these sciences were the circumstances which turned Morley from the pulpit to the college laboratory, where he became the greatest experimental chemist of his day.

In 1869 the authorities of what was then Western Reserve College at Hudson, after long deliberations and some opposition, decided to arrange for a department of chemistry, and after looking about for a teacher they persuaded Mr. Morley, then a young graduate in Divinity from Williams College, but a man who had shown while in college much interest and ability in chemistry, to leave the ministry and become the first professor of chemistry and the natural sciences in Western Reserve College.

Professor Morley was an excellent teacher, peculiar in some ways, willingly perhaps, but always stimulating and attentive to details, and possessed with a keen sense of humor. He kept a dictionary on his desk, and if a student in reciting stumbled upon a pronunciation or made an error in his blackboard work Professor Morley would hand him the dictionary with a chuckle and await his report. He aimed at efficiency, although the word wasn't heard of in those days. In order to save his limited time for research he was accustomed to correct his mathematics papers while hearing a recitation in chemistry. However, mistakes in the recitation did not pass unnoticed.

While Professor Morley has since regretted what he considered a waste of energy in his early teaching, which included what was then pretty nearly the complete range of physical science, mathematics, physics and chemistry, besides geology, mineralogy, medical chemistry (in the Medical College at Cleveland), and botany, it is possible that this wide range of work led him further along the lines that were later helpful when his work became more specialized, and it undoubtedly accounted in part at least for his wonderful breadth of knowledge on all scientific subjects. He probably has a far greater fund of exact, as well as ready, information on all kinds of scientific questions than any of his contemporaries.

Professor Morley early interested himself in the everyday problems of chemistry, such as the determination of the nature of the crystals in the substance left in the evaporating pans of the maple-sugar makers, but gradually his work turned to more important topics and centered on the accurate manipulation and study of gases. The attention of chemists was first attracted by his work on a very accurate series of analyses in which he made a study of the composition of air.[1] He obtained specimens of air from all parts of the world and demonstrated that the per cent of oxygen in the air varies between very narrow limits and is probably smaller in the higher strata of the atmosphere. He worked on this in coöperation with chemists in Europe, and as the result of his work announced the so-called Morley-Loomis hypothesis, which accounts for the variation in the composition of the air with changing barometric pressure.

Professor Morley began his famous determination of the atomic weight of hydrogen and oxygen while the college was still at Hudson, and finished it some time after the college moved to Cleveland. With characteristic thoroughness Morley carried out preliminary researches on the amount of moisture which sulfuric acid leaves in a gas,[2] and the amount of moisture left in the gas by phosphorus pentoxide.[3] These researches on the density of oxygen and hydrogen and the ratio of their atomic weights, published in 1895 as *Smithsonian Contribution to Knowledge No. 980*, remain to this day unequaled for accuracy and thoroughness, and are the same as the accepted values for these constants upon which our present system of atomic weights is based. He devoted more than ten of the best years of his life to the measurement alone of this elaborate determination, with the result that his health broke down under the strain of overwork before the researches were completed. He later designed an accurate gage for measurement of small pressures,[4] which he applied to the careful determination of the coefficient of thermal expansion of gases in collaboration with Dayton C. Miller. He also made a very careful determination of the vapor pressure of mercury[5] from zero to 100° C.

While working on the problems of gases, he was coöperating with A. A. Michelson on experiments to determine the relative motion of the earth and the luminiferous ether,[6] and performed the famous so-called "ether drift" experiments, which are the basis of the modern theory of relativity and have made physicists question the existence of the ether. Later Professor Morley, in coöperation with Dayton C. Miller, repeated these experiments in view of the Lorentz-Fitzgerald suggestion that the size of bodies may depend on translation through luminiferous ether.[7] He first proposed establishing a light wave
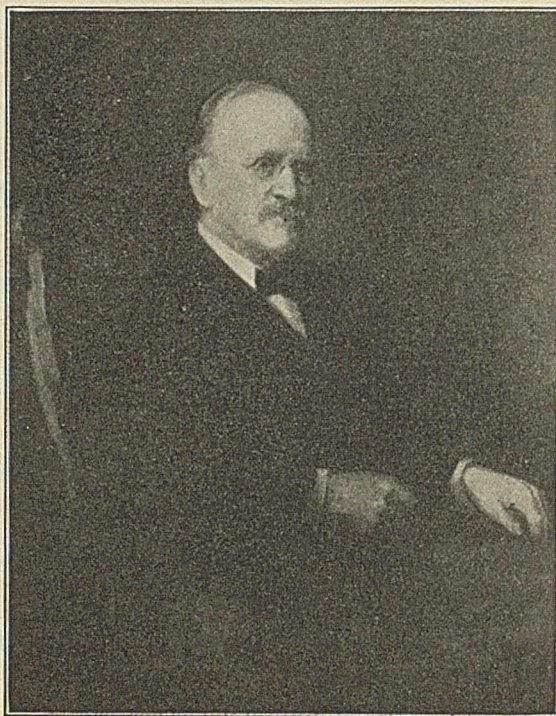
EDWARD WILLIAMS MORLEY

[1] *Am. J. Sci.*, [3] **18** (1879), 168; **22** (1881), 417; **22** (1881), 429.
[2] *Ibid.*, [3] **30** (1885), 140.
[3] *Ibid.*, [3] **34** (1887), 199; *J. Am. Chem. Soc.*, **26** (1904), 1171.
[4] *Am. J. Sci.*, [4] **13** (1902), 455.
[5] *Ibid.*, [4] **18** (1904), 83.
[6] *Ibid.*, [3] **31** (1886), 377; [3] **34** (1887), 333.
[7] *Proc. Am. Acad. of Arts and Sci.*, **41** (1905), 321.

as the ultimate standard of length,[8] and later developed the apparatus and method in collaboration with A. A. Michelson.

Of the fifty-two papers he has published, twenty-three are in pure physics, twenty-seven in pure chemistry, and two on general subjects. He had four collaborators in scientific work—all physicists. The physicists have always felt that they have a strong claim on Professor Morley as one of their group.

Professor Morley has been an indefatigable worker, frequently spending three-fourths of the night in his laboratory and then being on hand in the morning for his classes. In his work, he had the active, intelligent, and sympathetic interest of Mrs. Morley, who during her lifetime frequently spent the evenings helping him look up the literature of his investigations and in many ways assisted him in his work.

With his habits of clear thinking, precision, thoroughness, and carefulness, which led him to clear-cut plans of operation, there was combined a mechanical skill of a very high order,

which was evidenced in his expert glass-blowing, in his skillful manipulation, and in the elaborate attention to details in his experimental work.

Fortunate indeed are the chemists and physicists who have had the privilege of knowing him and working with him. Not only has he a mind of rarest quality, but a kindliness equally great. This has frequently been evidenced by the assistance he has always been ready to give his friends and acquaintances.

One of his friends, C. F. Mabery, has said, "Such examples of devoted application to the expansion of knowledge concerning the fundamental forces of nature as that of Dr. Morley's wide range of effort are greatly needed as an inspiration to the present generation. For, with the aid of all the modern appliances, the present worker must understand, first of all, that there never has been and never will be but one way to overcome the resistance of natural forces—by the application of persistent and well-directed labor."

HAROLD SIMMONS BOOTH

[8] *Am. J. Sci.*, [3] **38** (1889), 181.

PERKIN MEDAL AWARD

The Perkin Medal was presented to Dr. Milton C. Whitaker at a meeting of the American Section of the Society of Chemical Industry on January 12, 1923, with introductory remarks by Dr. Ralph H. McKee.

The Perkin Medal is awarded for the most valuable work in applied chemistry. This medal was founded in 1906 at the time of the Perkin semicentennial celebration of the coal-tar dye discoveries. The first medal was awarded to Sir William H. Perkin himself in 1906. All other awards have been and must be to chemists resident in the United States. As will be seen in the following list, the men who have since received this award form a nearly complete roster of the great industrial chemists of America of this century.

DATE OF AWARD	AWARDED TO	PRINCIPAL FIELDS OR 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 aluminium
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; electro-deposition of metals; flaming arc
1916	L. H. Baekeland	Velox photoprint paper; bakelite and synthetic resins; caustic soda industry
1917	Ernst 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	Achievements in oil industry: efficient conversion of high-boiling fractions into low-boiling fractions

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Impressions

By A. A. Backhaus

The committee has suggested that I give an impressionistic view of the Medalist, or, as someone has put it, "a close-up out of focus." A close-up on so large a subject is very likely to be out of focus.

During the summer of 1914, Dr. Whitaker, then head of the Chemical Engineering Department at Columbia University, was seeking an assistant. Professor Chambers, with whom I had done my undergraduate work, recommended me. The job was offered me and I accepted it. The entire negotiation consisted of but two letters, one in which the position was offered me, the other in which I accepted, although neither of us knew the other. I arrived in New York on the morning of September 16, and in the afternoon I reported to Havemeyer Hall, Columbia University, wondering what my new boss was going to look like. Dr. Whitaker was in his office, seated at his desk, completely filling a roomy chair. He had his coat off, sleeves rolled up, hair ruffled, and was hard at work as one usually finds him. I was impressed, not only by the size of the man, but also by his speed, "his velocity coefficient," for before I knew it I had been hustled into the laboratory and put to work. From that day until now I have been honored in calling Dr. Whitaker my boss.

Dr. Whitaker has an unusually keen insight into chemical processes and chemical plants. He can size up a plant operation, see the weak spots, and suggest remedies or improvements. He invariably turns the spot light on jokers in proposed new processes. His mind not only grasps broad features and general principles, but also takes in minute details. In this respect he sometimes exhibits an almost uncanny faculty of pouncing upon some minor detail. Such an instance occurred in connection with the installation of a new plant unit not long ago. The equipment for this installation had all been ordered and deliveries were being made when a letter came from Dr. Whitaker asking if the packing material for a certain part of the installation had been ordered. Investigation showed that it had been overlooked. Another instance of this kind came up in connection with a newly designed heater. This job was in the shops under construction when Dr. Whitaker asked whether manholes had been provided for inspection and repair of the tubes. While the drawings did not show these manholes, the equipment came from the shops provided with manholes. Experiences of this kind have at times made Dr. Whitaker impatient with engineers. Dr. Whitaker's viewpoint is distinctly that of the operator. He visualizes the operation and in his imagination goes through

all the operator's motions, and in this way usually picks out defective designs in equipment or installation.

Dr. Whitaker has said on several occasions that the successful plant or works superintendent must have the faculty of instinctively "happening on the spot" at the psychological moment. Nothing grates on his sense of the fitness of things more than to see a wooden case opened with a hatchet. One day while touring the plant he happened on a man breaking open a case. He immediately had orders issued to have nail-pulls purchased for every department receiving cases and a ban put on the use of any other tool for this purpose. These instructions were drilled into all the men handling cases until the practice of using the nailpull was firmly established. Three months after establishing this rule Dr. Whitaker again visited the plant and in one of the storerooms happened on a man mutilating a case with a hatchet. This was probably the only instance of breaking the rule in the entire three months.

I have often been impressed with the fact that Dr. Whitaker can make a little chemistry go farther than any man I know. This applies not only to chemistry but to other information. The ability of applying knowledge or practice from an unrelated field to a problem at hand comes up again and again.

It is probably not necessary to dwell upon the ability of Dr. Whitaker to express himself in clear and forcible English. His clearness in expression is due to his extensive vocabulary and his apt choice of similes and metaphors. Many here have probably heard him speak of research chemists as prima donnas who must be handled with kid gloves. The internal revenue regulations require records which will enable them to trace every individual package of alcohol from the plant where it is made to the ultimate user. This Dr. Whitaker calls "tagging the molecules." He describes a consulting man as one who comes into your plant, looks around, bellyaches about everything, and sends a bill. Unfortunately, his most picturesque expressions would not appear well in print.

In the beginning I referred to my meeting Dr. Whitaker. I recall very vividly his first remark, "Well you reported on time." Dr. Whitaker is very punctual in his appointments and expects others to be the same.

Dr. Whitaker is big hearted and sympathetic and always willing to help anyone in trouble. A few years ago while professor at Columbia University he was aroused out of bed late one night by the telephone. The son of one of his college-professor friends was at the other end of the wire. He said he was being locked up because of some scrap on the Bowery and wanted help. Dr. Whitaker dressed, went down town, and arranged for bail with a professional bailer and got the lad out.

No doubt a considerable part of Dr. Whitaker's success is due to his ability to pick men. On a recent visit to the Welsbach Plant at Gloucester, N. J., where Dr. Whitaker was plant superintendent from 1903 to 1910, I was impressed with the fact that the men forming the backbone of the present Welsbach organization were the men developed and installed by Dr. Whitaker during the time that he was connected with that company. In his make-up Dr. Whitaker is essentially an organization or corporation man. He does not take personal credit, but rather shares it with his co-workers. He not only stimulates thought on the part of those associated with him, but also inspires confidence, loyalty, and willingness to work. He goes at his work with enthusiasm and makes everyone working with him enthusiastic. I have often heard men say that if it were for anybody else they wouldn't do it, but seeing it is for Dr. Whitaker they will do it.

Dr. Whitaker differs from many other executives in that he thinks his problems out clearly and completely. He not only fixes a definite goal, but also works out in his own mind at least one good way of reaching it. In all his dealings with his men he plays the game with all the cards on the table.

Milton C. Whitaker

By Arthur D. Little

Men are sometimes distinguished for what they do and sometimes for what they are. More rarely are we permitted to honor them for both. Milton C. Whitaker is a chemist, who has earned distinction by his works, but he is first, last, and all the time a man.

The realm of chemistry is not a single and isolated state, nor are its workers unionized. It is, instead, a commonwealth of federated nations, each rich in resources of its own which require special aptitudes for their development.

So it happens that chemistry can only realize the potentialities of her estate through the coördinated efforts of workers of many types and with diversified endowment. Some must be patient and persistent garnerers of facts and gleaners of detail; others, highly skilled manipulators to divide that which we have called the indivisible. Some must be students and thinkers, whose thinking leads to generalizations. There must be teachers and expounders, to spread the truth; and doubters and disputants, lest error pass for truth. Finally, that mankind may derive material benefits from these accumulations of knowledge, there must come the organizer and doer, whose bottles are tank steamers, whose test tubes are digesters, and whose beakers, 50,000-gallon tanks. As student, teacher, editor, Milton C. Whitaker has won high place in our esteem, but to-night it is primarily for his position and achievement as the organizer and the doer that we are met to honor him.

Those of us whose professional activities center in the study, the classroom, or the laboratory are commonly inclined to award a disproportionate meed of merit to that one whose discovery of fact, material, or reaction supplies the basis for a great industrial development. They seldom recognize or appreciate the obstacles and difficulties along the steep and rocky road which leads from the laboratory to the plant. They do not see the caulkers on the first Burton still closing the leaking seams between hot boiler plates in an atmosphere of gasoline. They do not know how it feels to work sixty-four hours at a stretch to push along repairs, or how Saturday looks on Friday with no money in the bank to meet the pay roll. It is a wise invention that knows its own father. Countless examples can be adduced to show that the organizer, the adapter, the engineer, plays a part in the development of industry that is often vastly more constructive than that of the discoverer. We commonly and properly attribute the telephone to Bell, but the instrument, as we know and use it, is the child of many minds and the godchild of the organizer. Braconnot, in 1819, effected in a laboratory operation the conversion of cellulose to sugars and through them to alcohol. It required thereafter nearly a century of effort to transform that relatively simple laboratory procedure into a commercially operative process. The vast and intricate coal-tar industries, which have so greatly stimulated chemical science, owe their many-sided development as certainly to the organizer and administrator as to the laboratory worker, even though that worker be Perkin himself. It is, therefore, peculiarly fitting that the medal which commemorates Perkin's great contribution to our science and to industry should this year be bestowed on one who has shown superlative ability in the application of chemistry to industry on the grand scale; who has the faculty of sensing fundamental principles and necessities in their broad commercial and economic relationships and of building on them great producing agencies.

Milton C. Whitaker was born in Frazeysburg, Ohio, December 16, 1870. Doubtless there were boys in Frazeysburg who tried to lick him, but history records none who did. Later, his family moved to Colorado, and during the four years beginning with 1890 young Whitaker worked in the various lumber mills of

Stubbs and Jakway, cherishing always the ambition for a college education and a degree in chemistry. The youth showed the quality of the man, and concerning his work the testimony of his employer may be thus summarized: Ability as a mechanic was evident from the first and with it a natural and unusual power to grasp details and detect and remedy defects in plant and operation. He soon became master-mechanic, and when a little later, owing to the exhaustion of the local supply of timber, it became necessary to dismantle the mill, transport the equipment, and reërect and house it on a new site, the task was assigned to Whitaker. So well did the youth repay the confidence that the new mill proved the most successful that the company had operated. In 1896 the company decided to build another mill, and for this Whitaker, though then at college, prepared the working plans and during his summer vacation supervised construction. It was a good mill, of which its owners said years afterward, "It has not lost a single day because of faulty construction."

So Whitaker earned and saved and studied until in 1897 he was graduated from the University of Colorado with the coveted B.S. degree. Degrees have this in common with olives in a bottle and the kisses of a girl—the first one is hard to get, but the others come more easily. An M.S. from Colorado followed in 1900 and an LL.D. in 1913, and to these the University of Pittsburgh added Doctor of Chemical Engineering in 1915.

Following his graduation Whitaker became instructor in chemistry at Colorado, and in 1898 tutor in chemistry at Columbia. Here he came under the benign and stimulating influence of that honored and beloved dean of applied chemistry in America, Dr. Charles F. Chandler, whom he was privileged to serve as private assistant for nearly four years. That in itself was a liberal education.

Whitaker's intimate contact with chemical industry and his constructive influence thereon began in 1902, when he went to the Welsbach Company as chemist, on the recommendation of Dr. Chandler, who had for years been its consultant. From Whitaker's associates in this new connection one learns that his impress on the organization was almost immediate and ultimately profound. He was at first engaged on work of a purely chemical character in the laboratory under the direction of Dr. H. S. Miner, but through the laboratory he was gradually brought into general touch with the operations of the plant. Whitaker had been with the company only five or six months when Dr. Miner came down with typhoid fever, and the responsibility for production fell upon the shoulders of his assistant. As we should now expect, Whitaker handled affairs in the plant in a masterly way, going at once to fundamentals, and, as troubles arose, finding the means and methods for the prevention of their recurrence. Collodion was the bugbear of the industry. Its viscosity with the same solvent and concentration varied over wide and confusing range. As with most colloids, at that time little was known concerning methods of controlling this disturbing factor. Whitaker promptly secured a man experienced in the manufacture, installed a small plant, and worked out the problem of control with large resultant savings and the elimination of many difficulties elsewhere in the factory.

It was not long before he was made general manager of the company, and he immediately initiated a general campaign for the improvement of the hidebound methods of the mantle industry. He worked out a new flow sheet and rearranged the factory. He enunciated the principle that "a man is as good as his boss," and with this sense of responsibility for their performance, he picked leaders with a wise discretion and developed them into departmental heads. His ambition was to evolve a self-contained plant and an organization he could leave. He fixed responsibilities and demanded results, organized weekly conferences, established systems of reports that

stimulated healthy rivalries, wrote historical and educational bulletins for the sales department, developed a research laboratory and a system of control throughout the plant, built a clubhouse for girl employees, installed a hospital, invented testing machines. He put in a print shop to obviate delays, a lamp shop to broaden sales, a development shop for the incubation of new mechanical ideas. By standardizing the process of collodion dipping he saved twenty per cent of the collodion used. He substituted the electric drive for rope transmission, developed machines to replace hand labor, invented the present system of packing the fragile mantles, and improved the equipment and methods of the bleaching room. In short, he was responsible for betterments in practically every stage of the manufacture in the company's plants at Gloucester, N. J., Chicago, and Columbus, Ohio, and he left his impress on the industry from the time the order was received until the goods went out on the platform. It is an achievement to handle material efficiently. Whitaker did far more. He developed *esprit de corps* in men and women, created an organization from human beings, and secured and held their warm affection. Small wonder is it that during his connection with the Welsbach Company costs of production went down steadily and its business more than doubled.

It was with such a background of achievement and experience that Whitaker returned to Columbia in 1910 as professor of chemical engineering. Of his work and influence while there we cannot do better than record the impressions of a student whom he inspired, of a close associate who worked with him in understanding sympathy, and of Dr. Nicholas Murray Butler, his administrative chief.

The student says:

It was heretical to cut one of Dr. Whitaker's lectures, and there were never any heretics. A class convening for a quiz on multiple-effect evaporation would find, after the bell had rung, that the subject of discussion was the longshoremen's strike just declared that day in New York City. The quiz on evaporation would be given at the following session. In the meantime, wages, living conditions, labor policies, and legislation were moved down stage for closer inspection. A chance remark by someone in the class would cause the interruption of the order for the day while some principle of professional ethics, industrial justice, or downright decency was explained in a manner that left an indelible impression on the minds of young men. The verbiage of technical texts was never heard in Dr. Whitaker's classes. Even in the routine of teaching fundamentals, things sounded different, more tangible, more homely. And when those fundamentals were brought forth for application to practical problems the pedagogic atmosphere was dispersed completely. Dr. Whitaker's students have perhaps forgotten where they first learned how to select the right type of filter press, but they will always remember who taught them to think like engineers and to behave like men.

The estimate of the associate is this:

Nothing but a long talk could possibly cover the subject of Whitaker and his work. I suppose his outstanding characteristic might be called moral and professional courage, with a very high order of sales ability. He loved a problem, he loved to dig out its solution even more, but most of all he loved to put his solution across, to sell it against opposition. At Columbia he made Chemical Engineering. Without him it would never by any feature of identity have been distinguishable from Industrial Chemistry. This is history that went beyond Columbia.

Dr. Butler writes:

I rejoice at the good news that Dr. Whitaker is to receive the Perkin Medal. He certainly has earned it. He showed while with us marked initiative, administrative capacity, and single-minded devotion to science. He realized to the full the close interrelations between what is sometimes called pure science and what is sometimes called applied science, and he labored effectively to promote and to develop these relations. So vigor-

ous was his work and so large his influence that a Department of Chemical Engineering was in fact, even earlier than in form, set off from the Department of Chemistry and put under his direction. We look upon him as one of our own and follow his career with pride and satisfaction.

Dr. Whitaker had always maintained that the effective teaching of chemical engineering required of the teacher close and continuing contacts with industry. In developing such contacts for himself, he soon established relations with those who stood within the circle of opportunity. His executive ability, soundness of judgment, and technical attainments were quickly recognized. He gained the confidence of capital and effected that difficult synthesis which involves the combination of chemistry and finance. As a result, he was called in 1916 to become manager and in 1917 president of the Curtis Bay Chemical Company and, following reorganizations, president of the United States Industrial Chemical Company, and vice president and director of the United States Industrial Alcohol Company. In this latter capacity his position is, in one respect, undoubtedly anomalous. Most manufacturers strive to pass on to their customers the best they can produce. Whitaker turns out a product of surpassing purity, for which the demand is well-nigh universal, and he then deliberately, if not indeed maliciously, adds to it objectionable and insalubrious compounds which remove it from our sphere of nonprofessional interest.

The technical operations for which Whitaker is ultimately responsible in these two great companies are conducted on a scale of amazing magnitude. They afford convincing evidence of the fundamental importance of alcohol as an industrial raw material, and justify the demand of our profession for less burdensome and more intelligent regulation of its industrial use.

The basic activity of these plants is, of course, the manufacture of alcohol from molasses, which in the sugar-producing countries was formerly thrown away in vast amounts. Obviously, however, when alcohol is made on the grand scale, fermentation by-products, though of small percentage value, assume a large significance. Here aldehydes, as well as alcohol, are utilized in vinegar-making, fusel oil is split into its component alcohols, the carbonic acid, carefully purified, is compressed in cylinders, sulfate of ammonia and potash are recovered from the distillery slop by evaporation in multiple effect and furnacing.

The alcohol itself is marketed in many forms, each involving special operations. It may go out as tax-paid alcohol, 95 per cent or absolute, or as spirit denatured to meet the requirements of special industries or uses. Much is converted to the familiar solid alcohol and such amounts to tincture of iodine as to require a separate plant for the purification of the element by steam distillation. Many thousands of gallons of anhydrous alcohol are daily mixed with gasoline to produce the motor fuel, alcogas. To those who, like ourselves, have regarded absolute alcohol as a laboratory luxury and who are familiar with the refinements required for its preparation, its production on this scale and at a cost permitting such use stands forth as a conspicuous technical achievement.

Nowhere in the world is vinegar produced on so vast a scale as here; yet the vinegar plant has the solemn stillness of a deserted church. The innumerable operatives engaged in transforming alcohol to acetic acid are raised upon the ground. Their contract with the management is brief, but definite. It is "No beer, no work."

This colossal production of vinegar began early in 1916 as a war measure to relieve the strain upon acetate of lime and the wood distillation industry, owing primarily to the British demand for acetone as the colloidizing agent for cordite, and intensified by the requisitions for cellulose acetate as a dope for airplane wings. The initial difficulties encountered resulted

in Whitaker's engagement and demanded the utmost of his technical knowledge and administrative skill. With the hearty and generous support of his directors the immediate problems of production were soon solved. An especially liberal appropriation for continuing research was secured, laboratories were built and organized, and in six years all the present diverse activities of the United States Industrial Chemical Company were developed. The laboratories themselves constitute an impressive and educational example of the organization of industrial research. There are laboratories for chemical and bacteriological control, others for research and development, with finally a semi-works laboratory with development equipment of all sizes. The assembled unit plants, in which the multifold operations of the company are now conducted, are a monument to the earning power of such wisely directed and generously supported research when coupled with sound chemical engineering and sober business sense. The products of the company now include five alcohols, about forty different esters, some of which are made by notable new processes, acetone, ether, compressed ethylene, diethyl carbonate and phthalate, potash and ammonia salts, mixed fertilizers, and other materials related to the alcohol industry. That is what M. C. Whitaker has developed from an ailing war baby, whose purpose in life was the making of vinegar and acetone.

The range of Whitaker's professional work is further demonstrated by the varied subject matter of the twenty-two patents granted him as sole or joint inventor. Of these, fourteen are in the former class. Among the inventions covered are containers for fragile gas mantles and those for gases and volatile liquids; processes of gas manufacture, distillation, pulping resinous woods, recovering catalysts, and making ethylene; apparatus of varied types and motor fuels. With it all he has found time to publish important papers, to the number of twenty-five, dealing with such diversity of topics as the rare earths and their place in industry, water gas and oil gas, the war supply of nitrogen, the cracking of hydrocarbons, the carbonization of coal, and many others.

As members of the AMERICAN CHEMICAL SOCIETY, we gratefully acknowledge our own signal indebtedness to Whitaker for his upbuilding of *The Journal of Industrial and Engineering Chemistry*, and for the stimulus of his editorials during the six years ending with 1916. If you would know Whitaker himself and his professional and business attitude, go back to his famous editorial of September, 1912, on "Fussy Administration." If you are an executive, or if you hope to be one, it will give you something to think about.

To the profession generally Whitaker has given generously of his time and effort. In 1911 he served as chairman of the New York Section of the Society of Chemical Industry, and in 1914 as president of the American Institute of Chemical Engineers. He was for several years a member of its Committee on Chemical Engineering Education, and in December, 1910, presented clean-cut, constructive suggestions in a paper on "The Training of Chemical Engineers." From 1915 to 1917 he was president of the Chemists' Club, and that honorable office is no sinecure. While carrying his great responsibilities for the production of war materials at Curtis Bay, he served for two years as advisor to the War Industries Board.

Such, in brief outline and under dim illumination, is the career of the man whom we are proud to honor to-night. We award the Perkin Medal to him because he has shown himself to be a great constructive force in the field of applied chemistry, but it is his intensely human quality for which, after all, we value him most dearly. His corpuscular count is high. He knows men and handles them with consummate skill. He can call a spade a spade, and if necessary he can call it something a whole lot worse.

Presentation

By Charles F. Chandler

It is my privilege as the senior past president of the Society of Chemical Industry residing in this country to make the actual presentation of the Perkin Medal to my very dear friend and our distinguished brother chemist, Milton C. Whitaker.

He was born in Frazeysburg, Ohio, December 16, 1870. His father was R. B. Whitaker, Lieutenant, 51st Ohio Volunteers, during the Civil War. His mother was Jennie Magruder, of West Carlisle, Ohio. His two brothers, Orvil R. and Frederick, are mining engineers. The family moved in 1880 to Colorado, and Whitaker attended the Durango public schools. He graduated from the Boulder School in 1887, and from the Colorado State Preparatory School in 1890.

During the next three years he worked as mechanic and millwright in the lumber mills of the Southwest, where he designed and erected two large mills for the Mancos Lumber Company. In 1893 he returned to college, at the University of Colorado. Prof. Charles S. Palmer was at the head of the department of chemistry, and he made chemistry so interesting, even fascinating, that Whitaker could not resist the impulse to choose chemistry for his life work. So he made chemistry his major subject, studying at the same time mineralogy, geology, petrology, metallurgy, assaying, mechanical and electrical engineering. He also assisted in the chemical laboratory, and as instructor in chemistry did some teaching in this department.

He received from this university the degree of Bachelor of Science in 1897, of Master of Science in 1900, and in 1913 the degree of LL.D. In 1915 he received from the University of Pittsburgh the degree of Doctor of Chemical Engineering. He was married in 1900 to Mabel Martin of Denver, member of the class of 1898 of the University of Colorado. He has two sons, aged twenty and sixteen.

In 1898, when seeking a suitable chemist to take charge of the sophomore class in Columbia College, I had the good fortune to make the acquaintance of Dr. Whitaker. I decided at once that he was the man for the position, and had him appointed an instructor in chemistry. As we became better acquainted I was surprised to discover what a capable and reliable chemist he was, and I induced him to give me his spare hours and days as my associate in consulting and expert work in my private laboratory.

In 1902, Waldron Shapley, chemist for the Welsbach Light Chemical Company at Gloucester, N. J., died, and Mr. Sidney Mason, president of the company, applied to me for a competent chemist to fill the position, which was a very important and responsible one. Very reluctantly I felt obliged to tell him that by far the best and most reliable man for the position was Dr. Whitaker. When he met him and talked the matter over with him he was so impressed by him that he engaged him at once. He was immediately installed as chemist, and in 1903 was made superintendent of all the manufacturing departments.

He devoted the following seven years to directing research work, solving chemical and engineering problems, and the development of the factories at Philadelphia and Columbus. During 1908, 1909, and 1910, he was a special lecturer on works management at the Massachusetts Institute of Technology.

On my retirement from my duties at Columbia University in 1910, Dr. Whitaker was appointed professor of industrial chemistry and chemical engineering, a position which he filled to the great satisfaction of the department and of the students. He converted the basement of Havemeyer Hall into a most comprehensive chemical engineering laboratory by setting up a typical chemical plant equipment. His outfit included: single- and multiple-effect evaporators, filter presses, agitator tanks, siphon and air-effect pumps, absorption towers, centrifugals, separators, vacuum stills and dryers, multiple-series percolators, distilling columns, crystallizers, grinding equipment, machine shop, pipe shop, and private research laboratories.

In 1916 he became general manager of the Curtis Bay Chemical Co., and in 1917 its president. In November of that year he became president of the U. S. Industrial Chemical Co., successor to the Curtis Bay Co., and also vice president and director of the U. S. Industrial Alcohol Co., positions which he still retains. He was for a time advisor to the War Industries Board.

He remained at the head of the Chemical Engineering Department of Columbia for six years, until 1917, and when he left it he had built up an efficient and well-organized department, comparable with any similar organization in this country or abroad.

From 1911 to 1916 he was also editor of *The Journal of Industrial and Engineering Chemistry*, one of the official journals of the American Chemical Society. He improved this journal very materially, put it on a paying basis, and largely increased its circulation.

He was chairman of the New York Section of the Society of Chemical Industry, vice president of the American Institute of Chemical Engineers, and president of the Chemists' Club.

U. S. Patents Granted to M. C. Whitaker and Associates

Patent No.	Date Patented	Subject
1,030,954	July 2, 1912	Protective container for mantles
1,031,219	July 2, 1912	Protective container for mantles
1,003,559	September 19, 1911	Storage of acetylene[1]
1,123,827	January 5, 1915	Water-soluble coffee extract[1]
1,123,828	January 5, 1915	Coffee extract[1]
1,110,850	September 15, 1914	Process of distillation
1,242,624	October 9, 1917	Removing nickel from hydrogenized fat or oil
1,142,922	June 15, 1915	Process of treating resinous woods[2]
1,327,001	January 6, 1920	Manufacture of gas[3]
1,348,766	August 3, 1920	Apparatus for manufacture of gas[3]
1,405,809	February 7, 1922	Liquid fuel mixture
1,400,192	December 13, 1921	Process of obtaining potassium compounds
1,376,662	May 3, 1921	Process of obtaining alcohol and potassium compounds
1,396,389	November 8, 1921	Catalyzer apparatus
1,421,640	July 4, 1922	Ethylene from alcohol[4]
1,402,329	January 3, 1922	Apparatus for producing ethylene[4]
1,421,879	July 4, 1922	Liquid fuel
1,420,006	June 20, 1922	Internal-combustion-engine fuel
1,423,058	July 18, 1922	Fuel for internal-combustion engine
1,420,007	June 20, 1922	Fuel for internal-combustion engine
1,400,193	December 13, 1921	Container for volatile liquids

	Design	
58,281	June 28, 1921	Design for fuel container

[1] Whitaker and Metzger.
[2] Whitaker and Bates.
[3] Whitaker and Rittman.
[4] Whitaker and Backhaus.

Articles by M. C. Whitaker, *et al.*

"Olivinite and Picrotitanite from Magnolia District," *Proc. Colorado Sci. Soc.*, **1898.**

"The Rare Earths, Their Production and Application," *J. Ind. Eng. Chem.*, **1** (1909), 235. (Whitaker and Miner.)

"Improved Working Conditions in the Welsbach Company's Works," *Progressive Age*, August 15, 1910, p. 710.

"Incandescent Gas Mantles." Lecture delivered at Johns Hopkins University, October and November, **1910.**

"Incandescent Gas Lighting," *Trans. Ill. Eng. Soc.*, **5** (1911), 429.

"Chemical Engineering and the New Laboratories at Columbia University," *J. Ind. Eng. Chem.*, **5** (1913) 304. (Whitaker and Murphy.)

"Encouragement of American Development," *Chem. Eng.*, **18** (1913), 223.

"Chemical Utilization of Southern Pine Waste," *J. Ind. Eng. Chem.*, **6** (1914), 289. (Whitaker and Bates.)

"Thermal Reactions in Carbureting Water Gas," *Ibid.*, **6** (1914), 383, 472. (Whitaker and Rittman.)

"Some Professional Obligations." Presidential Address before American Institute of Chemical Engineers. *Chem. Met. Eng.*, **12** (1914), 437.

"Time Factor in Making Oil Gas," *J. Ind. Eng. Chem.*, **7** (1915), 484. (Whitaker and Alexander.)

"Albert Plaut Obituary," *Ibid.*, **7** (1915), 715.

"Bibliography of the Chemistry of Gas Manufacture," *Bur. Mines, Tech. Paper* **120** (1915). (Whitaker and Rittman.)

"High Explosives," *Columbia News*, **7** (1916) 581.

"Decomposition of Hydrocarbons and the Influence of Hydrogen in Carbureted Water-Gas Manufacturing," *J. Ind. Eng. Chem.*, **8** (1916) 593, 601, 684, 695. (Whitaker and Leslie.)

"Industrial Alcohol's Promising Future," *Journal of Commerce*, February 5, 1917.

Address on Alcohol before the Franklin Institute, November 21, 1917.

"Our Nitrogen Demand and Supply in the Event of War," *J. Ind. Eng. Chem.*, **9** (1917), 204.

"The Effect of Temperature and Duration of Reaction in the Formation of Light Oils in Coal Carbonization at Atmospheric Pressure," *Ibid.*, **9** (1917), 261. (Whitaker and Crowell.)

"Comparative Study of the Thermal Decomposition of Coal and of Some of the Products of Its Carbonization," *Ibid.*, **10** (1918), 431. (Whitaker and Suydam.)

"Manufacturing Consumers Make Pleas for Change in Alcohol Regulations," *Oil, Paint Drug Rep.*, **98** (1920), 29.

"Personalities." Award of Perkin Medal to Dr. C. F. Chandler. *J. Ind. Eng. Chem.*, **12** (1920), 183.

"Protest against New Volstead Bill Manufactures. Denounce Pending Measure as Menace to Drug and Chemical Industries. Enforcement Officials Lack Knowledge of Legitimate Uses of Nonbeverage Alcohol," *The Pharmaceutical Era*, **54** (1921), 233.

"Industrial Alcohol and Its Relation to Prohibition Enforcement from the Manufacturers' Standpoint," *J. Ind. Eng. Chem.*, **13** (1921), 647.

"Charles F. Chandler, Dean of American Chemists," *Ibid.*, **14** (1922), 977.

Conferring the Medal

Dr. Milton C. Whitaker,

My dear Friend:

It gives me the greatest pleasure, as the representative of the Society of Chemical Industry and the affiliated chemical and electrochemical societies of America, to place in your hands this beautiful Perkin Medal, as a token of the appreciation and affection of your fellow chemists.

Acceptance

By Milton C. Whitaker

I have always believed that the Perkin Medal is the greatest honor that can be conferred upon a chemist by his fellow workers. I am accordingly deeply appreciative of the distinction which your committee has bestowed upon me, and doubly grateful to receive the beautiful symbol of the honor from you, sir, a Perkin Medalist yourself and by unanimous consent the beloved dean of our profession.

It has been my good fortune to be an organization man rather than an individual worker. Achievements which have resulted in the award of the Perkin Medal to me are necessarily, therefore, achievements of the men with whom I have worked. It would be a pleasure to catalog the names and individual accomplishments of these men, but the list would be so long and involved that it is probably better at this time to generalize. Accordingly, the medal is accepted by me, in a representative capacity, as a distinguished honor conferred by the American chemical profession on these men with whom I have been associated in the thirty years devoted to study and practice in the field of applied chemistry.

Organization for Chemical Production

Organization for this or that purpose is a venerated topic for speech makers—especially efficiency experts and others with more or less amateur standing. Organization for chemical development and production has been spared much of this limelight, probably because of the new elements introduced and the greater difficulty in understanding the problem or even the language of chemical industry.

Nevertheless, the fact must be recognized that no program of chemical production can be carried through without an adequate organization, any more than mechanical production can be accomplished without operators, or railroads run without men. While research chemists and physicists are laying the foundations for products, processes, and plants, it is incumbent upon somebody to develop, study, and perfect, concurrently, a suitable

organization to carry their research results through the various stages of development and finally to profitable production. Furthermore, organized effort is obviously more rapid, efficient, and thorough than single-handed work, and this applies to every step from research to sales.

Accordingly, it seems appropriate, in spite of the overworked character of the subject of organization, to outline some of the methods which my associates and I apply to chemical development in order to arrive at the results which your committee has accepted as collectively justifying the great honor of the Perkin Medal.

Arthur Little once said, "There is great danger in an organization chart—someone might mistake it for *an organization*." After this apt, if somewhat blunt, awakening, we would not venture even to submit an organization chart. For the purposes of developing and coördinating the work of organization, the problems requiring individual treatment and timing may be arranged under the following general heads: (1) objective, (2) direction and policy, (3) research and engineering, (4) construction, (5) operation, (6) office and accounting, (7) sales and promotion, and (8) general seasoning.

Time will not permit a detailed analysis of the methods of development for each of these organization headings, but the system which we have followed may be illustrated by selected examples.

Objective

The objective of an organization requires the most careful analysis. This applies to all organizations, whether old or new. What is it supposed to do and where is it headed for? Obviously, the scope and extent of an organization should be adjusted to the facts developed by such an analysis. Over-organization seems to be the most general fault. We saw many cases during the war where there was so much organization that no one was left to do the work. We still frequently find organizations "all dressed up and no place to go."

This condition of organization seems to be largely due to the fact that almost everybody in a company, from chemists and engineers to office boys, has some pet theories in regard to organization that he would like to try, and will try if permitted. It is difficult for some of us to understand why men with highly specialized technical talent, which puts them in a class by themselves, surrounded by most fascinating problems and with worthwhile achievements easily within their reach, have a hankering to do "executive work," which in so many cases means to sit at a desk and function as a "traffic cop" for correspondence.

Direction and Policy

The direction and policy of an organization for chemical production is obviously, on account of its basic position, the most important element of the whole program. An organization without proper and carefully defined policy is like a ship without a rudder. It may gyrate around without going anywhere in particular, or it may, in close quarters, do a great deal of damage, both to itself and to its neighbors. Furthermore, a policy should be carefully worked out in the beginning, and it must "stay put." Missteps in the formulation or execution of policy may be of little consequence at the time, but may at some future date loom up like a rock in the channel. In any project of development, therefore, direction and policy deserve and must receive, far in advance, the most profound and intelligent consideration.

Research and Engineering

Research and engineering are the logical preliminaries to the development of any new program of chemical production, and, we believe, are equally necessary to improvement in the efficiency of established operations. Volumes have been written on the subject of organization for research. We claim no originality

for the systems which we have adopted, but take this occasion to record some typical schemes followed in our work, in the hope that they may serve as guides to others in what to do or what not to do according to their desires or tastes.

The overhead set-up for research must be analyzed as a preliminary to any plan to develop a research organization. The objective, interest, and resources available to the directors and executives are of primary importance in any research program. Their ability to understand the scope of our activities, their confidence in our abilities, their determination to see the thing through, and their capacity to stand disappointments, are qualities which must be measured and will form the foundation on which the program may be built. In short, ambitious researchers must exercise care in the selection of their bosses.

Many research projects are doomed to failure before they start, because of the lack of interest or understanding on the part of the overhead. If research is to be a part of an organization at all, it is entitled to the full benefits of coöperative support of every man in that organization from overhead to office boy. Research men are liable to be sensitive and sometimes temperamental. They respond to encouragement and wholehearted support, while, on the other hand, a single knocker may wreck the works.

Underwood & Underwood
MILTON C. WHITAKER

The greater portion of our organized research effort has been with the Welsbach Co., Columbia University, the U. S. Industrial Alcohol Co., and the U. S. Industrial Chemical Company. The confidence and undivided support which we have received from the directors and officers of these organizations, and the mistakes they have stood for and paid for, form the basis on which we have been able to build recent organizations.

We always see to it that officers and directors understand what we are trying to do and how we are trying to do it. We discuss our projects and policies and program with them. We do not even deny them the privilege of sharing our disappointments and understanding our failures. We have received in return encouragement, confidence, support.

A president of a corporation or a chairman of a board who reads and understands the research reports, knows and follows the progress of the work of every chemist and engineer in the organization, who champions the fellow who is down and encourages the fellow who is up, and who interprets these results and conditions to his directors, may be a rarity in some programs for the development of chemical production, but in our cases it has been the inspiration. We attribute these conditions to the care we have exercised in the selection and training of our bosses. They doubtless will ascribe it to other reasons.

Our research organizations consist of personnel, equipment, problems. Diversification of all three of these elements, within the scope of the project, is both necessary and desirable.

We have no formula for the selection of the men. We do not believe any one can pick a winner every time from a group of available chemists. Our best guess, based on training, experience and temperament as disclosed by the candidate, is given a trial in the organization and is given reasonable time to adjust or eliminate himself by a process of natural selection. Many chemists who think they are research men are not qualified either by training, ability, or temperament to handle research problems. Yet these same men may be or may develop into

excellent plant men. It likewise follows that many chemists who think they are qualified by nature to handle plant problems are essentially research men. Some men are not fitted for either research, plant, or sales, and would probably do better in insurance or music.

A man who is essentially a plant man is liable to be a nuisance in a research laboratory, and, on the other hand, a man with research inclinations is a hazard to any production process.

Diversification of training and experience among the members of a research organization is of the utmost value when the organization works as a group. While each investigator may have his particular problem, team work is a necessary element in order to achieve the greatest results.

The man who is inclined or prefers to play a lone hand, who is selfish or secretive, is out of place in any organization. Individual effort is limited to the capacity of a single person, whereas the advantages of an organization should be capitalized by producing results which represent the combined effort and experience and knowledge of a number of men participating. Thus it is that many successful developments come from the laboratory for which it is difficult to award the credit to any individual. This is sometimes reflected in the difficulties encountered in an effort to unscramble an invention for the purpose of securing patents. While the United States patent law has not kept pace with coöperative effort in research, and the problem of allocating the inventions to individuals in such an organization is becoming increasingly difficult, on the other hand a knowledge of the underlying principles of these patent laws broadens the field of vision of the investigator.

Construction

Equipment for industrial research is selected according to the number and scope of our problems, and the amount available is made or acquired in accordance with our needs and the progress of our work. A laboratory for the development of new processes and products should contain all necessary physical and chemical apparatus for the investigation of each fundamental principle involved in the projects under study. Every theory and fact contained in the literature and bearing directly on the problem or related problems is made available to the investigator before work is actually undertaken. We regard this as much a part of our research equipment as the apparatus and desks. Most of these chemical and physical facts and theories have to be checked and confirmed, and the laboratory equipment should be ample to meet these requirements.

As the results of the laboratory work are completed, checked, plotted, and discussed, plans are considered for an elaboration of these principles into a small laboratory apparatus. Confirmation of theories and reasoning at the laboratory desk, and further consideration and discussion of results bring us to the point where coöperation is required between the chemists and the engineers.

Operation

We believe that the place to start and finish a real chemical engineering problem is in the research laboratory. For this reason our engineers work with and rank with our research chemists. Personal contact and discussion during the laboratory
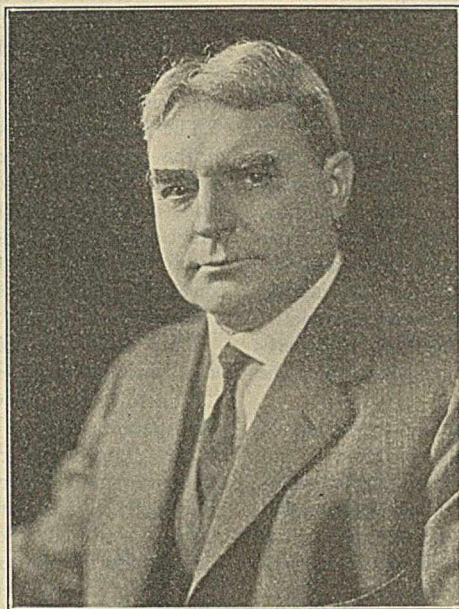
development and close coöperation in the planning of a semi-commercial unit have avoided many misunderstandings and failures.

Our experimental units have for their purpose much more than the checking of the laboratory results obtained by the research chemist. These units are scaled to a size which will permit of a continuous operation over a considerable period of time, in order definitely to establish engineering data for use in the design of commercial units, and to determine capacity, quality of product, and materials of construction. They must also produce a sufficient quantity of the product to enable it to be sold and, finally, to determine if it meets the supreme commercial test, that is, to *stay sold*.

We operate these experimental units from six months to two years, depending upon conditions, changes required, market tests, etc. During this period, the operation is under the close observation of the research chemists who established the basic data for the process, the engineers who coöperated and designed, and, if possible, the mechanics who built the apparatus. Even the plant organization which may ultimately be expected to erect and operate the commercial units, and the sales department which has to sell the product and make it stay sold, are kept in contact with the work.

Incidental to this experimental operation, all questions of quality, specifications, market requirements, containers, and natural sales units, are determined. The purchasing office becomes familiar with the problems involved in locating, specifying, and buying raw materials, the apparent hopelessness of the problem of costs and accounting in the operation becomes clarified for the auditors, and, finally, the clerks, stenographers, and office boys add the new names to their vocabulary and discuss the prospects of the new process with assurance.

Innumerable other elements such as I. C. C. regulations, insurance risk, workman hazards, keeping qualities, etc., are determined so that when commercial units are finally undertaken, all the elements from design to sale of products are settled and behind us.

Concentration on research problems, based on the needs and requirements of the organization and its policy for development, requires courage and persistence, but it must be regarded as necessary in industrial work. An industrial research laboratory has a different objective from that of the academic institution. We endeavor to achieve constructive results within a limited field, and in a reasonable time, which aim at the building of a plant and the production of a product at a profit. The academic investigator, on the other hand, may choose his problem from the unlimited field and for the purpose of making a contribution to science or of qualifying for a degree. The objective of the industrial investigator is a *process* and a *plant* to which he can point with the pride of achievement, whereas the objective of the academic investigator is a *contribution* to science and publications to which he can with equal fairness point with the pride of authorship. The former measures his success by the amount of factory noise and smoke his work creates, while the latter may modestly acknowledge the cheers of his peers, or may measure his success by the amount of printer's ink he has caused to be consumed.

Such a research organization as outlined was established in the fall of 1916 in the industrial outskirts of Baltimore. We selected as a building site a large potato patch and surrounded it with a high fence enclosing several acres. Here we developed what might be called a *research plant*.

We were inflicted with neither neighbors nor architects. The lighting, heating, ventilation, and drainage were planned by and for chemists, with the result that we have an abundance of each. Architecturally, it is below par, but it is what it was built for.

By the beginning of the year this plant was in full operation, manned by chemists specially qualified by analytical, organic,

physical, or biochemical training, and brought together from Maine to California with a liberal allowance for intermediate points. The chemists were reinforced with engineers, assistants, mechanics, and bottle washers.

The specific problem placed before this organization was the development of uses of alcohol and the utilization of the by-products of the alcohol industry.

The work of the laboratory was soon interrupted by war problems, and the entire time of the organization was devoted for over a year to the development and improvement of processes for the production of acetic acid, acetone, methyl acetate, ethylene, and solvents for airplane dopes.

The acetone process, which at one time supplied 60 per cent of the war requirements for acetone, was discontinued at the signing of the armistice. Methyl acetate and solvents for airplane dopes were no longer in demand and the process for the direct production of acetic acid was abandoned in favor of the by-product acid. Ethylene has since achieved considerable commercial development as a gas for cutting and welding and as a standard chemical.

Thus, at the end of 1918 we were like many other research organizations—going strong, but not in the right direction.

While the surveyors were staking out the site for the laboratory, a competent group of chemists was building up our equipment on the "state of the art." Every literature or patent reference, directly or indirectly related to our problems, in every country and language, was studied, translated if necessary, abstracted, classified, indexed, and made available to the laboratory staff. This file now includes over forty thousand references kept strictly up to date. These searchers are in constant contact with the laboratory, supplying them with advance information, helping over the humps, and bringing up the rear on patents. The department has since been expanded into a general information service for the entire business, including contemporary progress, commercial development, statistics, foreign relations, etc.

Having passed the research, engineering, and construction stages of a new development, we now come to the problem of developing and coördinating, in their proper order and to the proper extent, our operating organization.

Good operating chemists and engineers are in a class by themselves. Patience, caution, and conservatism are not natural to a chemist who has been trained to visualize the invisible, to theorize, and to experiment. Too much imagination and inventiveness are qualities which if applied to a production operation will eventually wreck it. We prefer men who are hard-headed, poker-faced, unimaginative citizens, possessed of an obsession to make the wheels go round.

A good operating man will study every detail of his operation with a view to increasing its efficiency and output. This includes the efficiency and dependability of his operators. Each man, woman, or boy in his subunits is studied to determine his or her fitness for the job. They must be made to fit the job or the job made to fit them. This leaves no room on the inside for misfits.

The operating chemist's problems are production, incessant production, quality and costs, including the costs of his losses of equipment, materials, and time. If he has a burning desire to investigate something about a going process, let him take his problem to the research laboratory and keep it there till he gets the answer. Let him remember that the business of the plant is to produce and the business of the research laboratory is to experiment and develop, but that it takes a wiser man than he is to make the two function together and avoid the clutches of the sheriff.

OFFICE AND ACCOUNTING

Plant offices are often neglected, in spite of the fact that they are capable of being made one of the most necessary and important elements in a plant organization. They should be the con-

necting link between all internal units of the organization and between the organization as a whole and the public. Some office organizations, if allowed to drift, seem to have a genius for developing a high nuisance value and getting themselves disliked both inside and outside the plant. The exercise of a little common sense and some of the same care on the office personnel and its functions as that used on the development of research or operation, will make an office staff what it should be—the pivotal point around which the whole finished organization will smoothly and noiselessly rotate. We believe that accountants, in addition to holding post-mortems on past performances, should supply *live* figures and facts designed to assist, direct, and control going operations; that their costs need *not* be a blind assemblage of figures, but that they should reflect a working knowledge of the operation and what the costs ought to be—at least enough knowledge to enable them to get the decimal point in the right place. This policy means that the office becomes a working part of our research engineering construction operating organization, and not the "short-hour aristocrats" of the plant. Orders, billing, and correspondence come in for their share of systematic attention, and the "foreign relations" of the organization are handled with a minimum of "alibi building" and "buck passing."

Purchasing agents, in addition to their usual prerogatives of brow-beating salesmen, are expected to function as advance agents for research and engineering, to know the stocks of materials and supplies in the plant, and to anticipate balance and look forward. Their job does not end with writing an order and dropping it in the mail, but they are expected to know when and where the goods will be delivered, see to it that they are delivered, that the stuff delivered is what was purchased and, more important, what is wanted, and, finally, to see that the man who wants the stuff knows it is in and where it is to be found. This may look like a big contract but it can be done and is being done wherever purchasing offices function according to our plan.

SALES AND PROMOTION

Having achieved the development of new products and processes and reached the point of production, the largest problem of all is sales. Unless proper attention has been given to the development of sales, which includes the promotion and introduction of the products to the trade, disaster awaits a budding chemical industry.

Sales development is a long and tedious process. It takes time and talent for a new producer to butt into an old market, and it takes more time and more talent to introduce new products. New products must be guided through the introductory stages by the research laboratory and especially by those men most responsible for the development. This knowledge and paternal interest must be capitalized in order to furnish salesmen, even those with technical training, with the proper sales points and the necessary enthusiasm.

SEASONING

General seasoning of a new organization is the most elusive and, therefore, the most interesting problem of them all. It has many discouraging and some mysterious features. Experience and patient hammering seems to be the solution if one can live through it. General plant sense, mechanical horse sense, legal liabilities as applied to purchase, sales and employment contracts, insurance, fire risks, employees' risks and safeguards, do not fall within the training and experience of the young plant chemist or engineer, yet it is incumbent upon the organization as a whole to understand and handle these and many similar problems.

The element of mystery is involved in such things as running a suction pipe sixty-five feet into a well, trying to push a loaded conveyor belt, installation of pipe sizes which add 100 to 200 per cent of friction load to the normal head load of a pump, connecting operating units directly to underground sewers, omitting safety valves from steam-jacketed equipment, trusting labor to function 100 per cent perfect. To the seasoned factory man such things are hard to account for. Whatever may be the cause of these apparent lapses, continued hammering, an occasional steam roller, and frequently some sad experiences seem slowly to wear down the list. In time they will learn to apply their physics, to think things through, to develop the "high points" in supervision so as to "just happen around" at a critical time, and finally to leave nothing to chance—to hold four aces at all times. No organization will ever be free from seasoning problems, as long as we have the human element to deal with, but the "rate of frequency" may be used as a measure of perfection.

. . . .

(EDITOR'S NOTE: The last part of Dr. Whitaker's address, giving a detailed description of his process for the production of ethyl acetate from acetic acid and alcohol, illustrated by curves showing some of his observations on esterification, will appear as a separate article in a subsequent issue of THIS JOURNAL.)

Technical Records of Explosives Supply, 1915–1918. IX—Heat Transmission. 48 pp., 15 illustrations, 4 alignment charts. 19 × 28 cm. Ministry of Munitions and Department of Scientific and Industrial Research, London. H. M. Stationery Office, 1922. Price, 5s, 3$\frac{1}{2}$d.

The right application of the laws governing the transmission of heat, and especially the flow of heat through the walls of pipes, constitutes one of the most important physical problems in chemical factory practice, since in a large number of instances heat must be supplied to initiate and to maintain chemical action, while in some instances heat must be removed in order to prevent undue acceleration in the rate of the reaction. There is an optimum temperature for each chemical operation and in good practice it is sought to maintain this condition by the control of the heat transmission.

The object of this publication is to make available to the industries the results of experience gathered in the operation of the national factories during the war, this being the last of a series of nine such publications prepared from the records of the Department of Explosives Supply of the Ministry of Munitions. In the treatment the subject is divided into "Theoretical Section," dealing with fundamental principles, criterion for turbulence, determination of coefficients of transmission, application of method of dimensions and coefficient of transmission to specific problems, and the construction of alignment charts; "Experimental Section," dealing with the methods of investigation and examination of experimental results as applied to acid coolers at the Queen's Ferry plant, lead coolers, and a superheater in a denitration plant, and to surface condensers, with consideration of water economy and efficient cooling, the effect of stirring, surface loss, and the heat interchange in a cylinder in which a heat-producing reaction takes place; and a third section devoted to a detailed study of the application of the principle of Quinan's bubbler scrubber to the cooling of condensing water.

Like its predecessors in this series, the pages bristle with data, many of which are really comprehensive comparative catalogs of factory devices, while the step-by-step solution of fundamental problems is recorded in so plain and detailed a manner that they may be followed and made use of by those having but a limited knowledge of mathematics. A copy of this book should be at hand for ready consultation in every factory and works.

CHARLES E. MUNROE

SCIENTIFIC SOCIETIES

Pioneer Yale Chemists

At the spring meeting of the AMERICAN CHEMICAL SOCIETY in New Haven, the center of interest will be the great Sterling Chemistry Laboratory of Yale University. It should be realized that the reason for this laboratory is the long record of scientific attainments and productive research in chemistry, which has built up a department requiring such a building for its adequate maintenance and future development.

From a considerable number of the past and present men of Yale whose work has been notable, four representatives have been chosen who were pioneers and who typify the spirit and achievements of Yale in chemistry. First is the elder Silliman, a teacher and lecturer who founded the departments of chemistry, mineralogy, and geology in Yale College. Samuel W. Johnson was a great agricultural chemist who originated the first agricultural experiment station in the United States. J. Willard Gibbs gave to the world the mathematical derivation of the Phase Rule and many other far-reaching and valuable principles of theoretical chemistry. Russell H. Chittenden was the first great physiological chemist in the United States.

BENJAMIN SILLIMAN, SR.

Yale's first professor of chemistry was a young lawyer, made into a scientist by two winters' sojourn in Philadelphia as a pupil of Dr. James Woodhouse and a few months in London and Edinburgh. Benjamin Silliman was in 1802 a tutor in Yale College, just completing his apprenticeship in the reading of law, when President Dwight prevailed upon him to take up the study of chemistry in order to found a department and teach the subject in his Alma Mater. Silliman was a bright and versatile young man of genial and winning personality, and intensely devoted to Yale. He had shown no special interest in science, and, in fact, on being granted his second degree in Yale had submitted as an original contribution a poem entitled "Columbia."

The notebook which Silliman used for his first lectures with Dr. Woodhouse, of the Medical College of Philadelphia, is preserved in the Yale Library, and is a most interesting record of the subject matter, as well as the method of presentation of chemistry in the earlier years of the science. Two men whom Silliman met in Philadelphia had a great deal to do with his interest and enthusiasm—Robert Hare, inventor of the oxyhydrogen blowpipe, who was a fellow student, and the great Priestley, who entertained the embryo Yale professor in his home.

In 1804 Silliman entered upon the full dignity of his position as professor of chemistry and natural philosophy in Yale College, delivering his first lecture on April 4, 1804, an event commemorated by the dedication of the Sterling Chemistry Laboratory on the same date in 1923. The next year the college found itself in possession of the sum of $10,000 to be expended in Europe for books and apparatus. Silliman asked to be permitted to undertake this mission, and at the same time to continue his scientific studies. During the few months spent largely in London and Edinburgh, the young American professor made the most of his opportunities, not only in attending lectures but in meeting people worth knowing, such as Dalton, Sir Humphrey Davy, and Henry, as well as men of note in literary and official circles. During this time Silliman also became greatly interested in mineralogy and geology.

Returning to America, he plunged with vigor and enthusiasm into his teaching. He believed strongly in visual instruction, and devised and skillfully performed spectacular experiments before his classes. He secured a splendid collection of minerals for the college, first by loan and afterwards he raised by public subscription the money to purchase his beloved "cabinet." His first laboratory was originally a deep and gloomy cellar, the architect in Silliman's words "having imagined that the deeper down in Mother Earth the dangerous chemists could be buried, so much the better." This was remodeled and made fairly habitable, serving him for lecture room and laboratory for fifteen years.

As he grew more mature Silliman became widely sought as a public lecturer. He spoke to large audiences in Boston, New York, Philadelphia, Baltimore, St. Louis, Mobile, and New Orleans. In this way he met and became intimate with many great men of the day. His correspondence included financiers, ministers, government officials, and many scientists in America and Europe.

In 1818 Silliman founded the *American Journal of Science*, and throughout his lifetime was intimately connected with this publication. This was the first permanent scientific publication in America, and its influence has been beyond estimation in furthering the cause of science in this country. In addition to the editorship of this journal Silliman found time to edit and publish Henry's text on the "Elements of Chemistry," to issue his own lectures as a text in two volumes, and to edit Bakewell's "Geology." He was a charming popular writer, his "Journal of Travels in England, Holland, and Scotland," and much later his "Visit to Europe in 1851," running to several editions and finding wide circulation.

Silliman, using Hare's "deflagrator," showed that carbon was volatilized in the electric arc. He was the first man in America to produce hydrofluoric acid, and was also the first to discover bromine in American brines. His first published work was a very thorough investigation of the chemical composition of a meteor which fell near New Haven. At one time he was employed by the national government to investigate the manufacture of cane sugar. His interest in the industrial applications of chemistry is well illustrated by his friendship and encouragement of Charles Goodyear during a time when the inventor was sorely tempted to give up his investigations.

It was largely due to Professor Silliman that the Sheffield Scientific School was founded. He personally presented to the corporation a plan for the founding of a school of science, and the institution was actually founded and struggling for existence when the liberal gifts of Mr. Joseph Sheffield assured its future.

For more than fifty years Benjamin Silliman maintained the work in chemistry, mineralogy, and geology at Yale. He was a man of enormous energy and varied interests. He was prominent in civic life, active as an editor, nationally known as a delightful popular lecturer, and was loved by generations of Yale
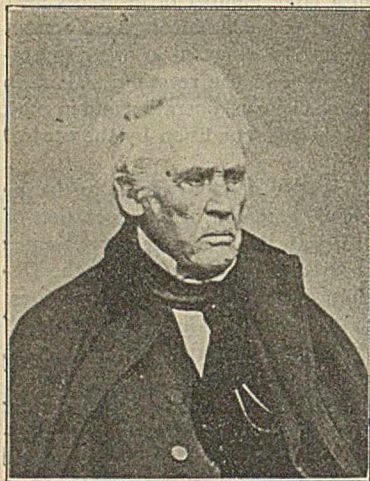
BENJAMIN SILLIMAN, SR.

men as a great and inspiring teacher. At the time of the unveiling of a statue of Silliman, Andrew D. White, then president of Cornell University, said: "It is no more disparagement to say that Benjamin Silliman was not a great original investigator than to say that a king is not a cabinet minister. When Sir Charles Lyell wrote from the South expressing amazement at the number of men whom he found in the most remote parts of the country who had received an impulse in scientific studies from Silliman, he had a vision of the real work of his honored friend."

SAMUEL W. JOHNSON

Samuel W. Johnson, for forty years professor of agricultural chemistry in Yale University, was the first director of the first agricultural experiment station in the United States. Largely through his efforts the Connecticut State Agricultural Experiment Station was founded in 1877. The movement once begun extended rapidly to other states, and in a few years the results of the work of these stations became a substantial and far-reaching contribution of applied science in this country.
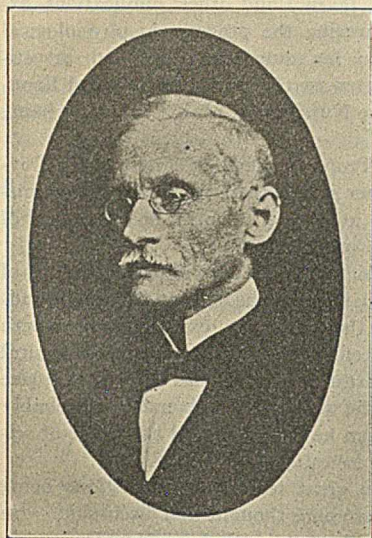
Professor Johnson is probably best known to those familiar with the development of agricultural chemistry in the United States through his two books, "How Crops Grow" and "How Crops Feed," which have met with wide approval, not only in this country but in other lands.

From his earlier years, Johnson was an enthusiastic advocate of the application of scientific principles to agriculture. He wrote extensively for farm papers, especially for *The Country Gentleman*. As he progressed in his study of chemistry, his papers, published in scientific journals and official reports, became more technical in their nature, and cover a wide variety of topics, such as the constituents of fertilizers, soil analyses, methods of agricultural analysis, laboratory apparatus, and even the detection and separation of rare earths. He edited two editions of Fresenius' "Qualitative Analysis."

In addition to his scientific investigations and his duties as experiment-station director, he concerned himself especially with the training of men as chemists. Among his distinguished pupils were Russell H. Chittenden, who subsequently became a great physiological chemist; W. O. Atwater, who later became a prominent worker along lines similar to those followed by Johnson; and Thomas B. Osborne, whose work on vegetable proteins and vitamins is classic.

After leaving Yale, Samuel Johnson spent two years in Europe, studying with Erdmann at Halle, with Liebig at Munich, and a short time with Frankland in England. Returning to the United States, he became in 1856 a professor in the Yale Scientific School, a position which he held until 1896. He continued his duties as director of the Connecticut State Experiment Station for four more years, much of the labor being taken from his shoulders by Dr. E. H. Jenkins, the present director. His last years were spent in reading and correspondence, his failing health forbidding active scientific work. Professor Johnson died in 1909.

His letters, edited by his daughter, Mrs. Thomas B. Osborne, reveal much of the nature and experience of the man from his early years up to old age. He had a keen sense of humor and a wonderful capacity for expressing his thought clearly and concisely. His work as an investigator was sound and thorough, and he showed especial talent as an author. Although for many years agricultural chemistry has not been taught at Yale, the field developed by Professor Johnson has been transferred to agricultural colleges and experiment stations, the work of which stands as a memorial to this pioneer author, teacher, and investigator.

J. WILLARD GIBBS

Unquestionably the greatest single contribution to theoretical chemistry by an American came from a man who was not in the strictest sense of the word a chemist at all. J. Willard Gibbs, professor of mathematical physics in Yale University for thirty-two years, published in 1876–1878 a series of papers on "The Equilibrium of Heterogeneous Substances." Because of the strictly mathematical treatment of the subject and the prevailing lack of familiarity of chemists with higher mathematics, its value was not recognized nor was the great principle involved used by chemists for several years. It was thus that some of the natural laws clearly stated for the first time in these papers were rediscovered by others, both from theoretical considerations and by actual experimentation. It remained for Roozeboom to evolve from the mathematical discussion of Gibbs the principle now known as the "Phase Rule."
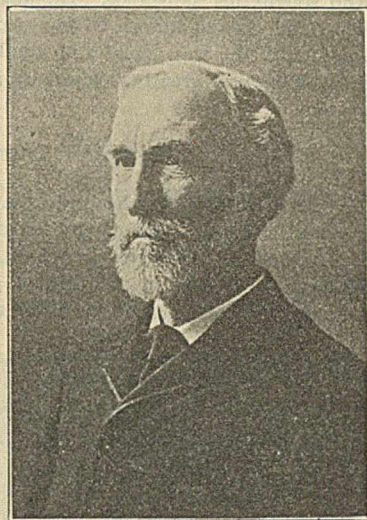
This remarkable series of papers contained other important theorems which have proved of immense value in scientific research. The late Professor Bumstead, in writing of the work of Gibbs, says:

It is not surprising that a work containing the results of such consequence should have excited the profoundest admiration among students of the physical sciences; but even more remarkable than the results, and perhaps of even greater service to science, are the methods by which they were attained; these do not depend upon special hypotheses as to the constitution of matter or any similar assumption, but the whole system rests directly upon the truth of certain experiential laws which possess a very high degree of probability. To have obtained the results embodied in these papers in any manner would have been a great achievement; that they were reached by a method of such logical austerity is a still greater cause for wonder and admiration. And it gives to the work a degree of certainty and assurance of permanence in form and matter which is not often found in investigations so original in character.

The great value of the Phase Rule in theoretical chemistry is recognized by all working in that field. The average man, however, does not realize the enormous practical use which is made of this principle first developed by Gibbs. The familiar carbon-iron diagram, which is the basis of the metallurgy of steel, is based upon it. The whole subject of alloys and, indeed, the science of metallography is founded on the Phase Rule. The classic work which has explained the constitution of portland ce-

SAMUEL W. JOHNSON

J. WILLARD GIBBS

ment was only possible through the Phase Rule. These are but a few examples of its value and versatility.

The father of Professor Gibbs was himself a professor in the Divinity School of Yale University, and a painstaking and thorough scholar. Willard Gibbs graduated from Yale College in 1858 with high honors, in 1863 he received the doctorate from Yale and was appointed a tutor teaching Latin and later natural philosophy. At the end of his term as tutor he spent three years in Europe, studying under Magnus, Kirchhoff, and Helmholtz. In 1871 he was appointed professor of mathematical physics in Yale University, a position which he held until his death in 1903.

Many honors came to Professor Gibbs in later life in the way of degrees and medals, notable among these being the Rumford Medal from the American Academy at Boston, and the Copley Medal from the Royal Society of London.

As a teacher, Professor Gibbs was thorough, his lectures being carefully prepared and filled with apt and striking illustrations. He was never too busy to attend faithfully to his duties as an officer of the college, or to devote his energy to students who sought his assistance. He was a quiet and unassuming man, and though known to few people outside the university community, he was genial and kindly in his relations with his fellow-men, and greatly beloved by all with whom he came in contact.

Russell H. Chittenden

Professor Chittenden has only the past year retired from active service as professor of physiological chemistry and director of the Sheffield Scientific School of Yale University. He was distinctly a pioneer in the field of physiological chemistry in America. When he began his duties as a professor in Yale in the early eighties, physiological chemistry was scarcely known as an independent field. Now the subject is being taught in all medical schools and large universities in the country.

In 1875, his senior year in the Sheffield Scientific School of Yale, he proved the presence of glycocoll and glycogen in scallops. This is considered a piece of research of the highest grade, being the first case of the isolation of a free amino acid in living tissue. His first graduate work was with Prof. Samuel W. Johnson in the field of toxicology. As a result of this training, Professor Chittenden later became one of the leading toxicologists of the United States, his services being in great demand in medico-legal cases. In order to render intelligent judgment, each case became the subject of valuable original research.
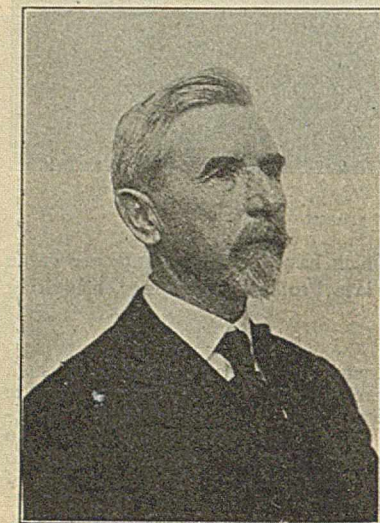
In the late seventies he went to Germany and took up, in collaboration with Kuehne, of Heidelberg, a study of the products of digestion. In 1880, returning to Yale, he was awarded the doctorate degree and continued his connection with the department of chemistry. In 1882 he became professor of physiological chemistry, a position which he held for forty years, until his retirement last session. He early succeeded in interesting young men in the research aspects of physiological chemistry, attracting numbers of graduate students who collaborated with him in original investigations.

At that time the teaching of chemistry to medical students consisted in the mere elements of chemistry, together with occasional urinary analyses. The splendid courses which were given by Professor Chittenden attracted many able young men, who preferred to remain for one or two years after graduation in order to receive training from him in physiological chemistry before going on with their medical course. As a result his students stood out preëminently in the various medical schools to which they went.

Professor Chittenden was early interested in the chemistry of digestion and became especially attracted to problems of nutrition, which led to his elaborate investigations in the so-called "physiological economy in nutrition." In this he was encouraged by the belief that the minimum amount of nitrogen requisite for man was much less than had been generally assumed. His work received wide attention and has been made the basis of the so-called "low-protein" in nutrition.

In the earlier part of his career Professor Chittenden prepared for the *American Chemical Journal* and other publications extensive yearly abstracts covering the progress in physiological chemistry. In addition to his numerous published investigations at Yale, he has written two books, "Physiological Economy in Nutrition" and "The Nutrition of Man," the latter being a series of Lowell Lectures.

During the World War, Professor Chittenden served the Government abroad as a member of the Inter-Allied Food Commission. He is a member of a number of scientific societies, and of several of these he has been president.

In 1898 he became director of the Sheffield Scientific School of Yale University. During his deanship he built up this undergraduate professional school of the university, extending the length of its course, and adding tremendously to its size and physical equipment. His great interest in science has served to place emphasis upon this part of the work of the university. Probably more than any other one man he has advanced the cause of scientific studies and scientific investigation in Yale.

Professor Chittenden is a great teacher, his questions being asked in such a way as to promote thought and discussion. He developed in his students enthusiasm and the spirit of research. As an investigator he has always been noted for brilliance, originality, and thoroughness. As an executive, his keen business sense and judgment of men have been a great asset to Yale. As a dean, possessed of mingled kindness and firmness and a thorough understanding of the psychology of young men, his wholesome and inspiring influence on Yale students has in a measure compensated for the years in which he was removed from active scientific work.

Russell H. Chittenden

Division of Cellulose Chemistry

At the first meeting of the new Cellulose Division at New Haven in April, it is proposed to hold a symposium on "Oxycellulose, Cellulose Hydrate, and Hydrocellulose." A good many papers have already been promised, but others are desired, especially those dealing with cellulose esters or the pulp and paper industry. Authors will please send the title and a short abstract to the secretary of the division, L. F. Hawley, Forest Products Laboratory, Madison, Wis.

Symposium on Insecticides and Fungicides

At the Pittsburgh meeting of the AMERICAN CHEMICAL SOCIETY, the Division of Agricultural and Food Chemistry voted to hold a symposium on insecticides and fungicides at the New Haven meeting in April. This will be the first gathering of chemists working along these lines, and an interesting program is being arranged. The symposium will be held on Thursday, April 5, and in order to allow for adequate discussion of the papers an all-day meeting will probably be held. Members wishing to present papers or to offer suggestions should address Dr. F. C. Cook, Bureau of Chemistry, Washington, D. C.

Symposium on the Synthetic Coal-Tar Dye Industry in the United States Prior to 1914

At the spring meeting of the AMERICAN CHEMICAL SOCIETY, to be held in New Haven, April 2 to 7, 1923, the Division of Dye Chemistry is planning a symposium to tell of the accomplishments of the Americans in the dye industry before the war.

So much has been said and written about our doings since 1914, that we are apt to underrate and pass over the truly interesting and worth-while results obtained by those who pioneered.

The aim is to have the symposium so complete that it will give a history of the pre-war activities. Accordingly, anyone who knows of the facts pertaining to the manufacture or chemistry of artificial dyes in the United States prior to 1914, is asked to communicate with R. Norris Shreve at 342 Madison Ave., New York City.

Chemical Education Section

At the Pittsburgh meeting of the AMERICAN CHEMICAL SOCIETY, a resolution was passed to have a symposium on "Tests in Chemistry" at the New Haven meeting. Professor Glenn, of Teachers College, Columbia University, will arrange this symposium.

Papers have already been scheduled for the discussion of the status of analytical chemistry in our universities and colleges.

It is expected that there will be a report of the committee on the "Correlation of High School and College Chemistry." It is also expected that there will be a report of the committee working on a list of research problems that are fitting for those teachers who have a limited amount of time or equipment for research. Professor Chapin, of Oberlin College, is chairman of the committee.

Papers containing constructive work for the teaching of chemistry are invited.

NEIL E. GORDON, *Secretary*

NOTES AND CORRESPONDENCE

Generation of Artificial Gas. A Guess at the Future

Editor of Industrial and Engineering Chemistry:

It has been suggested that, when cheap oxygen becomes available, it will be possible to carry out the complete gasification of coal in an apparatus like a blast furnace, to which oxygen and steam are fed. This will give a gas which might be described as a mixture of coal gas, water gas, and producer gas, minus the diluting nitrogen of the present producer gas. It should be possible to control the temperature by varying the proportions of oxygen and steam, and to flux the ash so as to eliminate the troublesome clinkering of the present water-gas process. This most promising idea for a large-scale gas generator is wholly dependent on cheap oxygen.

Cheap oxygen can also be applied to the gas so produced in two or three other ways which do not seem to have been suggested in this connection—i. e., to the removal of hydrogen sulfide and to the drying and enrichment of the gas.

By feeding a sulfur burner with pure oxygen instead of air, thus producing pure sulfur dioxide, we can utilize the reaction:

$$2H_2S + SO_2 = 2H_2O + 3S$$
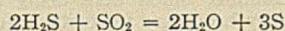
The precipitated sulfur can be taken out by Cottrell precipitation, or by bagging. Any excess sulfur dioxide can be removed from the gas by washing.

Cheap oxygen probably means that calcium carbide can be efficiently produced in a blast furnace. If such a furnace were operated as a part of the gas plant, the carbon monoxide from the carbide furnace could be added to the gas from the main gas generator. The carbide produced could be used as an efficient drying agent for the gas. Not only will the substitution of acetylene for water vapor in the gas do away with all the pipe and holder troubles, such as stoppages and freeze-ups, but the gas will thereby be enriched. Of course, further enrichment beyond the acetylene equivalent of the removed water can be made, if desired.

These subsidiary uses for oxygen add to the feasibility of the main scheme and seem worth while bringing to the attention of your readers.

FREDERICK G. DAWSON

5740 WOODROW AVE.
DETROIT, MICH.
November 25, 1922

New Calculating Chart

Editor of Industrial and Engineering Chemistry:

With regard to the article by me in the November, 1922, issue of your journal on "A New Calculating Chart," some have had difficulty in handling improper fractions or fractions in which the first digit of the numerator is greater than the denominator. Such divisions are performed at the left of the heavy "1" line; or, where the readings are too fine by this method, by dividing the denominator by the numerator and then obtaining the reciprocal. In the reciprocal method, the vertical is the denominator, the radial the numerator, and the radial from the intersection of the slant over the vertical "1" is the value of this fraction.

E. L. RICE

WASHINGTON, D. C.
January 15, 1923

Report of the Viscosity Committee of the Cellulose Division—Correction

In this report, published in THIS JOURNAL, **14** (1922), 1164, in the list of specifications, the eighth item should be changed to read:

Temperature of solution	25° C.
Temperature to be maintained by water jacket within	±0.5° C.

WASHINGTON NOTES

CALCIUM ARSENATE DEMAND

The all-absorbing topic of the moment seems to be calcium arsenate. On January 18, the Senate ordered to be printed the report prepared in compliance with Senate Resolution No. 377 passed by the Congress authorizing and directing the Bureau of Entomology, Department of Agriculture, and the United States Geological Survey, Department of the Interior, to investigate the available supplies of arsenic in the United States.

Briefly summarized, the situation as we see it is somewhat as follows:

During 1922, 8000 short tons of calcium arsenate, requiring about 3200 short tons of white arsenic, were consumed on cotton in controlling the boll weevil. It has been estimated that the consumption of calcium arsenate on cotton in 1923 will be between two and three times the quantity used in 1922, or, in terms of white arsenic, between 6400 and 9600 short tons, and that the United States requires about 8450 tons of white arsenic for purposes other than in the manufacture of calcium arsenate. The best information obtainable from governmental sources indicates that between 15,000 and 18,000 short tons of white arsenic will be required to meet our 1923 demand. The task is not a simple one.

It is difficult to obtain accurate figures of the world's total production of white arsenic, but available information shows that in the past not more than 50,000 tons were produced in the world during any one year.

The stocks of domestic white arsenic on hand October 1 (at smelters), and contemplated production from then until May, 1923, have been estimated by V. C. Heikes, of the Geological Survey, at 4630 short tons. To this quantity must be added imports which, for the first nine months of 1922, were about 3500 short tons. Only 900 tons of this amount, however, were imported during the third quarter of the year. Imports at this same rate should add an additional 1500 to 2000 short tons of white arsenic by the first of May, 1923. Imports, stocks, and potential production up to May, 1923, will, therefore, approximate 7500 tons of white arsenic. There is also a possibility of domestic smelters increasing production.

Information cabled to the Department of Commerce in November, 1922, indicated that practically no stocks of white arsenic were available for export from Mexico, Spain, and Japan; also, that the monthly output of 130 tons in Japan was contracted for up to the end of April, 1923.

The following table shows the domestic production of white arsenic and imports of all forms of arsenic from 1910 to 1922:

WHITE ARSENIC

Year	PRODUCTION Short tons	CONSUMPTION Per cent	IMPORTS, ALL FORMS[1] Short tons	APPARENT CONSUMPTION Short tons
1910	1,497	22.6	5,139	6,636
1911	3,132	43.3	4,096	7,228
1912	3,141	33.8	6,156	9,297
1913	2,513	34.8	4,701	7,214
1914	4,670	56.3	3,628	8,298
1915	5,498	63.3	3,183	8,681
1916	5,986	73.5	2,163	8,149
1917	6,151	60.9	3,955	10,106
1918	6,323	48.6	6,689	13,012
1919	6,029	48.0	6,540	12,569
1920	11,502	59.5	7,820	19,322
1921	4,786	48.9	5,012	9,798
1922	10,947	70.6	3,500[2]	15,500[3]

[1] Includes imports of white arsenic, arsenic sulfide, metallic arsenic, and arsenic acid. Can be considered chiefly *white arsenic.*
[2] Imports for first nine months of 1922.
[3] Estimated on basis of nine months' imports.

The consumption of calcium arsenate depends to a large degree upon the price the cotton farmer will receive for his cotton. It is the opinion of Dr. B. R. Coad, of the Department of Agriculture, that the cotton farmer during 1923 cannot afford to pay more than 18 cents per pound for calcium arsenate. This means that insecticide manufacturers must sell calcium arsenate to the dealers (middlemen) in the South at around 14 cents per pound. At this price, the insecticide manufacturers could not afford to pay more than 9 to 10 cents per pound for white arsenic. The bulk of domestic white arsenic, which can be produced by May, 1923, has been contracted for by insecticide manufacturers at net prices to the producer of about $8^1/_2$ cents per pound. Additional supplies of domestic white arsenic are bringing about 13 cents, and spot lots are selling around 15 cents per pound. The transactions at these higher prices are so small as to have little effect on the price of calcium arsenate.

It is undoubtedly true that the consumption of calcium arsenate could be materially increased if the prices were sufficiently low, but in view of the contract prices of white arsenic, it is impossible to see how the price of calcium arsenate can be less than 15 cents per pound delivered to dealers at southern points during 1923. Trade-journal quotations and manufacturers' advertised prices indicate that the price will be nearer 20 cents.

RESOLUTION TO PUT GOVERNMENT IN CHEMICAL BUSINESS

On January 13 the Senate passed a joint resolution appropriating $10,000,000 to permit the President to buy and sell to the farmers, at cost, nitrate of soda and calcium arsenate. While the initial appropriation is $10,000,000, the President is permitted to use the money as a revolving fund, so that the sales of these commodities to farmers may be pyramided and the business conducted on a large scale. The House has not yet taken action on this resolution.

MANUFACTURE OF FURFURAL

New uses for furfural made from corncobs are being sought by the Bureau of Chemistry, since it is now possible to produce it at a price that makes it of interest to a number of industries. Experiments are also under way on the manufacture of furfural from other agricultural wastes, such as hulls of rice, buckwheat, cottonseed, and peanuts. Peanut hulls yield less than one-third the amount of furfural that would be expected from a comparison of their pentosan content with that of corncobs. The yield with steam alone is so low as to preclude any commercial consideration of the use of peanut hulls as a source of furfural by the process as used for corncobs. There are indications that this yield may be considerably increased by the use of certain catalysts, and their effect will be studied.

MUSCLE SHOALS DEVELOPMENT BY THE GOVERNMENT

The Army Bill as passed by the House carries funds for the completion of Dam No. 2 and for the installation of eight power units which are all that the War Department considers will be needed for several years at Muscle Shoals. The bill appropriates $6,998,000 for work during the next year and in addition authorizes the Secretary of War to incur obligations on contract to the amount of $10,501,200. The bill is so worded that the money appropriated can only be used for the completion of the dam and installation of locks and hydroelectric machinery, and not for general construction. Development of the Muscle Shoals project by the Government, without regard to pending offers by Henry Ford and others, is bound to meet with stubborn resistance on the floor of the Senate.

BUREAU OF STANDARDS HAS BIGGEST TESTING MACHINE IN THE WORLD

A crushing force equal to the weight of fifty loaded coal cars of a hundred tons each can be exerted by the largest testing machine in the world which is now being installed at the Bureau of Standards. This machine has been in use for several years at the branch laboratory in Pittsburgh and has recently been moved to the main laboratory in Washington, D. C.

The machine will continue to work on the specimens for the towers of the Delaware River Bridge now under construction at Philadelphia. After that it will be used on the remainder of seventy-two steel columns which were being tested at Pittsburgh. It has recently been used for tests on forty-five samples of brick walls laid in different ways and with different kinds of mortar.

Such tests result in a great saving of money. It is believed that by careful experimental work, a method of design can be found which will allow the strength of steel columns for bridges and buildings to be calculated before they are built.

STANDARDS ADOPTED BY DEPARTMENT OF AGRICULTURE

Standards for condensed or evaporated milk, butter and renovated butter, ginger-ale flavor and ginger ale, cacao products, cacao butter, breads, cayenne pepper, and oil of cassia, as recommended by the Joint Committee on Definitions and Standards, have been approved by the Secretary of Agriculture for the guidance of officials in the enforcement of the Federal Food and Drugs Act.

January 19, 1923

PARIS LETTER

By CHARLES LORMAND, 4 Avenue de l'Observatoire, Paris, France

NITROGEN AND FERTILIZER NEEDS

The deficient harvest, especially in wheat, which we have had this year, has made it necessary for us to insure our needs for the coming season.

The consumption of nitrogen in France before the war was 78,000 tons (measured in nitrogen) per year. A consumption of 125,000 tons is estimated for the year 1923. The annual production is only 19,000 tons (about 55,000 tons of ammonium sulfate), and the production of 36,000 tons by the Haber process at Toulouse will only be realized by 1924 at the earliest.

In view of these conditions the French government made a contract with the German government to obtain from them deliveries of ammonium sulfate by virtue of the reparations, in conformance with the agreements of Wiesbaden. These contracts have not been fulfilled. Furthermore, the French government has offered in exchange deliveries of phosphate fertilizer, but here again without success.

The mission in charge of these negotiations included in its membership Eugene Roux, director of the Sanitary and Scientific Service of the Ministry of Agriculture. We obtained from him, on his return from Berlin, the reasons given by the German government for not accepting this delivery of nitrogen. In general, they use for fertilizer, one part of nitrogen and two parts of phosphorus. Before the war, for example, Germany used annually 210,000 tons of nitrogen and 610,000 tons of phosphoric acid. In order not to deliver nitrogen to France, she consumed in 1922, 340,000 tons of nitrogen, and will even reach in 1923, 500,000 tons. In other words, she is going to use equal quantities of nitrogen and phosphoric acid. Professor Wagner, an eminent agronomist of Darmstadt, has for a long time been pointing out the danger of this measure, which will result fatally in two or three years with a total diminution of yield.

When Frederick II committed unlawful arts, he claimed that he acted first and that he found professors of law afterwards to legitimize his act. It is the same in Germany now, for the German government has found two professors, Areboe and Wrangel, who, contrary to all the other agronomists of the world, sustain this theory and are carrying on experiments to legitimize this squandering of nitrogen.

In this same realm of nitrogen, an interesting study has just been made by Maze, of Pasteur Institute.

It is known that one of the principal reasons why cyanamide is rejected by agriculturists is its toxicity to the plant. Maze has shown that it is possible to entirely remove this toxicity by mixing the cyanamide with peat. A fermentation process which he has studied, permits the use of this cyanamide-peat mixture as a fertilizer without any harmful action to the plant.

SEASONING OF WOOD

One of the great difficulties of the wood industry lies in the seasoning. Wood is difficult to dry because the small cellules deep in the wood remain alive for a long time and a living cell does not easily lose its water; it can only lose it through plasmolysis under the action of a gas or a vapor which kills the cellule. Maurer has subjected some fresh wood to the vapors of benzene in an autoclave. He obtained in this way the death of the cellule and under the action of hot air the drying of this wood then took place very rapidly.

LOUIS PASTEUR CENTENNIAL

On the 27th of December, 1822, was born at Dôle, a small village in the Jura mountains, Louis Pasteur, whose centenary France is going to celebrate in 1923. The official ceremonies will take place in the month of June, but meetings have already begun this year which France wishes to place under the protection of Pasteur.

Although the most celebrated works of his relate to the field of biology, we chemists cannot forget that Pasteur was at first of our profession. He was an assistant chemical worker at the Ecole Normale Supérieure when he published his works on the unsymmetrical molecule.

At that time a great problem revolutionized the science— that was the enigma of Mitscherlich. Para-tartaric acid (now known as racemic acid), although having the same percentage composition as tartaric acid, did not act in the same manner under polarized light. Pasteur explained this anomaly—as a physicist, thanks to his profound knowledge of crystallography, he mechanically separated the right crystals and the left crystals of tartaric acid; as a chemist, he separated the right acid and the left acid in the tartrates of cinchonine, and having found that that separation of the right and left acids could be effected by fermentation, he thus introduced biology.

Not mentioning his works on medical biology, we cannot forget that to him we owe the fermentation industries—lactic acid, vinegar, wine, beer. He was the real founder of biological chemistry, and the disciples which he won, and who worked at the Pasteur Institute, are continuing his work. This work is great, not only because of the results achieved, but also in the field which it has covered, and we Frenchmen are proud to see Pasteur the benefactor of all humanity which claims him.

At the ceremonies which preceded the visit to the tomb of Pasteur, Dr. Albert Calmettes, assistant director of the Pasteur Institute after having summed up his work, said:

> Pasteur has saved, by his discoveries, millions of human lives. It is sufficient, in giving an account, to compare the former mortality by contagious maladies with the present mortality. Starting from 1885, it is stated, for all the nations, in spite of wars, there has been a progressive increase in the average duration of human life. Where fifty years ago, two persons died, per thousand population, only one dies now. At the middle of the last century, every person fifteen years of age could look forward to only thirty-six years of life, he now has an average of forty-eight ahead of him.

The progress in the domain of hygiene is also greatly due to Pasteur. Unfortunately, in our country of low birthrate, we do not apply enough the information furnished by science and the laboratories. Leon Bernard, professor of hygiene at the Faculté de Médecine of Paris, has just returned from a visit to the United States, and he has published a report of what he has seen. The organization of hygienic service in America is absolutely perfect, especially from a point of view of the organization of the laboratories and the extent of the research which is being pursued. The average mortality in America is less than that in France, and that statement in the country of Pasteur is not one to be proud of.

The government expects to take advantage of this year consecrated to Pasteur by conducting a lively campaign in behalf of hygiene, and also to interest the public in regard to the needs of the laboratories—that is, to encourage scientific research which the young generations, driven by the necessities of life, are unfortunately abandoning more and more.

December 28, 1922

Schedule of Trip of President E. C. Franklin

The following schedule has been arranged for a speaking trip for President Franklin. In most cases his subject will be "The Ammonia System of Compounds—Experimentally Illustrated."

Los Angeles, Calif.	March 16	Buffalo, N. Y.	April 21
Houston, Texas	March 19	Akron, Ohio	April 23
New Orleans, La.	March 21	Cleveland, Ohio	April 24
Nashville, Tenn.	March 22	Detroit, Mich.	April 25
St. Louis, Mo.	March 24	Ann Arbor, Mich.	April 26
Pittsburgh, Pa.	March 26	Midland, Mich.	April 27
Morgantown, W. Va.	March 27	East Lansing, Mich.	April 30
Maryland	March 29	Notre Dame, Ind.	May 1
Boston, Mass.	April 9	Lafayette, Ind.	May 2
New York, N. Y.	April 11	Urbana, Ill.	May 4
Philadelphia, Pa.	April 12	Evanston, Ill.	May 7
New Jersey	April 13	Milwaukee, Wis.	May 8
Lehigh Valley	April 14	Madison, Wis.	May 9
Rochester, N. Y.	April 16	Iowa City, Ia.	May 11
Syracuse, N. Y.	April 17	Ames, Ia.	May 14
Cornell, N. Y.	April 18–19	Minneapolis and	
		St. Paul, Minn.	May 16–17

LONDON LETTER

By Hugh Griffiths, 15 New Bridge St., London, E. C. 4, England

PARLIAMENTARY ELECTION

While the leaders of the Conservative party pledged themselves during the recent election not to introduce any essential alterations in the fiscal laws of the country, it was only to be expected that a very early opportunity would be taken to attack the Safeguarding of Industries Act.

It is generally realized that as long as this act is operative it is easily possible to introduce tariff reform in its most active form, without introducing any new legislation, but simply by extending the operation of the present act. During the first few days of December an attempt was made to get this act repealed, but this attempt was defeated. The speeches claimed that this act had served to foster certain special industries which previously could not be exploited in this country, notably the manufacture of tungsten metal powder and optical instruments. Nevertheless, the opinion is growing that there will be an inquiry into the application of this act.

There is something Gilbertian in the present system of considering the appeals held in connection with chemical products, and the ever-recurring solemn discussions turning on the meaning of the word "synthetic" would be comical if their consequences were not so serious. The nature of these discussions may be judged from the subject matter of recent complaints on such materials as sodium phosphate, oxalic acid, and calcium carbide.

In spite of the much-vaunted assistance of this act, most of the smaller manufacturers of chemical products, and particularly those engaged in the production of dyestuffs and synthetic drugs, consider that the pledges made to them have not been fulfilled, and they undoubtedly suffer very keenly—in spite of the provisions of the act—from the competition of imported materials, and the sale of dyestuffs delivered as "reparations."

The reports of several chemical firms which have recently appeared have shown dismal losses.

ARTIFICIAL SILK

The manufacture of artificial silk by the viscose process has for many years been a very important industry in England. The position is now more interesting because in addition to the viscose silk, which is a well-established article of commerce, the cellulose acetate silk is on the market, and at least one firm is preparing to exploit a cuprammonium process. The acetate silk is apparently being sold in large quantities and in a number of different colors. Hitherto, the dyeing of acetate silk has not been free from difficulties, but it was known that this material showed some affinity for basic amido-azo dyestuffs.

The process of dyeing, however, depends essentially upon empirical principles, and it is therefore specially interesting to hear of a new class of dyestuffs for acetate silk, discovered by A. G. Green and K. H. Saunders.

These dyestuffs are now manufactured by the British Dyestuffs Corporation, and, while full details of their constitution have not been made public, it is understood that in principle they are azo dyestuffs, depending for their solubility on water in the presence of ω-sulfonic groups. These dyestuffs are now available in a wide range of shades, and it has also been possible to develop these colors on the fiber in a similar manner to the primuline derivatives.

THE THERM INQUIRY

About twelve months ago the sale of coal gas was established upon a thermal basis, and the present system consists in charging the consumer for the number of "therms" consumed, one therm being equal to 100,000 British thermal units.

In recent months a fierce controversy has been going on as to whether this system is just to the consumer, and some wild statements have been made to the effect that most consumers have found their gas bills to be higher since the introduction of the system. A government inquiry is to be held on this question.

It is clear that the value of gas for heating or for incandescent lighting depends, not only upon the calorific value, but also upon the calorific intensity. It is therefore probable that some of the low calorific-value gas supplied by some of the companies does not give such good results, and the charge for therms is not necessarily fair to the consumer.

LUBRICATION

A most important contribution to the theory of lubrication and the constitution of lubricants has been given in the Thomas Hawksley lecture, delivered last week before the Institution of Mechanical Engineers by Dr. T. E. Stanton, of the National Physical Laboratory.

It was pointed out that the theory of Osbourne Reynolds was insufficient to explain correctly the phenomena of lubrication, and particulars of experiments made at the National Physical Laboratory were given. It was shown that seizing is not necessarily an indication of the proximity of the surfaces, and some interesting observations were made upon the difference between the fixed oils and the mineral oils. It has long been known, for example, that even when the viscosities are the same, such oils as castor and sperm show superiority over mineral oils, and it is suggested that the formation of a proper film takes place more readily with the fixed oils, owing to their chemical constitution.

The paper confined itself chiefly to actual results rather than to theoretical considerations, and some of the experiments reported show very interesting results of an unexpected character.

DEWATERING OF PEAT

From time to time discussions arise as to the best method of dewatering peat, and it is generally claimed that compression methods are more economical than centrifugal methods, and that all mechanical processes are superior to the purely thermal methods.

It has been proposed in this connection to employ the vapor recompression system of evaporation, but as this system must finally depend upon the maintenance of a low-temperature difference, it is somewhat difficult to believe that satisfactory results could be obtained on peat.

It should be noted, however, that vacuum drying by multiple effect is a practical proposition, and progress among the thermal methods is to be expected.

Some interesting particulars of the results obtained with an experimental chamber press of special construction were given by Professor Hinchley at the last meeting of the Chemical Industry Club. He stated that, working at a temperature of about 100° C. and employing pressures up to $1/2$ ton per square inch, materials were obtained containing 35 to 45 per cent of moisture, and on the basis of these figures it was estimated that an installation for the production of dried peat, constructed on the same lines as the experimental plant, would require only about 25 per cent of the finished material for the production of the necessary power.

This is a very interesting result, and if the expectations are realized on a larger plant, a big step will have been made toward the solution of the peat problem.

December 14, 1922

The largest sum ever raised to honor a man of science has been contributed to the memorial for Sir William Ramsay, which amounts to more than $500,000. £57,645 has been collected in cash, and this has been augmented by research fellowships instituted by various dominion and foreign governments to the value of about £60,000. The money is to be devoted to the erection of a chemical laboratory at University College, London, and to founding the Ramsay Memorial Fellowships in Chemical Science for British students.

Calendar of Meetings

American Ceramic Society—Annual Meeting, Pittsburgh, Pa., February 12 to 17, 1923.

American Institute of Mining and Metallurgical Engineers—Annual Meeting, New York City, February 19 to 22, 1923.

American Chemical Society—65th Meeting, New Haven, Conn., April 2 to 7, 1923.

American Electrochemical Society—43rd Semiannual Meeting, New York City, May 3 to 5, 1923.

Personals

Dr. Charles D. Walcott, secretary of the Smithsonian Institution, was elected president of the American Association for the Advancement of Science. Ten vice presidents were elected, each representing a section, Prof. E. W. Washburn being elected vice president for the chemical section.

Mr. G. P. Metz and Mr. E. R. Pickrell, both of H. A. Metz & Co., Inc., are spending several weeks visiting France, Germany, and England.

Prof. O F. Stafford, head of the department of chemistry of the University of Oregon, has returned to his university work at Eugene, after a four years' leave of absence devoted to industrial research in the field of waste wood utilization by destructive distillation.

Mr. Carl G. Schluederberg, president of the American Electrochemical Society, left recently for a four months' trip in the Orient to study business conditions.

Dr. Josiah H. Penniman has been elected provost of the University of Pennsylvania. He had been acting provost since the resignation of Dr. Edgar Fahs Smith about three years ago.

Mr. Hugh Kelsey Moore, director of research, Brown Co., Berlin, N. H., has been elected a member of the New Hampshire State Legislature.

Mr. E. F. Davis, formerly of the Dye Works Planning Department, du Pont de Nemours & Co., has just returned from Mexico where he has been installing a chlorine plant.

Mr. W. A. Baude has left the Dye Works of du Pont de Nemours & Co., to become assistant professor of chemical engineering at the University of Cincinnati. His position in the Dye Works is being taken by Mr. Frank Ernst from the Experimental Station.

Mr. M. S. Benjamin, lecturer in agricultural chemistry at the Hawkesbury Agricultural College, New South Wales, is spending some weeks in the United States visiting agricultural colleges and laboratories devoted to agricultural chemistry.

Mr. Milo R. Daughters, chief chemist and manager of research for the Dominion Canners, Ltd., is spending the winter in Florida.

Mr. C. Robert Moulton has resigned his position at the University of Missouri to become head of the Bureau of Nutrition for the Institution of American Meat Packers in Chicago.

Leave of absence has been granted by the Corporation of Yale University to Dr. Lafayette B. Mendel to enable him to deliver a course of lectures at the University of California. Professor Mendel plans to leave New Haven after the dedication of the Sterling Chemical Laboratory in April to join the faculty of the University of California for the intersession, which continues from May 14 to June 23, 1923. Professor Mendel has chosen for his subject "New Aspects of the Physiology of Nutrition."

Mr. L. C. Cooley has accepted a position as plant engineer with the U. S. Industrial Chemical Co., Baltimore, Md.

Mr. T. F. Banigan, formerly acid superintendent for the Hercules Powder Co., at Kenvil, N. J., and lately in acid work at Hercules, Calif., has accepted a position with the firm of Meigs, Bassett, and Slaughter, Inc., of Philadelphia, Pa.

Dr. John W. Caldwell, formerly head of the department of chemistry in Tulane University of Louisiana, died at his home in New Orleans on January 2, 1923.

Mr. Duncan Stewart has left the Mechanical Engineering Department of the Shell Company of California to join the chemical staff of the W. P. Fuller Co., South San Francisco, Calif.

Mr. D. D. Berolzheimer, formerly assistant technical editor of the Chemical Engineering Catalog, is now one of the editors of the Consolidated Textile Catalogs.

Mr. A. E. Marshall has resigned his office as president of Marshall Rieha, Inc., and will devote his attention solely to plant design, consultation, and report work for the chemical industry.

Dr. Irving Langmuir, research chemist of the General Electric Co., has been elected an honorary member of the Royal Institution, London.

Prof. Frank B. Wade, of the faculty of Shortridge High School, Indianapolis, Ind., was recently elected president of the Central Association of Teachers of Science and Mathematics.

Mr. H. H. Replogle has resigned his position as manager of the Intermediates and Certified Food Color Divisions of the National Aniline & Chemical Co., to assume the sales management of the Wamesit Chemical Co., Lowell, Mass.

Industrials

The Columbia Steel Corporation has been organized at San Francisco, with a capital stock of $20,000,000, to consolidate the Columbia Steel Company with the Utah Coal & Coke Company. The corporation is to build a blast furnace and by-products coke oven in Utah for the manufacture of pig iron to supply the California mill.

The United States Pulp Producers' Association, a new organization replacing the old Pulp Manufacturers' Association, began operation on January 1, taking over all the functions of the old organization and assuming some new ones. Changing conditions in the paper industry were given as the cause for the organization of the new association, which is the direct result of the American Paper and Pulp Association's policy of furthering organization among the several branches of the paper industry in order that the industry as a whole might be in a position to act uniformly and coöperatively in matters of local and national importance to the industry and its several branches. The purposes of the new organization are to provide a means for concerted action by pulp manufacturers in matters of tariff, taxation, legislation, etc.; to continue the distribution to members of reports containing all available data regarding the production and importation of wood pulp and pulpwood; to expand these reports to cover not only domestic but foreign production, shipments, exports, etc.; to further the uniformity of cost-finding methods in the pulp industry; and to increase the effectiveness and economy of pulp production. The officers of the organization are: president, T. W. Ross, Hummel-Ross Fiber Co.; vice presidents, L. M. Alexander, Nekoosa-Edwards Paper Co., D. C. Everest, Marathon Paper Mills Co., E. W. Kiefer, Port Huron Sulphite & Paper Co., and W. H. Savery of the Harpers Ferry Paper Co.; executive committee, Herman Elsas, George W. Sisson, Jr., and W. H. Sullivan; secretary-treasurer, O. M. Porter.

The organizing committee of the recently formed British Association of Manufacturers of Noncorrodible and Anticorrosive Products are considering proposals for sectionizing the work of the association under the following heads: noncorrodible metals (nonferrous); noncorrodible ferrous materials; stone and allied preservatives; metallic coating processes; timber preservatives; anticorrosive paints and varnishes for metals; rust-removing methods; boiler-incrustation preventatives.

The American crude oil production in 1922 was the greatest in history, the output reaching 550,000,000 bbls., according to the Shipping Board's estimate. The unprecedented production was 81,000,000 bbls. in excess of the 1921 yield, and represented the greatest annual gain since the discovery of oil in the United States. It is predicted that 1923 will surpass 1922 in point of production.

The drop in the price of radium from $120,000 to $70,000 a gram, following the finding of a vast deposit of pitchblende near Katanga in the Belgian Congo, which is said to be superior to the Colorado ores, is given as the cause for the closing down of the carnotite properties of the Standard Chemical Co., Colorado.

The American Cotton Growers' Association has raised the sum of $2,500,000 to be available at once for the production of arsenate upon a large scale and for the perfection of the methods of distribution and use.

According to unofficial estimates, the automobile industry used 600,000 tons of alloy steel in 1922. The estimate is based on the assumption that 25 per cent of the steel in the average car is alloy steel, and that automobile makers consumed a total of 2,500,000 tons of finished steel in 1922.

The Standard Oil Company of California is soon to inaugurate a correspondence course of instruction for employees in all parts of the state, designed to fit the students for better technical positions. This course is optional with the employees.

The Soda & Potash Corporation has been organized at Los Angeles, and incorporated in Colorado, with a capitalization of 100,000 shares of common stock of no par value, and 250,000 shares of preferred stock. The company is to build a plant at Los Angeles estimated to cost between $1,500,000 and $2,000,000, to make industrial and pharmaceutical sodas and industrial potash for the domestic and export market. The raw material will be mined in Nevada, where the company owns deposits of sodium sulfate, carbonate, bicarbonate, and sesquicarbonate. The officers are: C. W. Culpepper, president; Chas. W. Berry, vice president; Edward P. Shaw, treasurer; F. J. McGuire, secretary.

BOOK REVIEWS

The Chemical Examination of Water, Sewage, and Foods. By J. E. Purvis and T. R. Hodgson. (Cambridge Public Health Series.) 2nd edition. 346 pp. University Press, Cambridge, 1922. Price, $8.00.

The large number of analyses of waters, purification plant effluents, sewages, polluted river and sea water, etc., cited, gives the first portion of the book a considerable value to one broadly interested in the subject of the analysis and purification of water and sewage. Since the methods and examples are so exclusively British, the book will hardly serve as a laboratory guide to chemists in this country. The importance of determining the pH of a water, as well as its titratable alkalinity or acidity, is now well recognized on both sides of the water; yet the authors make no mention of such a procedure. The term "temporary hardness" is incorrectly[1] described, as it was in the first edition. Under water softening no mention is made of the use of zeolites. A rather arbitrary set of tests is given for "works effluents" without reference to the character of the works discharging the effluent. Such important tests as "free mineral acid" are omitted.

The food chemists of this country will find little of service to themselves in this book, either in the classroom or as a laboratory guide. The range of subjects is limited and stress is laid on foreign methods of analysis, disregarding largely those which have been tested and recommended by our own A. O. A. C. In the selection of methods, many that are well known to lead to inaccuracies or approximations have been used. The use of Fehling's solution as a volumetric method for the determination of reducing sugars has been recommended almost to the exclusion of gravimetric methods, and in the gravimetric method the use of a constant conversion factor is suggested. The carefully worked out tables which we have so carefully followed do not appear in the work.

The chapter on milk is elaborate, but we find the Leffman-Beam centrifugal method given for butter fat with no mention of the Babcock process, while the Adams "paper coil" method, in spite of its well-known inaccuracies, is given equal weight with the Rose-Gottlieb procedure. In the chapter on alcoholic beverages the use of the immersion refractometer has not been referred to, and this rapid and accurate method for methyl and ethyl alcohols is not made available.

<div align="right">G. D. Beal and A. M. Buswell</div>

A Method for the Identification of Pure Organic Compounds. Vol. IV. By S. P. Mulliken. vii + 238 pp. John Wiley & Sons, Inc., New York, 1922. Price, $5.00 net.

The appearance of the fourth volume of this compendious work closes the chief part of Professor Mulliken's program, which involves the tabulation of 10,000 of the more important organic compounds with a view to their ready identification when encountered in the laboratory. In Volume I about 2300 compounds of carbon with hydrogen alone and in conjunction with oxygen are described, in Volume II about 4000 organic derivatives of nitrogen; Volume III dealt with pre-war dyes, and is now permanently out of print. In the present volume all other important classes of organic compounds, involving derivatives of the halogens and sulfur alone and in combination with each other and with nitrogen, amounting to about 3700 chemical individuals, are treated in the same way. On account of the

greater variety of possible group arrangements with the increased number of "additional elements," more widely divergent types are included in the generic classifications than in the first two volumes; as before, however, the orders are subdivided into groups of solid and liquid species, the latter being occasionally further resolved according to specific gravity. The reviewer cannot subscribe to the publishers' view that "the use of this book is not limited to those who have unusual experience in the organic field." As in the previous volumes, an integral part of the work consists in the admirable, though brief, discussions of general procedure and group tests, and the study necessary to make full use of the tabulated information constitutes in itself an unusual experience, being nothing short of a course in organic qualitative analysis. The presence of errors is of course inevitable, whether as misprints—e. g., the boiling point of "mustard gas," p. 185—or for other reasons—e. g., oxalyl chloride, p. 28—should be classed as a liquid of boiling point 63.5° to 64° C. and melting point −12° C., but from experience of the previous volumes a large proportion need not be anticipated. The early appearance of a supplementary volume containing new procedure and descriptions is promised.

<div align="right">H. T. Clarke</div>

Rothamsted Experimental Station. Reminiscences, Tales, and Anecdotes. By Edwin Grey, field superintendent. 14 × 22 cm. 155 pp. E. Grey, Laboratory Cottage, Harpenden, England.

The Rothamsted Experimental Station was a pioneer in scientific agriculture, and from a very small beginning in 1843, when a barn was used as a laboratory, it has developed to such an extent that the work accomplished there has gained universal recognition and admiration. It was the object of the author of this little volume to present in the form of a narrative his personal recollections of those who have participated in the development of the institution since his connection with it, which has now extended through a period of fifty years. In this account, therefore, not only the illustrious founders, Lawes and Gilbert, have been considered, but all who took any part in the numerous chemical and botanical experiments, and even the boys and girls to whom the humbler tasks of the field or laboratory were allotted have received their share of recognition.

One may thus follow the gradual change from the primitive conditions and methods of the early days to the present advanced state of development, for the station is now provided with commodious buildings, thoroughly equipped laboratories, and a staff of trained research workers who are capable of conducting the most elaborate scientific investigations. In the field work there has been a similar extension of facilities for the growth and study of agricultural products.

The narrative has been rendered exceedingly entertaining by the incorporation of many humorous incidents connected with the individual characters and events described in the text. A number of excellent illustrations have also been included, among which the portraits of Sir John Bennet Lawes and Sir Joseph Henry Gilbert are particularly deserving of mention. In conclusion, it need only be said that the story of Rothamsted which Mr. Grey has related will be of absorbing interest to all who are concerned with the development of pursuit of agricultural science.

<div align="right">F. B. Power</div>

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[1] A. M. Buswell, "Temporary Hardness in Natural Waters," *J. Am. Water Works Assoc.*, 3 (1916), 959.

Standard Methods of Chemical Analysis. A Manual of Analytical Methods and General Reference for the Analytical Chemist and for the Advanced Student. Edited by WILFRED W. SCOTT. Vol. 1, xxviii + 714 pp.; Vol. II, xvii + 564 pp. Illustrated. 3rd edition, revised and enlarged. D. Van Nostrand Co., New York, 1922. Price, $10.00.

The first and second editions of this book were reviewed in THIS JOURNAL, 9 (1917), 917, and 10 (1918), 250. The third edition appears in two volumes. Volume I contains the "Technical Methods for the Detection and Determination of the More Important Elements," the "Qualitative Tests of Substances," and the "Tables and Useful Data," which comprised Parts I and III of the second edition. Volume II is devoted to the "Special Subjects" which appeared in Part II in the earlier edition.

In Volume I a new chapter on radium has been introduced, and the chapters on cadmium, zinc, bismuth, selenium, tellurium, molybdenum, tungsten, uranium, gold, and platinum have been considerably revised and enlarged. In view of the general excellence of the methods which are given, it is unfortunate that the author still carries along in this revision such careless statements as: "Aluminium hydroxide is precipitated by the addition of a salt of a weak acid to its neutral or slightly acid solution, iron remaining in solution" (page 5); "Aluminium is precipitated as a carbonate by the addition of ammonium carbonate" (page 6); "Arsenous Oxide. The sample may be dissolved in caustic soda, the solution neutralized with hydrochloric acid, and the resulting sample titrated with iodine" (page 35); and "A number of elements such as phosphorus, arsenic, molybdenum, tungsten, vanadium, and the like, form fairly stable compounds with iron in neutral or slightly alkaline solutions " (page 249).

The author pays no attention in several instances to well-known facts—for example, no mention is made of the complex character of the cadmium sulfide precipitate obtained in acid solutions, nor is the necessity for the addition of excess phosphate precipitant before a second precipitation of aluminium phosphate noted.

The illustrations and color plates are for the most part very satisfactory; it is not clear, however, why the key-board type of balance was selected and labeled "Analytical Balance" (page 400), nor why the author still pictures in Fig. 20 (page 122) an air scrubber in which the air is dried by phosphorus pentoxide before its entry into 1:3 sulfuric acid.

In addition to the older chapters, Acidimetry and Alkalimetry, Fixed Oils, Fats and Waxes, Analysis of Paints, Cement, Methods of Analysis of Coal, and Gas Analysis, Volume II contains the new chapters, Asphalts and Allied Substances, Standard Methods of Sampling, Examination of Soap, Sanitary Examination of Water, Electrometric Titrations, Physical and Chemical Constants of Rubber, Solubility of Substances, and Examination of Explosives. In addition, the chapters on alloys and water analysis have been entirely rewritten and miscellaneous subjects, such as the examination of alcohol, introduced.

On the new chapters it is unfortunate that the chapter on the examination of soap was written before the recently completed final report of the Joint Committee.

In the chapter on rubber the methods are in general good, but too briefly described. It would have been better had a general outline for the analysis of rubber goods been given and then complete descriptions of the common methods. On page 1363 it should be noted that an acetone extraction removes only part of the mineral rubbers and substitutes as against the total removal which is inferred.

The volumes are attractive in appearance and will doubtless continue to have the deserved good sale of the previous editions.

G. E. F. LUNDELL

The Examination of Hydrocarbon Oils and of Saponifiable Fats and Waxes. By D. HOLDE, translated by EDWARD MUELLERS, PH.D. 8 vo., 572 pp. John Wiley & Sons, Inc., New York, 1922. Price, $6.00 net.

The first English edition was reviewed by the writer in THIS JOURNAL, 7 (1915), 555, and earlier in the *J. Am. Chem. Soc.*, 28 (1905), 550. He has used the book for more than twenty years.

The general methods of examination in this edition are collected into a single chapter, instead of being given under the different topics treated. Among the additions is a discussion of the electrical excitability of gasoline—a very important matter in the handling of this liquid. Lubrication is discussed at length, seventy pages being devoted thereto, including lubrication with graphite. Other additions have to do with cumarone and other artificial resins, rosin size, surface tension and its measurement. Many chapters, as those on viscosity, turpentine, wool grease and soaps, have been rewritten, the increase in the material amounting to about 20 per cent. Tables of comparison of the properties of the hydrocarbon, as well as the animal and vegetable oils, have been freely used.

A particularly useful feature is the description of methods of discriminating, not only between the oils, but also between various mixtures of different asphalts, coal tars, pitches, waxes, etc. American procedure and instruments are described in many cases; it would seem that Herschel's work upon viscosity should have been more fully discussed, and the MacMichael absolute viscometer included. Americans using the book should not overlook the fact that specifications given are as a rule European —German in many cases, as was naturally to be expected from the potential market for the work. Where A. S. T. M. methods have been described, these are usually those of 1921 or earlier.

It is one of the most satisfactory books about the subjects with which it deals that has appeared in any language. However, nothing else was to have been expected from either the publisher or author. It has almost always given the latest information, and in many cases either first-hand or Holde-tested methods, coupled with the citation of their source.

In translating "Motoroele" as "motor oils" (page 162) it would have been clearer to have rendered it "Diesel motor oils." "Motor oils" usually means "lubricating" rather than "fuel" oils. The translation is fully up to the high standard of the first edition, the translator knowing thoroughly both chemistry and the German language, and having a general knowledge of the subjects treated.

A. H. GILL

American Fuels. By RAYMOND FOSS BACON and WM. ALLEN HAMOR. Vol. I, 628 pp.; Vol. II, 629 pp. McGraw-Hill Book Co., Inc., New York, 1922. Price, $12.00.

This is an excellent and timely book and will be of value for reference to everyone who has the responsibility of the efficient use of fuels. Perhaps a more descriptive title would have been "The Technology of American Fuels." It is a compilation of articles on methods for the preparation and utilization of the different fuels available in America, each article being by a specialist in his particular subject. On this account there is some unavoidable lack of coherence or unity of treatment, but this is not such as to interfere in the slightest with its value to the reader seeking information.

The first two chapters are devoted to a broad survey of the almost limitless fuel resources of this country. Following these are chapters on the technology of coke, which is somewhat weakened by the author's showing himself so manifestly a protagonist of one particular type oven, and on the briquetting of fuel, and coal preparation.

The chapters following on gasification of fuels and on producer-gas technology might better have been combined, as the former discusses mainly gas producers with by-product recovery.

More attention might have been devoted to present-day practice in the treatment of producers, as there is still much ignorance of this subject to be dispelled, in spite of its long commercial history.

Low-temperature distillation of coal is interestingly treated and the information given becomes more valuable when it is considered that this method of carbonization has not yet reached the commercial stage either here or in England.

Two hundred and forty pages are devoted to the subject of pulverized fuels and a subsequent chapter to the recently developed colloidal fuel. Both discussions are well set forth and bring the knowledge of each field up to date. A good description is given of the Trent amalgam process which is attracting so much favorable attention of late.

Fuel oil, natural gas, and water gas, and their utilization are discussed, with particular reference to measures of conservation of the supplies of the first two. In connection with these the chapters on surface combustion and on water gas present many new ideas. The discussion of the "downward charge" is clearly presented. Chapters 21 and 22 deal with problems of heat treatment. The chapter on the economics of American fuel practice should be read by economists and financiers as well as by engineers and manufacturers.

Some errors, manifestly typographical, were noted, which should be corrected in a later edition. On page 44 appears the sentence, "The elementary substances encountered in combustion work are hydrogen and sulfur," which certainly deserves attention. The press work on the book is excellent, the type clear, and the illustrations well chosen.

The reviewer favors the use of the phrase "manufactured gas," rather than "artificial gas," the latter phrase having been used by a number of writers in the present book. The word "manufactured" is preferred to "artificial" by the American Gas Association, U. S. Bureau of Mines, and other authorities. "Artificial" unfortunately has two meanings, one of which suggests falsity or unrealness.

WM. HUTTON BLAUVELT

Researches on Cellulose, IV. By CHARLES F. CROSS and CHARLES DORÉE. 350 pp. Longmans, Green & Co., London, 1921. Price, $5.00 net.

This volume is a critical survey covering the period 1910–1921, inclusive, and with the preceding volumes is intended to supplement Cross and Bevans' original volume on "Cellulose" (1895).

A complete bibliography of the subject is not given, but "a selection of researches dealing with fundamental points" is made, and these, reproduced or abstracted, serve as a basis for constructive criticism.

Three independent aspects of cellulose as a subject of investigation are presented—namely, cellulose (1) as a colloidal substance, (2) as a chemical individual, and (3) under transformation (decay, distillation, fermentation). It is obvious that no sharp lines of demarcation can be drawn between these aspects of the subject, and, while the authors' criticisms are made primarily from the viewpoint of (1), they assign to the systematic chemist under (2) a rather narrower view of the subject than he takes.

The physical phenomena considered include structural breakdown, refraction of light, optical activity, specific volume, fluorescence, and solubility, but with the exception of the last the data permit of no general conclusions. Solution of cellulose in salt solutions is shown to be independent of the nature of the salt, but dependent upon the physical properties of the salt solution.

The material presented on "constitution" indicates glucose and cellobiose, or their anhydrides, to be important structural units in the cellulose molecule; yet the authors contend that "the polydextrose views of constitution are too positive and beyond the warrant of a critical comprehensive survey." Conse-

quently, they assume a "reasoned agnostic position which leaves open all the contributing avenues of observation, experience, and exact knowledge of the workers, who investigate 'cellulose' objectively and to whom the results of the systematic chemist are only one aspect of the matter."

The data on oxy- and hydrocellulose lead to the conclusion that there is no justification for using these terms as applied to chemical individuals. The contributions on lignocellulose leave the chemistry of lignone and lignin still in an indefinite state and add little in the way of answering the question, "Is there one cellulose only?" The consideration given to systematic analysis of the lignocelluloses takes little or no account of the work of Schorger, of Sieber and Walter, and of Schwalbe.

The book contains several unpublished researches by the authors and serves rather to present their point of view than to give an exhaustive review of the subject. One wishes that the material had been sifted more thoroughly and more completely and adjusted more carefully to the definite level, which the authors contend exact knowledge in this field has reached.

S. A. MAHOOD

Standard Specifications for Laboratory Apparatus Adopted by the Manufacturing Chemists' Association of the United States. Part I, Graduates and Thermometers. 49 pp., 13 figures. MANUFACTURING CHEMISTS' ASSOCIATION OF THE UNITED STATES, Woodward Building, Washington, D. C., 1922. Price, $1.50.

This publication gives specifications for volumetric flasks, boiling flasks with round bottom and with flat bottom, Kjeldahl flasks, distilling flasks, Erlenmeyer flasks, weighing bottles, transfer pipets, burets, graduated cylinders, Mohr pipets, laboratory porcelain, du Pont nitrometer, and thermometers. General specifications, including tests, are given for glass and porcelain ware. Dimensions are given for the different items.

The volumetric flasks are of the Giles type with a bulb in the neck about one-tenth the capacity of the body, but they have only the one capacity mark below the bulb. These flasks, the buret, distilling flasks, and the seven thermometers have not been stock articles. Practically all the other items are in general use and the work of the committee has been to select the sizes desired and adopt the dimensions given in the catalogs of manufacturers. With a few exceptions the Bureau of Standards tolerances for dimensions and accuracy have been adopted for graduated ware.

The dimensions for transfer pipets are chosen with reference to the heights of the volumetric flasks. The thermometers are all graduated for 76-mm. immersion and the centers of the tubulatures on the distillery flasks are 77 mm. below the top of the neck. The Barrett 200-ml. distilling flask, the burets, Mohr pipets, and the du Pont nitrometer are illustrated with drawings with complete dimensions.

The laboratories of the companies belonging to the Manufacturing Chemists' Association have been ordering apparatus according to the specifications and some of the new items are listed in catalogs of dealers. The book will be useful as a guide to those purchasing apparatus for commercial or educational laboratories. It should have a decided influence in unifying the practice of the manufacturers and dealers in regard to the pieces of apparatus described. Practically all the recommendations for stock items are in line with recommendations of the Committee on Guaranteed Reagents and Standard Apparatus of the American Chemical Society.

A foreword by Charles L. Reese, president of the Manufacturing Chemists' Association, gives credit to the untiring efforts of the chairman of the association committee, E. C. Lathrop, and to the other members of the committee for the painstaking care with which the work was carried through.

W. D. COLLINS

COMMERCE REPORTS

December

There are indications that the British have determined to become independent in the petroleum world as rapidly as possible. One noteworthy example of this is the action of a number of leading companies engaged in the oil industry which have contributed a large sum of money to the University of Birmingham to build up a great school of oil engineering. (P. 598)

Strong claims have been made by a professor of the Technical High School of Berlin to the effect that he has perfected a new method of obtaining gasoline from crude oil which depends upon unusually high pressures. (P. 598)

At the recent meeting of the French Société de Chimie Industrielle an attempt was made to decide upon questions of nomenclature, methods of testing petroleum products, etc. The organization of a technical and petroleum engineering institute at Pechelbronn has also been under discussion. (Pp. 598–9)

Italy's efforts to secure a measurable independence in petroleum supplies have led to the suggestion that the government subsidize exploratory drilling. (P. 599)

Oil shale as a fuel is being tried out by several railways and also by some of the larger industrial establishments in Esthonia. Recent tests in one of the largest factories showed that much better results could be obtained from oil shale than either wood or turf. (P. 600)

The wholesale drug trade of the West Coast of Mexico is almost entirely in the hands of California wholesale drug houses. (P. 616)

German manufacturers of chemicals and dyes are beginning the redevelopment of their trade in India. (P. 616)

Reports received from practically the whole area under indigo in British India indicate that the acreage for the 1922–23 crop is 226,900, which is 4 per cent below the estimate at the corresponding date of a year ago. (P. 616)

A Portuguese decree of October 24, 1922, prohibits until further notice the exportation of all kinds of fertilizers. (P. 622)

Further details are given regarding the revised import duties on coal-tar dyestuffs and fuel oil in Italy. (P. 622)

New export duties have been placed on oil seeds exported from Mozambique. (P. 622)

Arsenic, arsenate of lead, arsenate of lime, carbonate of soda, copper sulfate, Paris green, and all substances which are to be used for destroying insects injurious to cotton plants are exempted from import duties and taxes by Salvador. (P. 622)

The Soviet Russian mining industry, except salt and some gold and platinum mining, is practically at a standstill. A sharp decline is expected also in the basic chemical industry because of the lack of demand for acids and alkalies. An increase of output, ranging from 30 to 50 per cent, is contemplated for the rubber, dyestuffs, and drug industries. (P. 626)

Bird Lake District in Manitoba is estimated by mining engineers to contain millions of tons of high-grade copper ore, assaying 20 to 27 per cent copper, with a valuation per ton placed at $81.13. (P. 644)

Germany's vegetable-oil industry is so unstable that it seems possible many of the oil-crushing factories in the interior of Germany will be forced to close. (P. 649)

A uniform system of the technical training for textile workers is proposed for Australia. (P. 652)

Machinery has recently been installed in Mexico for conducting experiments for the commercial production of fiber, cellulose, and alcohol from the maguey plant. (P. 652)

The Petroleum Division of the Bureau of Foreign and Domestic Commerce has on file a pamphlet on the "Development of the Argentine Petroleum Industry and Its Importance to World Economy," which may be consulted by referring to File No. 75,641. (P. 657)

There is a good demand for fertilizer in Portugal. (P. 661)

Conditions in the French chemical market are reported to be satisfactory and improving. The fertilizer market is strong; the paint and dye industries are active; and the prices of naval stores show a rising tendency. (P. 661)

Italy has authorized her customs authorities to permit the exportation of ammonium nitrate to be used as fertilizer, calcium cyanamide, and olive residue after the oil has been removed. (P. 672)

Manganese ore may now be exported from Russia free of duty. (P. 673)

Inspectors have been employed in Haiti to enforce the Haitian presidential decree of May 9, 1922, establishing the metric system in all transactions in the Republic. (P. 682)

A translation of Presidential Decree No. 800, Republic of Guatemala, relating to hydrocarbons and amending the original petroleum law of May 27, 1922, may be consulted by referring to file No. 76,318 of the Petroleum Division of the Bureau of Foreign and Domestic Commerce. The same office also has on file, No. 76,429, a copy of an amendment to the Canadian regulations concerning the leasing of petroleum and natural gas rights. (P. 725)

The Rumanian Ministry of Industry and Commerce has granted permission for the exportation of petroleum products. (P. 725)

Although exports of American chemicals and allied products still fall a little short of the totals reached in 1921, indications are that chemicals are holding their own, and statistics to corroborate this statement are given. (P. 727)

The German potash situation is reviewed. (Pp. 727–8)

A further rise in German chemical prices is reported. (P. 728)

Two new ore deposits of considerable extent have been discovered in Sweden, one containing zinc ore and iron pyrites and the other revealing an unusually rich copper ore. (P. 776)

The artificial silk trade of Germany is reviewed. (P. 778)

A movement is on foot in Germany to do away with the chemical middleman, and "From manufacturer to retailer" is the slogan of the day. German chemical-market conditions are reviewed and statistics are given showing the exports of chemicals from Germany from January to September, 1922. (Pp. 779–80)

According to a French ministerial decision, oil of vaseline has been reclassified under tariff items. (P. 813)

Nigeria has added fuel oil other than kerosene to the list of articles which may be imported free of duty.

SPECIAL SUPPLEMENTS ISSUED

ADEN	ITALY	SWEDEN
BRAZIL	MANCHURIA	SYRIA
CEYLON	MEXICO	THE NETHERLANDS
CHINA	PERU	URUGUAY
INDIA	SPAIN	YUGOSLAVIA

STATISTICS OF EXPORTS TO THE UNITED STATES

PORT ELIZABETH, SOUTH AFRICA—(P. 603)	GERMANY (continued)	GERMANY (concluded)
Grease wool	Ammonium carbonate	Cyanides
	Caustic potash	Tartar and tartrates
GERMANY—(P. 780)	Potashes	Carbonate of strontium
Alkali metals	Chloride of lime	Zinc salts
White and red phosphorus	Potassium chlorate	Arsenous and arsenic acid
Lactic acid and lactates	Sodium sulfate and bisulfate	Magnesium sulfate
Tartaric acid	Potassium sulfate	Chlorides (calcium, magnesium)
Citric acid	Copper sulfate	Muriate of potash
Crude potash salts	Alums	Ammonium chloride
Fertilizer salts	Ammonium nitrate	Potassium and sodium sulfates
Barium chloride	Barium nitrate	Barium, lead, and nickel compounds
Bromides and bromoform	Potassium manganate and permanganate	
	Ferricyanides	

CURRENT PUBLICATIONS

NEW BOOKS

American Society for Testing Materials. Proceedings of the Twenty-fifth Annual Meeting. Part I. Committee Reports. New and Revised Tentative Standards. 1023 pp. Part II. Technical Papers. 501 pp. Price, each part, paper, $6.00; cloth, $6.50; half-leather, $8.00. American Society for Testing Materials, Philadelphia, Pa.

Catalysis in Organic Chemistry. Paul Sabatier. Translated by E. Emmet Reid. 405 pp. Price, $5.00. D. Van Nostrand Co., New York.

Chemical Age Yearbook and Diary for 1923. 40 pp. Price, 10s. 6d. Benn Bros., Ltd., London.

Coal: Methods of the Chemists of the U. S. Steel Corporation for the Sampling and Analysis of Coal, Coke and By-products. 2nd edition. 184 pp. Price, $3.00. Bureau of Instruction, Carnegie Steel Co., Pittsburgh, Pa.

Flavouring Materials: Natural and Synthetic. A. Clarke. Oxford Technical Publications. 166 pp. Price, 8s. 6d. Henry Frowde and Hodder and Stoughton, London.

Gas: The Flow of Gases in Furnaces. W. E. Groume-Grjimailo. Translated by A. D. Williams. 399 pp. Price, $5.50. 194 illustrations. John Wiley & Sons, Inc., New York.

Gasworks Recorders. Leonard Levy. 246 pp. Price, 35s. net. Benn Bros., Ltd., London.

Gas: The Romance of the Gas Industry. O. E. Norman. 203 pp. Price, $1.50. A. C. McClurg & Co., Chicago.

Gas: Fuel Research Board. Technical Paper 5. An Apparatus for the Measurement of Specific Gravity of Gases in Small Quantities. Alfred Blackie. 7 pp. Price, 3d. net. H. M. Stationery Office, London.

Molybdenum Ores. R. H. Rastall. 86 pp. Price, 3s. net. John Murray, London.

Oil: Ueber Fette Öle. Leinölersatzmittel und Ölfarben. Alexander Eibner. Price, $3.00. B. Heller, München.

Oxidations and Reductions in the Animal Body. H. D. Dakin. 176 pp. Price, 6s. Longmans, Green & Co., London.

Report of the Committee of the Privy Council for Scientific and Industrial Research for the Year 1921-22. 123 pp. Price, 3s. 2¹/₂d. H. M. Stationery Office, London.

Textiles: Betriebseinrichtungen der Textilveredelung. Paul Heermann and Gustav Durst. 164 pp. Price, $1.50. Julius Springer, Berlin.

X-Rays: The Industrial Applications of X-Rays. P. H. S. Kempton. 110 pp. Price, 2s. 6d. Sir Isaac Pitman & Sons, Ltd., London.

RECENT JOURNAL ARTICLES

Acid and Alkaline Chlorine Bleaching of Cotton. E. Ristenpart. *Textile Colorist*, Vol. 44 (1922), No. 528, pp. 783-84. Translated from *Textilberichte*.

Ammonia as a Refrigerant. W. H. Motz. *Canadian Chemistry and Metallurgy*, Vol. 6 (1922), No. 12, pp. 260-64.

Bibliography of Stainless Steel and Iron. Victor S. Polansky. *Forging and Heat Treating*, Vol. 8 (1922), No. 12, pp. 560-65.

Blast-Furnace Slag: An Investigation of Losses in Copper Blast-Furnace Slag. D. F. Stedman. *Engineering and Mining Journal-Press*, Vol. 114 (1922), No. 24, pp. 1023-27; No. 25, pp. 1072-74.

Catalysts: Some Recent Work on the Mechanism of Catalyst Poisoning. E. B. Maxted. *The Chemical Age* (London), Vol. 7 (1922), No. 182, pp. 816-18.

Chemical Industry: Some Achievements of Chemical Industry during the War in This Country and in France. William Macnab. *Journal of the Society of Chemical Industry*, Vol. 41 (1922), No. 23, pp. 353t-61t.

Chrome Refractories. J. Spotts McDowell and H. S. Robertson. *Journal of the American Ceramic Society*, Vol. 5 (1922), No. 12, pp. 865-87.

Cobalt Tungsten Alloys. Karl Kreitz. *The Metal Industry*, Vol. 20 (1922), No. 12, pp. 463-64. Translated from *Metall und Erz*.

Comparative Tests of English and Domestic Whitings. A. E. Williams and B. J. Woods. *Journal of the American Ceramic Society*, Vol. 5 (1922), No. 12, pp. 901-15.

Developed Dyestuffs. Julius Rath. *Color Trade Journal*, Vol. 12 (1923), No. 1, pp. 9-11. Translated from *Textilberichte*.

Gas Generators: Les Gazogènes à Fusion de Cendres depuis l'Origine jusqu'à 1921. A. Folliet. *Chimie et Industrie*, Vol. 8 (1922), No. 5, pp. 965-73.

Gases: Removal of Solid and Liquid Particles from Gases. A. F. Nesbit. *Blast Furnace and Steel Plant*, Vol. 10 (1922), No. 12, pp. 637-41.

Glass: The Application of Calorizing to Glass-making Processes. S. Frank Cox. *The Glass Industry*, Vol. 3 (1922), No. 12, pp. 243-45.

Glass: The Composition of Lime Suitable for Various Purposes in Glass-Making. Violet Dimbley and W. E. S. Turner. *Journal of the Society of Glass Technology*, Vol. 6 (1922), No. 23, pp. 221-28.

Glass: Some Practical Notes on the Manufacture of Colourless Glass in a Tank Furnace. F. W. Adams. *Journal of the Society of Glass Technology*, Vol. 6 (1922), No. 23, pp. 205-10.

Glass: The Weathering of Glass Containers. K. L. Ford. *Journal of the American Ceramic Society*, Vol. 5 (1922), No. 12, pp. 837-54.

Hosiery Dyeing. Arthur T. Brainerd and Water E. Brainerd. *American Dyestuff Reporter*, Vol. 11 (1922), No. 13, pp. 441-46, 463.

Hydrated Silica: La Silice Hydratée. Son Utilisation dans l'Industrie Chimique. G. Durocher. *L'Industrie Chimique*, Vol. 9 (1922), No. 107, pp. 533-36.

Lead: The Action of Natural Waters on Lead. John C. Thresh. *The Analyst*, Vol. 47 (1922), No. 560, pp. 459-68; No. 561, pp. 500-05.

Leather: The Influence of Moisture on the Extraction of Oils and Greases from Leather. Arthur M. Hey. *Journal of the Society of Leather Trades' Chemists*, Vol. 6 (1922), No. 11, pp. 385-89.

Leather: The Plumping of Hide Powder by Lactic and Acetic Acids. J. S. Rogers. *Journal of the American Leather Chemists' Assoc.*, Vol. 17 (1922), No. 12, pp. 611-22.

Leather: Time Reduction in the Tanning Process. R. O. Phillips. *Journal of the American Leather Chemists' Assoc.*, Vol. 17 (1922), No. 12, pp. 594-605.

Locomotive Brasses and Bronzes. Sir Henry Fowler. *The Metal Industry*, Vol. 20 (1922), No. 12, pp. 461-62.

Nitrometer Method for the Determination of Nitrogen in Nitrates and Nitric Acid. H. W. Webb and M. Taylor. *Journal of the Society of Chemical Industry*, Vol. 41 (1922), No. 23, pp. 362t-64t.

Sodium Cyanide: Fabrication du Cyanure de Sodium, par les Vinasses de Distillerie ou de Sucraterie de Melasses. De Jussieu. *L'Industrie Chimique*, Vol. 9 (1922), No. 107, pp. 530-33.

Starch Products and Malt Extracts Used in Textile Treatment. A. J. Hall. *Textile Colorist*, Vol. 44 (1922), No. 528, pp. 776-77, 781-82.

Steel: The Manufacture of Fine Forging Steels. Larry J. Barton. *Blast Furnace and Steel Plant*, Vol. 10 (1922), No. 12, pp. 612-18.

Steel: Practical Notes on the Heat Treatment of High-Speed Steel. H. K. Ogilvie. *Forging and Heat Treating*, Vol. 8 (1922), No. 12, pp. 551-52.

Thermal Efficiency and Heat Balance of an Open Hearth Furnace. C. L. Kinney and G. R. McDermott. *Blast Furnace and Steel Plant*, Vol. 10 (1922), No. 12, pp. 629-36.

Washing Benzol and Other Carbons out of Gas. Karl Bunte and E. Frei. *American Gas Journal*, Vol. 117 (1922), No. 3384, pp. 673-76, 678-9.

MANUFACTURERS' TECHNICAL PUBLICATIONS

Combustion. A 16-page pamphlet descriptive of the various fuel-saving devices marketed by the Combustion Engineering Corp., 45 Broad St., New York City.

Electrical Communication: The Bell System Technical Journal. A quarterly journal "devoted to the scientific and engineering aspects of electrical communication." (This journal, of which two numbers of 150 pages each have so far appeared, is designed for the publication of the researches conducted in the laboratories of the American Telephone and Telegraph Co. The papers so far published are of the high scientific merit in the special field which the journal serves.) Subscription price, $1.50 per year. Single copies, 50 cents. Published by the Information Department, American Telephone and Telegraph Co., 195 Broadway, New York City.

Electric Motors: L-A Motors, Type H. D. A 16-page booklet describing the heavy-duty electric motors of the Louis Allis Co. These motors are of the induction type and have a rotor winding punched in one piece from a solid copper sheet which prevents the usual trouble experienced with windings as ordinarily made up of many units. The Louis Allis Co., Milwaukee, Wis.

Essential Oils: Semiannual Report on Essential Oils, Synthetic Perfumes, etc. Booklet of 172 pages, giving notes on scientific research in this field. Schimmel & Co. (Fritsche Brothers), Miltitz, near Leipzig.

Plant and Products. 24-page booklet describing steam turbines, centrifugal pumps, blowers and compressors, and speed-reducing gears. De Laval Steam Turbine Co., Trenton, N. J.

Magnitude of the Power Plant's Chimney Loss. Relation between CO_2 and Money Wasted up the Chimney. Leaflets of Uehling Instrument Company, Paterson, N. J.

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 Mines

A Section through the New Albany Shale. J. B. REEVES. *Reports of Investigations* 2425. 5 pp. Issued December, 1922.

Comparative Steaming Tests of Nenana Lignite and Matanuska Bituminous Coals. J. A. DAVIS AND PAUL HOPKINS. *Reports of Investigations* 2412. 9 pp. Issued November, 1922.

Experiments on Back Pressure in Oil Wells. T. E. SWIGART. *Reports of Investigations* 2420. 9 pp. Issued December, 1922.

Mesothorium. HERMAN SCHLUNDT. *Technical Paper* 265. 57 pp. Paper, 10 cents.

Natural Gas as a Factor in Oil Migration and Accumulation in the Vicinity of Faults. R. VAN A. MILLS. *Reports of Investigations* 2421. 6 pp. Issued December, 1922.

Rock Strata Gases in Mines of a Nevada Mining District. E. D. GARDNER. *Reports of Investigations* 2427. 4 pp. Issued December, 1922.

The Explosibility of Methane-Air and Gasoline-Air Mixtures as Related to the Design of Explosion-Proof Electric Motors. E. J. GLEIM. *Reports of Investigations* 2422. 7 pp. Issued December, 1922.

The Production of Carbon Black from Natural Gas by the High-Voltage Arc. J. J. JAKOWSKY. *Reports of Investigations* 2417. 10 pp. Issued December, 1922.

Twelfth Annual Report of the Director of the Bureau of Mines to the Secretary of the Interior for the Fiscal Year Ended June 30, 1922. 33 pp. Paper, 10 cents.

Bureau of Standards

Annual Report of the Director of the Bureau of Standards, 1922. *Miscellaneous Publication* 50.

Bibliography of Scientific Literature Relating to Helium. *Circular* 81. Paper, 10 cents.

Fifteenth Annual Conference on the Weights and Measures of the United States. *Miscellaneous Publication* 51. Paper, 15 cents.

Gases in Metals: 1—The Determination of Combined Nitrogen in Iron and Steel and the Change in Form of Nitrogen by Heat Treatment. LOUIS JORDAN AND F. E. SWINDELLS. *Scientific Paper* 457. Paper, 5 cents.

Preparation and Properties of Pure Iron Alloys: II—Magnetic Properties of Iron-Carbon Alloys as Affected by Heat Treatment and Carbon Content. W. L. CHENEY. *Scientific Paper* 463. Paper, 15 cents.

Preparation and Properties of Pure Iron Alloys: III—The Effect of Manganese on the Structure of Alloys of the Iron-Carbon System. H. S. RAWDON AND FREDERICK SILLERS, JR. *Scientific Paper* 464. Paper, 10 cents.

Protective Metallic Coatings for Rustproofing of Iron and Steel. With Bibliography. *Circular* 80. 2nd ed. 12 pp. Paper, 20 cents.

Reclamation of Used Petroleum Lubricating Oils. W. H. HERSCHEL AND A. H. ANDERSON. *Technologic Paper* 223. Paper, 5 cents.

The Structure of Fucose. E. P. CLARK. *Scientific Paper* 459. Paper, 5 cents.

United States Government Specification for Turpentine (Gum Spirits and Wood Turpentine). *Circular* 86. 2nd ed. 11 pp. Paper, 5 cents.

Various Photoelectrical Investigations. W. W. COBLENTZ. *Scientific Paper* 462. Paper, 10 cents.

Bureau of the Census

Manufactured Gas. 14th Census of the United States: Manufactures, 1919. Prepared under the supervision of E. F. HARTLEY. 27 pp. 1922.

Paper and Wood Pulp. 14th Census of the United States: Manufactures, 1919. Prepared under the supervision of E. F. HARTLEY. 15 pp. 1922.

Congress

Sulfate of Ammonia. Extracts from Hearings on Proposed Tariff Act of 1921 (*H. R.* 7456), Schedule 1; Statements of C. G. ATWATER AND R. F. BOWER. 16 pp. 1922.

Tariff Act of 1922, with Index. *H. R.* 7456, to provide revenue, tó regulate commerce with foreign countries, to encourage industries of the United States, and for other purposes. *Public* 318, 67th Congress. 198 pp. 1922.

Department of Agriculture

A Physical and Chemical Study of Milo and Feterita Kernels. G. L. BIDWELL, L. E. BOPST, AND J. D. BOWLING. *Department Bulletin* 1129. 8 pp. Paper, 5 cents. Issued November 27, 1922.

Forest Products Laboratory, Madison, Wis. *Department Circular* 231. Reprint. 48 pp. Paper, 15 cents.

Report of the Insecticide and Fungicide Board. 8 pp. 1922.

Department of Commerce

Annual Report of the Director, Bureau of Foreign and Domestic Commerce. 114 pp. 1922.

Federal Trade Commission

Report on the Fertilizer Industry, August 19, 1916. Reprint with slight changes. 272 pp. Paper, 50 cents. 1922.

Geological Survey

Cement in 1921. B. W. BAGLEY. Separate from Mineral Resources of the United States, 1921, Part II. 14 pp. Published January 8, 1923.

Chromite of Kenai Peninsula, Alaska. A. C. GILL. *Bulletin* 742. 52 pp. Paper, 15 cents.

Forty-third Annual Report of the Director of the United States Geological Survey to the Secretary of the Interior for the Fiscal Year Ended June 30, 1922. 80 pp. 1922.

General Features of the Magnetite Ores of Western North Carolina and Eastern Tennessee. W. S. BAYLEY. Prepared in Coöperation with the North Carolina Geological and Economic Survey and the State Geological Survey of Tennessee. *Bulletin* 735-G. Separate from Contributions to Economic Geology, 1922, Part I. 60 pp. Published December 8, 1922.

Geology of the Ranger Oil Field, Texas. FRANK REEVES *Bulletin* 736-E. Separate from Contributions to Economic Geology, 1922, Part II. 60 pp. Published November 27, 1922.

Geology of the York Tin Deposits, Alaska. EDWARD STEIDTMANN AND S. H. CATHCART. *Bulletin* 733. 130 pp. Paper, 30 cents.

Gold, Silver, Copper, and Lead in South Dakota and Wyoming in 1921. Mines Report. C. W. HENDERSON. Separate from Mineral Resources of the United States, 1921, Part I. 6 pp. Published December 13, 1922.

Gold, Silver, Copper, Lead, and Zinc in Utah in 1921. Mines Report. V. C. HEIKES. Separate from Mineral Resources of the United States, 1921, Part I. 22 pp. Published November 27, 1922.

High-Grade Clays of the Eastern United States, with Notes on Some Western Clays. H. RIES, W. S. BAYLEY, AND OTHERS. *Bulletin* 708. 314 pp.

Lime in 1921. G. F. LOUGHLIN AND A. T. COONS. Separate from Mineral Resources of the United States, 1921, Part II. 14 pp. Published November 29, 1922.

Manufactured Gas and By-products in 1920. R. S. McBRIDE. Separate from Mineral Resources of the United States, 1920, Part II. 59 pp. Published December 12, 1922.

Sulfur and Pyrites in 1921. H. A. C. JENISON AND H. M. MEYER. Separate from Mineral Resources of the United States, 1921, Part II. 5 pp. Published December 29, 1922.

Surface Water Supply of the United States, 1919–1920. Part VII. Lower Mississippi River Basin. N. C. GROVER, ROBERT FOLLANSBEE, AND R. C. RICE. *Water-Supply Paper* 507. 49 pp. Paper, 10 cents.

Surface Water Supply of the United States, 1918. Part III. Ohio River Basin. N. C. GROVER, A. H. HORTON, AND C. G. PAULSEN. Prepared in Coöperation with the States of Illinois and Kentucky. *Water-Supply Paper* 473. 115 pp. Paper, 10 cents.

The Brooks, Steen, and Grand Saline Salt Domes, Smith and Van Zandt Counties, Texas. SIDNEY POWERS AND O. B. HOPKINS. *Bulletin* 736-G. Separate from Contributions to Economic Geology, 1922, Part II. 61 pp. Published December 23, 1922.

The Occurrence and Uses of Peat in the United States. E. K. SOPER AND C. C. OSBON. *Bulletin* 728. 207 pp. Paper, 50 cents.

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MARKET REPORT—JANUARY, 1923

[Supplied by Drug & Chemical Markets]

January, 1923, has been a generally slow month in the chemical business. Of course, there have been the usual exceptions, such as arsenic, the arsenates, bleaching powder, and one or two others, but, taken all in all, demand for spot chemicals has been quite dull. Contract business on caustic, soda ash, muriatic and sulfuric acids, and other industrial chemicals, however, which was very active preceding the turn of the year, has continued being closed in sufficient volume to keep the big manufacturers of these products busy at all plants. Prices ruling at the close of the month, when considered from the viewpoint of the whole, stand about at the same levels as those ruling at the end of 1922, and at approximately the same figures at which 1923 contracts are indicated to have been made in most instances.

Shortage of supplies in a number of materials is becoming more pronounced as improvement in buying becomes more general. White arsenic supplies are known to be far below the amount required by the insecticide manufacturers for calcium arsenate. A recent report that 25,000 tons of calcium arsenate would be available by July 1 is not given much credence in the trade and has had no effect upon the market price of arsenic which has sold at $15\frac{1}{2}$ cents per lb. to consumers. The largest consumers of arsenic, however, are not in the market very strongly at the present prices, and are content to make the best of the situation, but are not offering arsenate in very large quantities. Some makers are receiving supplies from previously placed contracts with smelters at lower prices.

The season for buying copper sulfate is approaching and a good inquiry has been noted, though the demand will be affected to a certain extent by the scarcity of arsenic for Paris green purposes. Makers of copper sulfate have advanced prices along with the recent advance in metallic copper. Lead acetate and other lead compounds have also been increased in price owing to advances of $3 per ton in the cost of pig lead. Bleaching powder and chlorine have been in strong demand and makers are well sold up in these commodities. Some manufacturers advanced their prices at the beginning of the new year. Oxalic acid has shown a weakness due to competition between domestic and foreign material. Prussiates weakened on slower demand and are quoted at lower prices.

Caustic potash has gained in strength after a long period of weakness. Large stocks have gradually passed into consumers' hands at prices below current shipment prices, and dealers are now quoting higher prices. Sodium nitrate is higher. Sodium sulfide is strong and in good demand. Makers have reduced sodium cyanide. Bichromates are in good contract demand. Copperas is very scarce in first hands while demand has been on the increase. Niter cake and salt cake are in small supply in all hands. Glauber's salt is in good demand. Tin crystals were advanced at the first of the month on the increased cost of the metal.

An acute scarcity exists in the market for coal-tar crudes. Benzene, toluene and solvent naphtha production is unable to keep pace with the strong demand for these products. The increased use of benzene for motor fuel is the main reason for the scarcity. All supplies of cresylic acid have been taken up and only imported material is available and this at the extremely high price of $1.60 per gal. Domestic production is small and is contracted for far in advance. Phenol is in much the same position as cresylic acid. Domestic production cannot meet the demand, and imported material is selling at 35 and 40 cents per lb. Demand has fallen off slightly due mainly to the high prices. The thirty million pounds which were on hand at the close of the war have passed into consuming channels. One year ago phenol was selling at 11 cents per lb. and since that time has advanced over 300 per cent in price. No definite steps seem to have been taken for the production of synthetic phenol in the U. S. as yet.

Intermediates have gained in demand and prices are firm. Old stocks are pretty well taken up and the tendency of prices is upward, owing to the increasing cost of production. In the oil market strength has been shown throughout the whole list since the first of the year. Animal oil and animal products have been especially strong and are higher in price. China-wood oil is very scarce and is selling at 15 and 16 cents per lb. Fish oils practically dropped out of the market with the closing of the fishing season. Turpentine has advanced again to $1.56 per gal. after a decline to $1.43.

Among the fine and medicinal chemicals, conditions have been more than ordinarily quiet during the past month. Manufacturers advanced prices for all salicylates in spite of an easier position for phenol. Salicylate prices have, for many months past, been far out of line with phenol costs, so the advance in the former, following a drop in phenol, is not as incongruous as it might appear on the surface. Sugar of milk is extremely scarce and higher.

Heavy chemical average chart for 1920, 1921, 1922.

- HEAVY CHEMICAL AVERAGE -
Simple Average of Twenty Representative Heavy Chemicals.
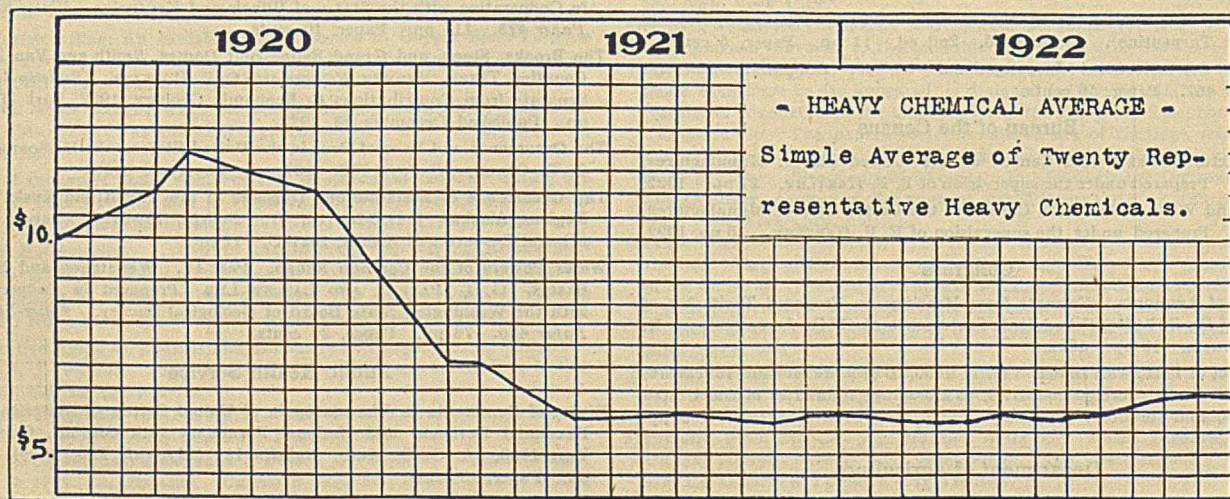
FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

INORGANIC CHEMICALS

	Jan. 1	Jan. 15	Jan. 1922
Acid, Boric, cryst. bbls.......lb.	.11¾	.11¾	.12¾
Hydrochloric, comm'l. 20° lb.	.01¼	.01¼	.01¼
Hydrofluoric, 30% bbls..lb.	.06	.06	.07
Hydriodic, sp. gr. 1.150...lb.	2.25	2.25	2.00
Nitric, 42°, cbys. c/l wks.lb.	.05½	.05½	.06
Phosphoric, 50% tech....lb.	.08	.08	.10
Sulfuric, C. P............lb.	.08	.08	.07
66° tks. wks........ton	15.00	15.00	16.00
Oleum 20%..........ton	18.00	18.00	19.00
Alum, Ammonia, lump.......lb.	.03½	.03½	.03½
Potash, lump...........lb.	*.03¼	*.03¼	*.03½
Chrome..........lb.	.06	.06	.07
Soda, ground............lb.	.04	.04	.03½
Aluminium Sulfate (iron-free).lb.	.02½	.02½	.02½
Ammonium Carbonate, pwd...lb.	.10¾	.10¾	.08
Chloride, white gran.....lb.	.07¾	.07¾	.07½
Ammonia, anhydrous ....lb.	.30	.30	.30
Ammonia Water, drums, 26°..lb.	.08½	.08½	.07½
Arsenic, white.............lb.	.15½	.15½	.08½
Barium Chloride............ton	*95.00	*95.00	*53.00
Nitrate................lb.	*.08	*.08	*.07
Barytes, white...........ton	33.50	33.50	28.00
Bleaching Powd., 35%, works ....100 lbs.	2.00	2.00	2.25
Borax, cryst., bbls........lb.	.05½	.05½	.05¾
Bromine, pure, wks..........lb.	.29	.29	.23
Calcium Chloride, fused, f.o.b. N. Y..........ton	24.50	24.50	28.75
Chlorine, liquid.............lb.	.06	.06	.06
Copper Sulfate..........100 lbs.	6.00	6.00	5.55
Iodine, resublimed...........lb.	4.50	4.50	3.80
Lead Acetate, white crystals..lb.	.12	.13	.11
Nitrate................lb.	.22	.22	.15
Red.................lb.	.10¼	.10¾	.08
White (Carb.)..........lb.	.08½	.08½	.07¼
Lime, live and hydrated, bbl..lb.	.01¾	.01¾	.01½
Oyster shell...........lb.	.03	.03	.02¾
Lime Acetate..........100 lbs.	3.50	3.50	1.75
Magnesium Carbonate, tech...lb.	.07½	.07½	.06
Magnesite, calcined..........ton	55.00	55.00	55.00
Phosphorus, yellow..........lb.	*.28	*.28	*.27
Red.................lb.	*.30	*.30	*.30
Plaster of Paris.............bbl.	4.25	4.25	4.25
Potassium Bichromate.......lb.	.10	.10	.10½
Bromide, imported.......lb.	*.19	*.19	*.13
Carbonate, calc., 80–85%..lb.	*.05½	*.05½	*.04½
Chlorate, cryst.........lb.	*.07½	*.07½	*.05½
Hydroxide, 88–92%.....lb.	*.06½	*.06¾	*.06
Iodide, bulk............lb.	3.50	3.50	2.90
Nitrate................lb.	.08	.08	.08
Permanganate, U. S. P....lb.	*.17	*.16	*.15
Prussiate, red.........lb.	*.90	*.90	*.29
Yellow.............lb.	*.38	*.38	*.24½
Salt Cake, bulk............ton	28.00	28.00	17.00
Silver Nitrate..............oz.	.43	.44½	.44½
Soda Ash, 58%, bags...100 lbs.	*1.80	*1.80	*1.85
Caustic, 76%, N. Y..100 lbs.	3.75	3.75	3.80

*Resale or Imported (not an American makers' price).

	Jan. 1	Jan. 15	Jan. 1922
Sodium Acetate.............lb.	.07½	.07	.04
Bicarbonate........100 lbs.	2.00	2.00	2.00
Bichromate..........lb.	.07½	.07½	.07¾
Bisulfite, powd..........lb.	.04¼	.04¼	.04¼
Chlorate.............lb.	.07	.07	.07½
Cyanide, 96–98%.......lb.	.23	.23	.28
Fluoride, tech..........lb.	.09½	.09½	.09½
Hyposulfite, bbls.....100 lbs.	3.20	3.20	3.50
Nitrate, 95%......100 lbs.	2.60	2.60	2.32½
Nitrite................lb.	.08½	.08½	.06½
Prussiate, yellow......lb.	.19	.18½	.16½
Phosphate (di-sod.),tech..lb.	.04½	.04½	.04¼
Silicate, 40°..........lb.	.01½	.01½	.01½
Sulfide, 60%, fused.....lb.	.05	.05	.05
Strontium Nitrate..........lb.	*.10	*.10	*.10
Sulfur, flowers..........100 lbs.	3.00	3.00	2.75
Crude, mines.......long ton	14.00	14.00	16.00
Tin Bichloride, 50% sol'n.....lb.	.10½	.10½	.09¾
Oxide..............lb.	.38	.38	.37
Zinc Chloride, U. S. P........lb.	.20	.20	.35
Oxide, bbls...........lb.	.07½	.07½	.08

ORGANIC CHEMICALS

	Jan. 1	Jan. 15	Jan. 1922
Acetanilide, U. S. P., bbls......lb.	*.34	*.34	*.29
Acid, Acetic, 28 p.c.......100 lbs.	3.17	3.17	2.37½
Glacial.............lb.	.12½	.12½	.10
Benzoic, U. S. P........lb.	.73	.73	.60
Carbolic, cryst., U. S. P., drs..............lb.	.35	.35	.12
50- to 110-lb. tins.....lb.	.38	.33	.18
Citric, crystals, kegs....lb.	*.49	*.49	*.43
Oxalic, cryst., bbls., wks...lb.	.13½	.13½	.14
Pyrogallic, resublimed....lb.	1.60	1.60	1.75
Salicylic, U. S. P......lb.	.45	.45	.24
Tannic, U. S. P., bbls....lb.	.70	.70	.75
Tartaric, cryst., U.S.P...lb.	*.30	*.30	*.25
Acetone, drums.............lb.	.21	.21	.12
Alcohol, denatured, complete.gal.	.42	.42	.45
Ethyl, 190 proof, bbls....gal.	4.75	4.75	4.75
Amyl Acetate...............gal.	2.50	2.50	2.00
Camphor, Jap, refined, cases...lb.	.91	.86	.90
Carbon Bisulfide, c/l........lb.	.06	.06	.06½
Tetrachloride.........lb.	.10	.10	.10½
Chloroform, U. S. P., drums...lb.	.35	.35	.43
Creosote, U. S. P............lb.	.40	.40	.40
Cresol, U. S. P.............lb.	.27	.27	.14
Dextrin, corn..........100 lbs.	3.09	3.09	2.70
Imported Potato........lb.	.09	.09	.06½
Ether, U. S. P., 100 lbs.......lb.	.14	.14	.14
Formaldehyde, bbls..........lb.	.16	.16	.10½
Glycerol, dynamite, drums....lb.	.16	.16	.14½
Methanol, pure, bbls.........gal.	1.30	1.30	.75
Methylene Blue, med.......lb.	2.25	2.25	4.00
Petrolatum, light amber......lb.	.04	.04	.05¼
Pyridine................gal.	2.00	3.00	1.75
Starch, corn, pow'd.....100 lbs.	2.47	2.47	2.13
Potato, Jap..............lb.	.07	.07	.06½
Sago...................lb.	.03½	.03½	.04

FINE CHEMICAL AVERAGE — Simple Average of Twenty Representative Fine Chemicals

Courtesy of Drug & Chemical Markets
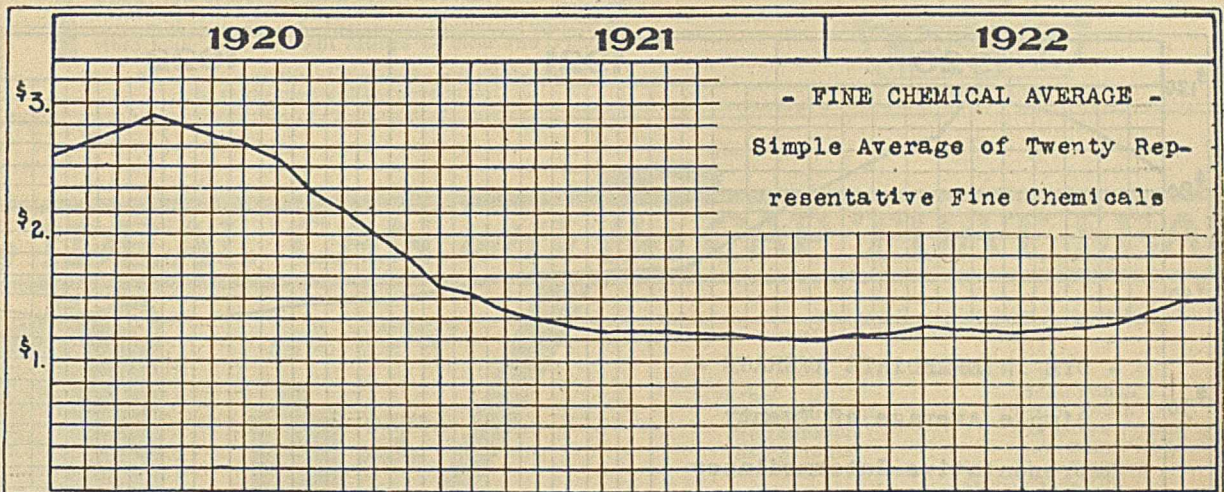
OILS, WAXES, ETC.

	Jan. 1	Jan. 15	Jan. 1922
Beeswax, pure, white........lb.	.37	.37	.33
Castor Oil, No. 3.............lb.	.12½	.12½	.10½
Ceresin, yellow..............lb.	.08	.08	.07½
Corn Oil, crude, tanks, mills..lb.	.09	.09¾	.06¾
Cottonseed Oil, crude, f. o. b. mill................lb.	.09¼	.09½	.07
Linseed Oil, raw, c/l.........gal.	.87	.90	.69
Menhaden Oil, crude, mills...gal.	.50	.52	.35
Neat's-foot Oil, 20°..........lb.	.18	.18½	.16¾
Paraffin, 128–130 m. p., ref.....lb.	.03¾	.03¾	.05
Rosin, "F" grade, 280 lbs....bbl.	6.30	6.25	5.30
Rosin Oil, first run..........gal.	.43	.45	.36
Shellac, T. N................lb.	.76	.80	.66
Sperm Oil, bleached winter, 38°.....................gal.	1.02	1.02	1.70
Stearic Acid, double pressed...lb.	.12	.12½	.09¾
Tallow Oil, acidless...........lb.	.12	.12¾	.10
Turpentine, spirits of........gal.	1.47	1.56	.82½

METALS

	Jan. 1	Jan. 15	Jan. 1922
Aluminium, No. 1, ingots.....lb.	.23	.23	.17
Antimony, ordinary......100 lbs.	6.50	6.75	4.55
Bismuth....................lb.	2.65	2.65	1.80
Copper, electrolytic..........lb.	.14⅝	.14¾	.13⅞
Lake...............lb.	.14⅝	.14¾	.13¾
Lead, N. Y.............100 lbs.	7.25	7.80	4.70
Nickel, electrolytic..........lb.	.36	.36	.45
Platinum, refined, soft........oz.	118.00	118.00	78.00
Quicksilver, flask......75 lbs. ea.	74.00	73.00	52.00
Silver, foreign.................oz.	.67	.67⅛	.65¼
Tin........................lb.	.38¾	.39	.32¾
Tungsten Wolframite....per unit	7.50	7.00	2.00
Zinc, N. Y..............100 lbs.	7.40	7.30	5.20

FERTILIZER MATERIALS

	Jan. 1	Jan. 15	Jan. 1922
Ammonium Sulfate, expt..100 lbs.	3.55	3.55	2.60
Blood, dried, f. o. b. N. Y...unit	4.65	4.65	3.50
Bone, 3 and 50, ground, raw..ton	28.00	28.00	30.00
Calcium Cyanamide, unit of ammonia	2.25	2.25	2.25
Fish Scrap, dried, wks......unit	5.25	5.35	3.25 & .10
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68%.....ton	3.00	3.00	5.00
Tennessee, 78–80%.....ton	3.00	3.00	8.00
Potassium Muriate, 80%...unit	.70	.70	*.75
Tankage, high-grade, f. o. b. Chicago...............unit	4.65 & .10	4.65 & .10	3.00 & .10

COAL-TAR CHEMICALS

Crudes

	Jan. 1	Jan. 15	Jan. 1922
Anthracene, 80–85%........lb.	.75	.75	.75
Benzene, pure, tanks........gal.	.30	.30	.29
Naphthalene, flake..........lb.	.06½	.06½	.07½
Phenol, drums..............lb.	.40	.40	.11

Crudes (*concluded*)	Jan. 1	Jan. 15	Jan. 1922
Toluene, pure, tanks........gal.	.30	.30	.30
Xylene, 2 deg. dist. range, tanks.................gal.	.45	.45	.45

Intermediates

Acids:

	Jan. 1	Jan. 15	Jan. 1922
Anthranilic..............lb.	1.10	1.10	1.10
Benzoic, tech...........lb.	.65	.65	.50
Cleve's.................lb.	1.25	1.25	1.50
Gamma................lb.	1.80	1.80	2.25
H.....................lb.	.78	.78	1.00
Metanilic..............lb.	1.00	1.00	1.60
Monosulfonic F........lb.	2.30	2.30	2.30
Naphthionic, crude......lb.	.62	.62	.65
Nevile & Winther's......lb.	1.15	1.15	1.30
Picric.................lb.	.20	.20	.25
Sulfanilic.............lb.	.20	.20	.26
Tobias'................lb.	1.30	1.30	2.00
Aminoazobenzene............lb.	1.15	1.15	1.15
Aniline Oil.................lb.	.16½	.16½	.17
Aniline Salt................lb.	.24	.24	.25
Anthraquinone (sublimed)....lb.	1.35	1.35	1.50
Benzaldehyde, tech.........lb.	.65	.65	.45
U. S. P.............lb.	1.40	1.40	1.25
Benzidine Base.............lb.	.85	.85	.90
Benzidine Sulfate...........lb.	.70	.70	.70
Diaminophenol.............lb.	3.75	3.75	5.50
Dianisidine................lb.	4.50	4.50	4.75
p-Dichlorobenzene..........lb.	.06	.06	.15
Diethylaniline.............lb.	.60	.60	.90
Dimethylaniline............lb.	.40	.40	.40
Dinitrobenzene.............lb.	.20	.20	.21
Dinitrotoluene.............lb.	.20	.20	.25
Diphenylamine.............lb.	.52	.52	.58
G Salt...................lb.	.65	.65	.70
Hydroquinol...............lb.	1.15	1.15	1.35
Monochlorobenzene.........lb.	.08	.08	.10
Monoethylaniline...........lb.	1.00	1.00	1.00
b-Naphthol, dist...........lb.	.24	.24	.30
a-Naphthylamine...........lb.	.29	.29	.30
b-Naphthylamine...........lb.	.95	.95	1.05
m-Nitroaniline.............lb.	.62	.62	.85
p-Nitroaniline.............lb.	.74	.74	.77
Nitrobenzene (Oil Mirbane)...lb.	.10	.10	.10
p-Nitrophenol..............lb.	.72	.72	.75
o-Nitrotoluene.............lb.	.11	.11	.15
p-Nitrotoluene.............lb.	.65	.65	.70
m-Phenylenediamine........lb.	.90	.90	1.10
p-Phenylenediamine........lb.	1.50	1.50	1.60
Phthalic Anhydride.........lb.	.35	.35	.38
R Salt...................lb.	.60	.60	.60
Resorcinol, tech............lb.	1.30	1.30	1.50
U. S. P.............lb.	2.00	2.00	2.00
Schaeffer's Salt............lb.	.60	.60	.70
Sodium Naphthionate........lb.	.56	.56	.70
Thiocarbanilide............lb.	.35	.35	.40
Tolidine (base)............lb.	1.00	1.00	1.20
Toluidine, mixed...........lb.	.30	.30	.30
o-Toluidine...............lb.	.15	.15	.20
p-Toluidine...............lb.	1.00	1.00	1.10
m-Toluylenediamine........lb.	.95	.95	1.10
Xylidine..................lb.	.42	.42	.40

DYE INTERMEDIATE AVERAGE — Simple Average of Twenty Representative Intermediates