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EDITORIALS

Helium *vs.* Hydrogen

A LITTLE while ago the French dirigible Dixmude set sail for a tour over the Mediterranean. The ship has never been found, but such remains as have been discovered are reported as charred, indicating that the same fate overcame this proud airship as has overcome most of those depending upon hydrogen. The Dixmude was in a storm and was probably struck by lightning. This would cause disaster only in case sufficient air had diffused into the bag to produce an explosive mixture, or in case there were a sufficient leak of hydrogen to become ignited by lightning or any other means, yet such conditions are the rule rather than the exception. But lightning is not the only danger to such a ship. The static electricity that accumulates is liable at any moment to produce a spark of sufficient intensity to ignite the gas mixture.

Some time later the United States dirigible Shenandoah, anchored to a steel mast, was subjected to the terrific strains and stresses of another storm perhaps comparable in its severity with that which overtook the Dixmude. After a time the force became too great for the mechanism involved and the ship was torn loose, one or two of the gas compartments being ruptured. Sparks twelve to eighteen inches in length indicated the presence of static, and all conditions were right for another catastrophe by fire and explosion such as overtook the Roma and the dirigible in England wherein many American and British lives were lost. But the Shenandoah did not burn. She returned safely to her hangar. Fortunately, she depended, not upon hydrogen, but upon helium, for which we are largely indebted to the foresight and constructive work of Admiral Moffett and the Army and Navy Helium Board assisted by the U. S. Bureau of Mines.

Why has this important fact been entirely overlooked in official discussions and press reports? What is back of the obvious effort to have American people forget helium? To say that people have now had impressed upon them the fact that helium is the most important and unique feature of the Shenandoah will not answer the question. Gas is gas to the nontechnical public. It has been claimed that the cost of helium is too high. Yet, by installing condensers to retain the moisture from the exhaust gases, the necessity of valving, with consequent loss of helium and consequent cost of helium for operation, would be obviated. Also, recent experiments on a semicommercial scale have indicated that helium can be produced at considerably less cost than at present. Still the opinion persists that the cost of helium is too high. What price will a man set upon his own life? To what extent would the American people support a commercial or even a military dirigible program after another catastrophe by fire? Can it be possible that those interested in commercial aviation are hoping to assure Americans of the safety of dirigibles by the performance of the Shenandoah, carefully suppressing details with reference to helium on the theory that they can then operate with hydrogen-filled balloons?

Is it possible that the apparent aversion to helium is due to the influence of a German engineer occupying a responsible place in our air service? America possesses a helium monopoly. It is conceivable that our good fortune is regarded jealously by those who remain loyal to other countries under all circumstances. True, helium saved his life as well as the lives of others who are at least lukewarm toward it,

but no doubt aviators become indifferent to danger for, notwithstanding the experiences of others, those living have never been burned nor had their necks broken.

This whole helium question should be brought frankly into the open. The people must be made acquainted with the great advantages of helium, and must not be allowed to forget that the greatest factor of safety in a balloon is this chemical element—helium.

Lend a Hand

H ERBERT N. McCOY, of Chicago, has accepted a place on the board of trustees for the publication of the International Critical Tables, and will act as field secretary with the special object of completing the campaign for the necessary funds as rapidly as possible. This marks a new and important step in this project which we have brought to the attention of our readers from time to time. It is the work now sponsored by the National Research Council which is of most interest to chemists. It aims to supply our research and technical men with extensive tables of physical and chemical constants critically evaluated and compiled from the viewpoint of American scientific needs. It will be the first comprehensive edition of tables in the English language, and for those who support the compilation it offers a real investment. What organization could search the literature for a given table of values for the sum which it might invest in this coöperative undertaking?

Those who have applied such data to industrial problems find it difficult to comprehend the lack of interest in a few quarters in this new undertaking. Industries without such experience have doubtless conducted expensive experiments or made unsuccessful installations because they did not know how to secure critical data. The project is so worthy from whatever angle it may be discussed that we surely need to do nothing more than announce that Dr. McCoy and the other members of the board of trustees deserve your support and assistance, not only in the future, but immediately. About seventy-seven thousand dollars is wanted in addition to that already pledged or paid. The work is going to be done and done properly. It will be a credit to America when finished. You will want to have had a part in it.

Gossip

I N TIMES that are tense and when both excitement and suspicion run high, there is a notable tendency, even among folks who should know better, to repeat gossip and speed rumor on its destructive way. The dangers of repeating hearsay have been the subject of age-old discussion, but nevertheless men are willing all too frequently to repeat a statement without first ascertaining the real facts. In the hope that some may be saved from such temptation we quote the following from *The Roller:*

Gossip is a humming bird with eagle wings and a voice like a foghorn. It can be heard from Dan to Beersheba, and has caused more trouble than all the ticks, fleas, mosquitoes, coyotes, grasshoppers, chinch bugs, rattlesnakes, sharks, earthquakes, cyclones, blizzards, smallpox, yellow fever, gout, and indigestion that all this United States has known or will know until the universe shuts up and begins the final invoice. In other words, it has got war and h—l both backed up in the corner and yelling for ice water.

The 1923 Dye Imports

THE review of the 1923 dye imports compiled by the Tariff Commission affords much food for thought and furnishes further argument for the specialization in manufacture which we discussed editorially in our July, 1923, issue. We quote from the review:

This list points out the leading dyes of foreign origin used by the domestic textile and dye-consuming industry. Of the sixty-six dyes in this table, totaling 1,617,052 pounds, seven were imported in excess of 50,000 pounds each and twenty-seven in excess of 20,000 pounds. The total imports for the fourteen leading dyes exceeded 700,000 pounds. Twenty-two of the sixty-six dyes in this table were of Swiss manufacture and 31 per cent of the quantity came from that country, while practically the entire remainder were manufactured in Germany.
The vat dyes lead in the quantity of imports. Indanthrene Golden Orange G and R, totaling 123,140 pounds, and the two vat pinks (Hydron and Helindone) 91,067 pounds, while the figures for Indanthrene Yellow were 83,208 pounds. Among the acid dyes the Patent Blues and Xylene Light Yellow totaled 120,059 pounds. Of the mordant and chrome colors, Alizarin Blue Black leads with an import of 56,332 pounds, followed by Alizarin, synthetic with 35,168 pounds, less than one-fifth of the pre-war imports. In the group of direct colors, Diaminogene Blue and the two Trisulfon Browns accounted for over 100,000 pounds. Of the basic dyes, Phosphine and Rhodamine 6G and B accounted for nearly 95,000 pounds.
Only two of the dyes in the comparison table, namely, Schultz 220 Buffalo Black PY and Schultz 392 Buffalo Direct Orange, were produced in the United States in 1914, whereas at present about thirty of this list are now being manufactured.

The figures further emphasize that more work must be done on a few important dyes if we are to have a well-rounded industry with a balanced production program. In the acid dyes, five were imported in quantities in excess of 25,000 pounds. In the vat dyes, twelve were imported in amounts above that figure, four among the mordant and chrome dyes, two in the class of direct dyes, and three classed as basic dyes. Our dye industry has doubtless been justified in concentrating upon dyes of greater tonnage instead of making large investments in research and development on these few that may be rated as the more costly, but the time when tariff is to be reduced from 60 to 45 per cent ad valorem is just around the corner. If these dyes have not been produced under the higher protection, it will be more difficult to perfect them with less protection. The seven cents per pound specific remains, but with the cheaper colors amply protected, their production will continue to be encouraged and the perfection of the more costly dyes will become less attractive. This is a condition we do not like to see, and from the start we have contended for a really balanced program.

The past two years have been active years and American companies have not only added specialties to their lines which duplicate some of those made elsewhere, but have actually added their own colors not heretofore produced in any works. All of this represents constructive effort, and we know that extensive research has gone forward on such popular items as Indanthrene Golden Orange and Hydron and Helindone Pink. There has been increased domestic production and increased exportation, both of which are encouraging. There has also been increased production in foreign countries and greater competition in the Far East. Since there is not the coöperation between our strong groups that is so much to be desired, perhaps it will come to pass that our greatest strength will be in the further specialization of manufacture undertaken by smaller plants with highly trained personnel and mutually high regard between the technical staff and the financial directors. Domestic manufacturers are still in competition with reparation dyes which continue to come to us from France and Italy, as well as with the German products and dyes made in other countries under German auspices.

The attitude in the dye industry toward the development of new things involving the support of the research laboratory reminds one of the old story of the roof which could not be patched in rainy weather and did not need patching in dry weather. When the dye industry is busy there is no time for research, and when it is not, there is no money for it. There is still a greater tendency to look backward than to look forward. We need all the lawful coöperation between our producers that can be obtained. We need a legitimate combination of facilities for export business. We need to establish our own standards, so that our products will properly command world business.

The Coal Question

IN COMMON with millions of other people we have been interested in the coal question and the speculation as to whether anything ever can or will be done that will appeal to the ultimate consumer as something really constructive. The ease with which the governor of a State primarily interested in coal production settled a strike in favor of the numerous voters of his State and at the cost of the general public will long be remembered. It was a disappointment to many who believed the country in a proper frame of mind to fight out a strike begun, so we are informed, primarily to prevent a reduction in wages, but which ended with the miners and the operators sitting on top of the world.

A recent discussion by a number of specialists left us with the feeling that no one knows the real way in which to better the situation. One eminent geologist believes that the outstanding trouble with coal is the waste—waste of resources, waste of capital, waste of man power, and waste of transportation. It is said that there are one hundred million tons of avoidable waste in the bituminous mines, and that the conservation of coal is going forward much more rapidly in utilization than in the mining and handling of this essential material. The central power stations in 1921 obtained 25 per cent more kilowatt hours from the same fuel than in previous years. Conservation of man power might be obtained through better management, a better spirit of coöperation, and such modifications of union rules as would remove limits that are now quite definite. The introduction of better machinery and the promotion of a longer working season are other factors. The waste of capital is due to the high cost of overdevelopment, the unnecessary waste through competition, and the failure to limit new developments. The combination of certain mines is advocated.

The desire for a long haul on the part of the railroads is said to play an important part in waste through transportation. Mines that were not needed have been opened and, in one case, six thousand cars were used for six months to haul five million tons to the Lakes from Tennessee and Virginia because of a twenty-five cent freight differential for the three hundred mile greater haul, whereas Pennsylvania coal would seem to have been satisfactory.

Others point out that the operators have taken every possible advantage of improved machinery, which has made progress paralleling the development of new electric devices, but that the unions have seriously interfered with the introduction of this machinery. In many places any saving due to the use of new devices has had to be paid to the unions in some form of wage. Another expert emphasizes that better utilization is one of the great possibilities and that the place to apply brains today is no longer in the engine room but in the boiler room. In some of the more modern plants 86 per cent of the heat in the fuel finds its way into the heat in the steam, whereas the average for the country is probably not 65 per cent. The storage problem is outlined as everybody's business and therefore nobody's business, and since

the consumer is underorganized, whereas both the operators and miners are organized, the question of storage becomes a problem for governmental solution.

Some believe that there should be a department of mines so that the President might have upon his Cabinet some one whose full time would be given to a consideration of mine problems. Another compares the large investment in a mine operating at the most two hundred and twenty days at eight hours per day with the investments in metal mines where two or three shifts are employed throughout the year, and suggests that perhaps, since the public must pay interest on the coal reserves, the Government should own all coal fields and grant licenses for their operation.

Out of all this a few things are certain. We have excess mines, excess miners, and overproduction. The opening of new mines should be ended, and we should abstain from recruiting more miners. But it is not the American fashion to control development. The seasonal factor in mining is not unique, for other industries confront the same situation. Perhaps the miners only exercise the same group influence which gives rise to the famous blocs in Congress. Perhaps, after all, miners are merely typical of that class of Americans who work as little as possible, get all they can for the work done, and preach the joy of leisure.

There seem to be two things that can be done at the moment. One is the constant collection and review of facts as the best method for continued attack on this difficult problem. The other is continued scientific research which, perhaps, will bring us eventually to consider coal as a raw material, subject to various treatments to obtain its best values. The search by the scientific method for adequate substitutes for anthracite initially and for a better production and transportation of power from its prime source eventually must continue. The whole fuel problem offers one of the best opportunities for experimental development and research.

Our International Journal

NO ONE should overlook the significance of the statement, "Published under the auspices of the American Chemical Society, the Chemical Society, and the Faraday Society," which appears after the title of the *Journal of Physical Chemistry* in the first number of its Volume 28. The listing of the associate editors without special reference to the societies to which they belong is another interesting feature of this first step in international coöperation in chemistry on a basis which gives us a journal devoted to a special branch of our science. The willingness of the Chemical Society and the Faraday Society to join forces with the American Chemical Society is something to which we have pointed with justifiable pride. This, together with the generous financial support of Francis P. Garvan, makes available an international journal which will bring regularly to our desks and laboratories discussions of the latest work in physical chemistry throughout the English-speaking world.

Not only those working and specially interested in physical chemistry, but all who desire to see the possibility of international coöperation in such matters fully demonstrated, should lend their support to this project, firm in the belief that it will prove beyond doubt a precedent for further joint effort. Such coöperation might include the publication of our monographs, reports, and reviews, and even abstracts. As the science continues to develop, there will be recurring need for publications in special fields and these needs can best be met on an international basis.

We predict that the *Journal of Physical Chemistry* will set a standard worthy of emulation by other scientific publications.

Right About Face

IT HAS been said that the negotiations between the Interessengemeinschaft and the British Dyes Corporation which have been in progress for two years have been consummated or are about to be consummated. This comes as something of a shock to all who relied upon our British friends to stick to their colors. The British Dyes Corporation was formed to prevent the German dye trust from regaining the virtual monopoly of the trade in the British Empire which it enjoyed before the war. Indeed, the British concern has been regarded as a semiofficial organization, has been supported with certain government grants, and at one time was protected by special legislation. A number of outstanding Britishers, including Lord Moulton, Sir William Pope, and James Morton, have steadfastly called the attention of the British public to the necessity of creating a dye industry in Great Britain. The British Dyes Corporation has had its difficulties, as have all others who have attempted to accomplish in a few years what it has taken their competitors several decades to achieve.

It is barely possible that in the hands of a Labor Government there is prospect of all the needed protection for the industry being withheld and that the corporation faced a choice between losing all it had or making an arrangement with the group it most feared in business. We predict that it will be another instance to which the old rhyme about the young lady from Niger will be applicable. It was to be expected that the Cartel would leave nothing undone to regain a world monopoly in synthetic organic chemical trade, but it would hardly be expected that our various allies would be so willing to enter into such close trade agreements. The *Manchester Guardian* reports that under the terms of the agreement the British company is given a monopoly of the British market and is also allocated a percentage share of the colonial and foreign markets in which to push its products without fear of German competition. It may also call upon the German concern for information as to manufacturing processes now in vogue in England and is entitled to the services of the German experts. In return for these concessions the I. G. is to receive half the profits after all obligations have been met.

We have repeatedly argued against such alliances and have pointed out their great dangers. The Germans, having found that they could not overcome the competition of these new manufacturing groups, proceeded to form an alliance with them in very much the same way as does a political boss who finds the opposition growing too strong and perfects his own organization by some such unholy alliance. The German dye interests now enjoy similar arrangements with French, Swiss, Italian, Soviet Russian, and British makers, and our industry doubtless faces several alternatives. Persistent rumor has it that one or two of our large companies have also been approached by representatives of German interests who seek to ratify a similar agreement with American interests. We devoutly trust this scheme will fail. Another alternative is to shut up shop. This cannot be considered. A third choice is to perfect our processes, put our chemicals on a high plane of quality, and build up such export companies as our laws allow, so that we can meet the competition of the world in foreign markets, particularly the Far East.

That the British public will be indignant over the right about face of the British Dyes Corporation is to be expected. Already an indignation meeting has been held. Results will be awaited with interest. Should a similar unfortunate arrangement be made with American firms, we predict that they would be immediately deprived of protection and left to the mercies of the tiger.

The Filtration of Activated Sludge[1]

By F. W. Mohlman

THE SANITARY DISTRICT OF CHICAGO, CHICAGO, ILL.

DES PLAINES RIVER TREATMENT WORKS

APPROXIMATELY 3000 pounds of dry activated sludge are produced daily at the Des Plaines Treatment Works. As removed from the aeration tanks the moisture content averages 98 per cent, although it frequently is as low as 97 per cent. Sludge is removed from the Dorr thickeners daily and stored in rectangular tanks containing Filtros tile aerators for pretreatment. From these storage tanks the sludge is pumped directly to the filters.

When the press house was put into operation, in September, 1922, two types of presses were available. The first was a 120-plate Simplex press, a typical recessed-plate filter press with a special type of grooved recesses. A perforated sheet-metal plate was riveted over the grooves, on which the filter cloth rested. The plates were center-feed, the thickness of the cakes 1 inch. The filtering area was 1815 square feet. Pressure could be built up to 125 pounds per square inch.

The other press was a Worthington platen press, similar to the one used at Milwaukee in 1918.[2] This press held eighteen bags, each 5 × 8 feet, supported between perforated platens. The filtering area was 1440 square feet.

The first few pressings were made with untreated sludge. The bags soon clogged and very slimy cakes were produced, even with a long pressing of from 7 to 8 hours. It became increasingly difficult to handle the sludge produced.

Experimental pressings in 1917 at the Stockyards Testing Station[3] of The Sanitary District of Chicago had shown that acidification with sulfuric acid greatly improved filtration of the activated sludge produced from packing-house wastes. Subsequent work by Wilson[4] and Copeland indicated that the degree of acidification required could be controlled most easily by pH determinations, also that only a short interval should intervene between acidification and filtration.

Acid was used for a number of pressings, and as far as practicable the pH was adjusted to the optimum value, approximately 3.5 as shown by laboratory tests with Büchner funnels. Results were very unsatisfactory, with wet, slimy cakes and dirty bags. It was necessary to press 24 hours per day, with a chemist present only during the day shift; consequently, perfect adjustment of the acidity could not be obtained. The sludge produced in the plant exceeded the output of presscake, and bags had to be washed frequently.

Small-scale work at Argo at the Corn Products Testing Station (*loc. cit.*) had indicated that filter alum was very effective in preparing activated sludge for filtration. Accordingly, laboratory tests were made with the Des Plaines sludge, using varying amounts of filter alum, $Al_2(SO_4)_3.18H_2O$.

A practical, simple method of treatment of activated sludge before filtration has been in use for the past year at the activated sludge plants and testing stations of The Sanitary District of Chicago. Several varieties of filters and filter presses have been tested, mostly on a full-size, working scale. The work has been carried on at the Des Plaines River Treatment Works, where operation began in August, 1922; at the Calumet Treatment Works, where operation of the activated sludge units began in April, 1923; and at the Corn Products Testing Station, which has been in operation since 1921. The procedure in use at each plant is discussed separately.

The results showed considerable improvement over the use of acid, and as soon as possible alum was used for pretreatment of all sludge produced in the plant. A marked improvement in filtration was noted immediately. The cakes were dryer, the time of filtration was shortened, and the bags were cleaner.

The use of alum was so satisfactory that it was adopted as routine procedure in the pretreatment of sludge.

A comparison of the relative efficiency of acid and alum for pretreatment is shown in Table I. These results were obtained by filtration of 250 cc. of treated sludge through a battery of Büchner funnels, using a sludge containing 99.06 per cent water.

TABLE I—RELATIVE EFFICIENCY OF ACID AND ALUM FOR PRETREATMENT

| | SULFURIC ACID 66° Bé. | | | FILTER ALUM | |
Cc. per Gallon	Time of Filtration, Minutes and Seconds	pH	Pounds per 1000 Gallons	Time of Filtration, Minutes and Seconds	pH
0	7:30	7.1	0	8:00	7.1
1	10:15	6.2	3	2:00	6.7
2	9:30	5.3	6	1:50	6.4
3	6:00	4.3	9	1:40	6.2
4	5:00	3.2	12	1:30	6.0
5	4:00	2.5	15	1:15	5.8

These results have been verified a number of times, and show facts which indicate why alum has proved so much more satisfactory than acid. An insufficient amount of acid or a drift back to a pH between 5 and 6 may actually cause an increase in the time required for filtration. On the other hand, the addition of even small amounts of alum produces a sharp decrease in time of filtration, with little tendency toward deflocculation and at no time an actual increase in time of filtration. The curve shows no "humps" and no sharply defined isoelectric point. Similar results have been noted by van der Meulen and Smith[5] in experiments on the use of alum for coagulating Imhoff sludge.

A rather interesting fact has been demonstrated by a number of laboratory tests and proved by months of practical operation—namely, that the sludge may be too concentrated for effective use of alum. For example, 97 per cent sludge treated with the usual amount of alum (say 10 pounds per 1000 gallons) will not filter so rapidly as the same sludge diluted to twice its volume—that is, to 98.5 per cent moisture and treated with the same amount of alum. The flocculation is visibly not so good in the heavy as in the light sludge.

These observations have resulted in the following procedure for the pretreatment of the sludge:

The sludge is drawn into the storage tank, where its moisture content is determined approximately by means of a special hydrometer which has been calibrated by many tests on sludges of various moisture contents. If the apparent moisture content is below 98.5 per cent, effluent or city water is added to bring the moisture up to that point. Alum is then added, never more than 10 pounds per 1000 gallons. If possible, the sludge is used up within 6 hours; if it has to

[1] Presented before the Division of Water, Sewage, and Sanitation at the 66th Meeting of the American Chemical Society, Milwaukee, Wis., September 10 to 14, 1923.

[2] Hatton and Copeland, Fourth Annual Report of the Milwaukee Sewerage Commission, p. 70 (January 15, 1918).

[3] Pearse and Mohlman, Report on Industrial Wastes from the Stockyards and Packingtown in Chicago, p. 160 (January 20, 1921).

[4] Wilson and Heisig, THIS JOURNAL, 13, 406 (1921).

[5] THIS JOURNAL, 15, 281 (1923).

stand 24 hours, more alum is added. A small amount of air is used to keep the sludge uniform in composition and aerobic.

The pH is usually decreased to 5.8 to 6.0, at which point practically all the alum is precipitated as $Al_2(OH)_6$. It will be noted that the function of the alum is thus as a coagulant as used in water filtration, and not for its salt effect, after the isoelectric point has been obtained by the use of acid. Much lower amounts are required if alum is used as outlined than if acid and alum are used together.

The amount of alum left in the sludge as a diluent of the valuable nitrogenous material is absolutely negligible. At the rate of 10 pounds per 1000 gallons of 98.5 per cent sludge, only about 30 pounds, or 1.5 per cent, of Al_2O_3 will be added to a ton of dried sludge.

The costs of alum and sulfuric acid are compared in Table II. Sludge moisture is taken at 98.5 per cent, the cost of alum at 1.75 cents per pound, and of acid at 1 cent per pound. These quotations are both high, due to the fact that the supplies were bought in small lots and had to be brought in by truck.

TABLE II—COMPARATIVE COSTS OF ALUM AND SULFURIC ACID

Sulfuric Acid 66° Bé.			Filter Alum		
Cc. per Gallon	Pounds per Ton Dry Sludge	Cost per Ton Dry Sludge	Pounds per 1000 Gallons	Pounds per Ton Dry Sludge	Cost per Ton Dry Sludge
0	0	$0.00	0	0	$0.00
1	65	0.65	2	32	0.56
2	130	1.30	4	64	1.12
3	195	1.95	6	96	1.68
4	260	2.60	8	128	2.24
5	325	3.25	10	160	2.80
6	380	3.80	12	192	3.36

Since at least 4 cc. of sulfuric acid per gallon at a cost of $2.60 per ton of dry sludge would probably be required, it is apparent that the cost of alum as it has been used here has been at least as low as if acid had been used.

Alum has been used as described above since October, 1922, with uniform success. No so-called "winter sludge" was encountered, pressing and pretreatment were for practical purposes just as satisfactory in January and February as in July and August. On the other hand, one period of difficulty was encountered in April, 1923. During this month an attempt was made to cut the air in the aeration tanks to the minimum amount capable of giving an effluent that would not decolorize methylene blue in less than 8 or 10 days. The air was gradually reduced to as low as 0.66 cubic foot per gallon, but as the air was cut the nitrates in the effluent were reduced from 7 or 8 parts per million down to 1 or 2 parts per million. The effluent was still clear, but stabilities began to drop off. The main difficulty was noted, however, in filtration of the sludge. Although the same pretreatment was continued— in fact, the alum dosage was increased—slimy cakes were obtained and filter cloths clogged rapidly. The air was soon increased to 1.2 cubic feet per gallon and the nitrates were built up to 5 to 10 parts per million. Coincidentally, the sludge began to press more easily, and soon was back to its former satisfactory condition. Confirmation of this phenomenon has been obtained a number of times at the Corn Products Testing Station.

The present trend of development of the activated sludge process seems to be in the direction of decreased aeration and minimum nitrification. Numerous mechanical and biological schemes are proposed which require less power than that required by aeration with compressed air, but generally no nitrification is obtained. The writer believes that thorough activation, as evidenced by formation of 5 parts per million or more of nitrate nitrogen, is essential for the production of a sludge that will filter easily, and that this factor must be remembered in attempts to turn out a satisfactory effluent without nitrification.

Calumet Treatment Works

The Calumet Treatment Works include two activated sludge units, each with a capacity of 1.75 million gallons per 24 hours. Sludge was built up and ready for pressing in June, 1923. An Oliver filter has been installed and has been filtering all sludge produced. This filter is 11 feet 6 inches in diameter and 14 feet long, covered with 495 square feet of filter cloth. It has not been possible to run for more than 7 or 8 hours continuously with this filter, as the sewage is quite dilute and the sludge accumulates very slowly. As at the Des Plaines Works, it was found that untreated sludge would not filter satisfactorily. Alum was used for preparation of the sludge, but it was found desirable to add more alum, up to 14 pounds per 1000 gallons. A number of tests with Büchner funnels indicated much more rapid filtration with alum treatment than with acidification. The filter has worked very satisfactorily during the short time it has been operated. The average rate of filtration has been approximately 0.011 pound dry sludge per square foot filtering surface per minute. This high rate of filtration combined with the fact that filtration is continuous and cleanly has indicated that this type of filter is preferable to the pressure filters in use at the Des Plaines Works.

Corn Products Testing Station

An unusual type of activated sludge has been produced at the Corn Products Testing Station from the wastes from the Corn Products Refining Company. This sludge is usually very light and voluminous, frequently containing over 99 per cent water. It contains over 75 per cent organic matter on the dry basis, and from 6.5 to 7.5 per cent nitrogen. The problem of pressing this sludge is unusually difficult because of its watery nature and the rapid changes in its character due to biological conditions.

Two filters have been used for pressing this sludge, a recessed-plate filter press and a small American continuous filter. The latter is a rotating leaf suction filter containing 20 square feet of filtering surface. In principle it is similar to the Oliver filter. Many substances have been used for pretreatment of the sludge before filtration. It was found in the winter of 1921–22 that frequently it was impossible to produce a cake in the filter press, no matter what pretreatment the sludge received. It would be absolutely impossible at times to produce a cake in a reasonable length of time with the recessed-plate type of press.

The American filter has offered more hope. Sludge has been pressed both hot and cold many times, using as filter aids sulfuric acid, alum, dicalcium phosphate, spent bone ash, sulfur dioxide, and Filter-cel. General conclusions were:

1—By suitable pretreatment of the sludge it should be possible at all times to produce a cake with a type of suction filter similar to the American filter.

2—A very dilute sludge (99.5 per cent water) or one not well activated cannot be pretreated with any of these substances, including heating to 150° F., so as to give a high rate of filtration—that is, a rate greater than 0.080 pound per square foot per minute. A well-activated sludge with a moisture content of 98.5 or 99 per cent can be treated with either alum or acid, with or without heating, and will give a satisfactory cake with a high rate of filtration. The moisture content without heat is usually about 85 per cent, with heat from 80 to 82 per cent. Apparently heating does not greatly increase the rate of filtration. Alum treatment is generally more effective than acidification.

3—Phosphates, bone ash, Filter-cel, and sulfur dioxide are of little value.

4—The ratio of time of pick-up to time of drying is fixed. It would be desirable to be able to vary the ratio—that is, to shorten the time of pick-up with a heavy sludge and to lengthen it with a dilute sludge. Control of the degree of vacuum and blanking off of one or more sectors are unsatisfactory methods for accomplishing such variations.

CONCLUSION

As a result of the uniformly successful use of alum for pretreatment of the activated sludges produced at Des Plaines, Calumet, and Argo, the writer believes it to be preferable to acid as a practical aid in filtration. It has the advantages of being safe to handle, there is no possibility of increasing time of filtration, it is as cheap as acid, it gives a very clear filtrate, and it is not necessary to control the amount used within narrow limits. The only disadvantage is that it may very slightly dilute the nitrogenous material of the sludge.

A Sectional System of Laboratory Desks[1]

By P. Borgstrom

TULANE UNIVERSITY OF LOUISIANA, NEW ORLEANS, LA.

IT is an interesting fact that chemical laboratory desks have changed but little in construction since the time of Liebig and Bunsen. The idea of sectional furniture, now universally adopted in modern office equipment, has apparently found no place in the workshop of the chemist. It frequently happens that in chemical laboratories rearrangement of desks becomes desirable, particularly in small rooms or instructors' laboratories, and with the classical style of furniture such changes are impossible without considerable expense. With this idea in mind, what may be termed a sectional type of chemical laboratory desk has been designed, which has been installed in the new laboratory of physiological chemistry at Tulane University.

Two sizes of sections, 18 and 30 inches, were chosen because they suited the conditions here—that is, a major and a minor course. The method of setting up, as well as type of section used, is shown in the drawing. At the end of the desk, A is a "finished end," stained and finished to match the desk fronts. This end is fastened to the desk by the same method as used to hold the section together—namely, three screws at D. B is a device to lock the drawers. C shows the section removed to receive a lead-lined trough that runs through the student desks. E is a shelf, a small one being used in the 18-inch and a larger one in the 30-inch section. The tops are 1.25 inches thick, built up of strips, glued and doweled. On the under side of the top are cleats to hold the sections in place, as well as to prevent warping of the top. Where a sink

was to be installed the section was made without bottom or back and with a drawer front only. As the water, gas, pressure, and vacuum lines all run above the desk, the sink can be installed independent of the desk and the desk can be removed without the aid of a plumber. In the instructors' laboratories a few 60-inch sections were made (combining two 30-inch sections) with a removable wall so that long apparatus which would not go into the 30-inch section could be stored.

The main advantage consists in its flexibility. When time of installation came it was found that some of the rooms had been altered in size due to changes in construction, and these changes caused no inconvenience or loss in installation. Moreover, ideas of equipment of the different rooms had changed in the two years that had elapsed since the plans for the building had been drawn. If the laboratory should be moved at any time in the future, the sections could be adjusted to the new building at relatively small expense.

The one objection advanced against this system is the cost. Actually, 629 linear feet of desks were installed and the expense would have been 5.00 per cent less if longer sections (8 and 12 foot) had been used. This is calculated on desk frontage only, independent of the tops, hoods, and plumbing. If these factors had been included in the calculation, the cost would have been 2.73 per cent less in the longer sections. It may also be said that these desks were made at a local cabinet works, whose specialty is office and store fixtures.
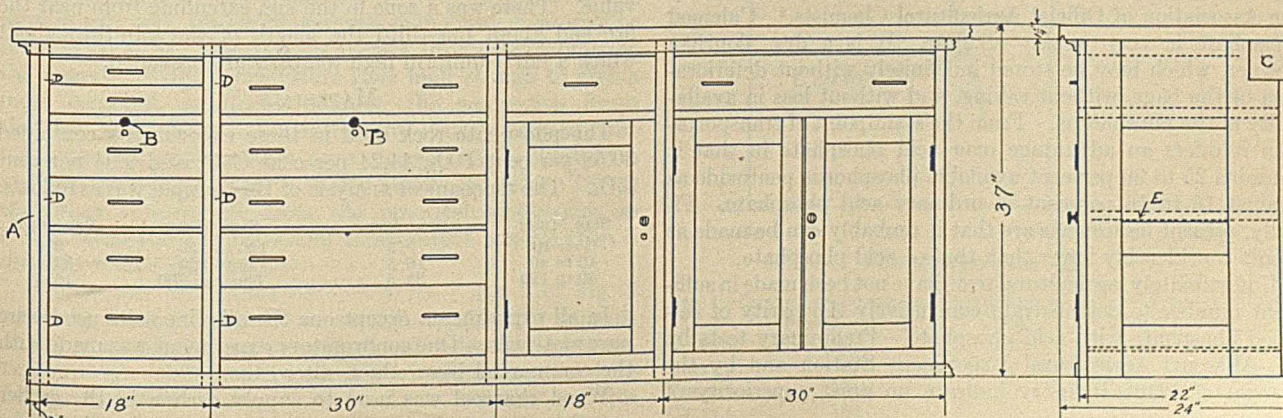
SECTIONAL LABORATORY DESK

The Preparation and Chemical Nature of Calcined Phosphate[1]

By E. W. Guernsey and J. Y. Yee

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THE interest of this laboratory in phosphate fertilizers arises chiefly from the necessity for finding a material which can be mixed directly with calcium cyanamide in the event of that substance being used as a fertilizer. Acid phosphate, the usual phosphorus carrier, cannot be mixed in the desired proportions with calcium cyanamide, since reactions occur which decrease the agricultural value of both phosphorus and nitrogen.

A considerable number of patents dealing with calcined phosphate have appeared during the past twenty-five or thirty years. A list of the United States patents on this subject is given at the end of this paper. They are for the most part quite similar in their claims, the chief variations being in the exact proportions of materials specified, the manner of manipulation of the charge, and other details of procedure. A material of this nature is said to have been put on the market in small quantity about fifteen years ago. Its manufacture on a large scale, however, did not prove successful at that time. Recent large-scale experiments have been conducted by at least two concerns. One of these concerns reports difficulty in getting a uniform product, while the other claims to have obtained an entirely satisfactory material. With the impetus which would be given to the development of a nonacid phosphate fertilizer in the event of the extended use of lime nitrogen as a fertilizer, it is believed that a technically feasible process could be worked out on a commercial scale.

While only a small portion of the phosphorus of calcined phosphate is water-soluble, a large part—at least 85 or 90 per cent in a properly prepared material—is available, according to the generally accepted test of solubility in 24 per cent ammonium citrate, under the conditions prescribed by the Association of Official Agricultural Chemists.[2] Calcined phosphate is very weakly alkaline. It is a dry, flourlike powder, which may be stored indefinitely without deterioration of the bags, without caking, and without loss in availability of the phosphorus. From the standpoint of transportation it offers an advantage over acid phosphate in that it contains 25 to 30 per cent available phosphorus pentoxide as against 15 to 16 per cent in ordinary acid phosphate. Finally, present indications are that it probably can be made at a cost considerably lower than that of acid phosphate.

Unfortunately, agricultural tests have not been made in sufficient number to demonstrate conclusively the parity of calcined phosphate with acid phosphate. Preliminary tests by the Missouri Agricultural Experiment Station and by the Bureau of Plant Industry indicate no great superiority of

Calcined phosphate is made by heating to a comparatively high temperature a mixture of phosphate rock, an alkali salt, and carbon or a carbonaceous material. It is a dry, powdery material which may be stored indefinitely without change. It contains 25 to 30 per cent P_2O_5, of which practically none is water-soluble but the greater part is soluble in ammonium citrate solution. It is weakly alkaline, and hence has the advantage over acid phosphate that it can be used in mixed fertilizer with calcium cyanamide without reaction.

This paper describes a series of experiments with a small rotary kiln made to determine the optimum conditions for the preparation of the material. It is found that with a charge of phosphate rock 100, sodium sulfate (as Na_2SO_4) 15, powdered coal 15, 90 per cent of the total P_2O_5 of the phosphate rock may be made citrate-soluble by heating at 1300° C. for 25 to 30 minutes. With a charge of phosphate rock 100, sodium sulfate (as $NaHSO_4$) 10, carbon 15, a conversion of 85 per cent can be obtained under the same conditions.

The conversion of the P_2O_5 to a citrate-soluble form is shown to be due in large part to a breaking down of the physical structure of the rock. A theory is offered to account for this action.

It appears probable that the manufacture of calcined phosphate is commercially feasible.

one over the other. It is probable that the chief difference may be a somewhat more prompt response of plants to acid phosphate due to its water-soluble phosphorus.

While the patent literature on calcined phosphate is extensive, no thorough study of the conditions best suited for the conversion of the phosphorus of phosphate rock to a citrate-soluble form has apparently been reported. The work described in this paper is intended to give more definite information on the optimum conditions for conversion—which conditions determine the cost of manufacture—and affords a somewhat clearer insight into the mechanism of the conversion and into the chemical nature of the material.

Some of the more important results of a systematic investigation of the relation between conversion (the portion of total phosphorus which is citrate-soluble) and certain factors, such as temperature, composition of the charge, and time of heating, will first be described.

Apparatus

In the later and more satisfactory experiments of the investigation, heating of the charge was carried out in an internally fired rotary kiln the internal dimensions of which were 9.5 cm. (3.75 inches) by 81.3 cm. (32 inches). The tilt and speed of rotation of the kiln could be varied to give any desired time of passage and degree of agitation of the charge. The kiln was heated in the earlier experiments by a gasoline burner and later by a simple type of gas burner. Temperature was measured at the hottest part of the interior of the kiln by a platinum, platinum-rhodium thermocouple protected by a porcelain tube. It was usually possible to maintain the temperature to within 10 or 20 degrees of the desired value. There was a zone in the kiln extending from near the fire end about one-third the length of the kiln throughout which a fairly uniform high temperature prevailed.

Materials

The phosphate rock used in these experiments contained 30.58 per cent P_2O_5, 44.24 per cent CaO, and 9.94 per cent SiO_2. The mechanical analysis of this sample was as follows:

Size Mesh	Per cent	Size Mesh	Per cent
Over 40	0.3	120 to 150	0.5
40 to 80	16.8	150 to 200	32.4
80 to 120	33.5	Through 200	16.5

In all experiments except one the alkaline salts used were pure materials. One confirmatory experiment was made with the commercial by-product, niter cake.

Wood charcoal was used to supply carbon in the earlier experiments, but was later replaced by powdered coal without affecting the results.

PROCEDURE

In the typical experiment 1 kg. of the thoroughly mixed charge was calcined, about 1 hour being required to feed the entire charge into the kiln. This rate of supply was such that the upper end of the kiln was kept about one-fourth filled. In some cases measured amounts of water were added to the previously dry-mixed charge and the whole was worked into a uniform paste. This paste was broken into small pellets and fed to the kiln at the same rate (on a dry basis) as was used for the dry charge.

The product of each run was thoroughly mixed and a 200-gram sample ground for an hour in a small ball mill. The ground sample (easily passing a 200-mesh screen) was analyzed in all cases for total and ammonium citrate-soluble phosphorus, and in many instances a rather detailed chemical examination was made in order to gain light on the composition of the citrate-soluble phosphorus compounds, and on the changes accompanying conversion.

RESULTS

About eighty experiments were made in the rotary kiln. Sodium sulfate was chosen as the alkaline salt to be used in a majority of the experiments, because it is more generally available and at a lower price than other salts suitable for this purpose. A considerable number of experiments were performed with sodium acid sulfate, since, at times and places where this salt could be obtained as a by-product (niter cake) in the manufacture of nitric acid, it would doubtless be cheaper than sodium sulfate. From one to three experiments were made with each of the other alkali salts, sodium carbonate, sodium hydroxide, sodium peroxide, potassium sulfate, and potassium acid sulfate. The purpose of the experiments with these salts was to demonstrate the general nature of the action of alkali salts on phosphate rock, rather than to determine the most favorable conditions for the use of the respective salts.

OPTIMUM TEMPERATURE—The optimum temperature for calcination varies with the composition of the charge. It is lower for charges containing higher proportions of sodium sulfate, as may be observed by comparing Curves 1, 2, 3, and 4 of Fig. 1. With 15 parts of sodium sulfate the temperature is quite definitely about 1300° C., while with 55 parts the best temperature is apparently less than 1200° C. Then again, the optimum temperature is lower with sodium carbonate than with sodium sulfate, the comparison being made between charges containing equivalent amounts of sodium oxide, as in the experiments represented by Curves 3 and 5. For sodium sulfate under these conditions the optimum temperature is about 1250° C., while for sodium carbonate it is less than 1200° C. and probably less than 1150° C.

In general, the optimum temperature for any charge is that temperature at which the charge just begins to sinter. Under the most favorable conditions the product yielded is in the form of very soft, friable clinkers which in many cases may be reduced to a very fine powder merely by crushing between the fingers. If the temperature rises high enough to give a more compact, semifused product, the conversion drops sharply. The range of temperature through which the maximum conversion with a given charge may be obtained is in most cases quite narrow, as the curves indicate. This is somewhat unfortunate from the practical standpoint, as it will necessitate more careful temperature control than is usual in rotary kiln practice.

PROPORTION OF ALKALI SALT—Curves 1 and 2 of Fig. 2 show the manner in which conversion at 1300° C. depends on the proportion of sodium sulfate and sodium acid sulfate, respectively. (1300° C. is about the optimum temperature for the low-alkali charges used in the experiments of this plate.) It will be noted that the conversion obtained is only roughly proportional to the proportion of sodium sulfate

(or acid sulfate), a slightly greater proportionate conversion being obtained with less sodium sulfate. As the proportion is increased a point is reached such that further additions yield no greater conversions. With sodium sulfate this maximum conversion of about 91 per cent is reached at 15 parts sodium sulfate per 100 parts phosphate rock. This charge contains an atomic ratio of sodium to phosphorus of about 0.5. With sodium acid sulfate a maximum conversion of about 83 per cent is obtained when the charge contains the equivalent of 10 parts of sodium sulfate per 100 parts of phosphate rock.

PROPORTION OF CARBON—The function of carbon in the charge seems to be twofold. In the first place, it facilitates decomposition of sodium sulfate, which, as will be seen later, is a necessary preliminary to conversion; and second, the escape of carbon dioxide from the charge due to combustion of the carbon appears to favor the production of a porous, friable clinker. Fig. 3 shows the relation between conversion and proportion of carbon. At 1300° C. the most favorable proportion is apparently about 15 parts per 100 parts of phosphate rock, which is the proportion used in most of the experiments. It will be noticed that the use of carbon is not essential at this temperature, a relatively high conversion being obtained with no carbon in the charge. At 1200° C., however, practically no conversion is obtained without carbon in charge. It is significant that in the experiment at 1200° C. the sodium sulfate remained undecomposed, while in all experiments in which appreciable conversion was obtained
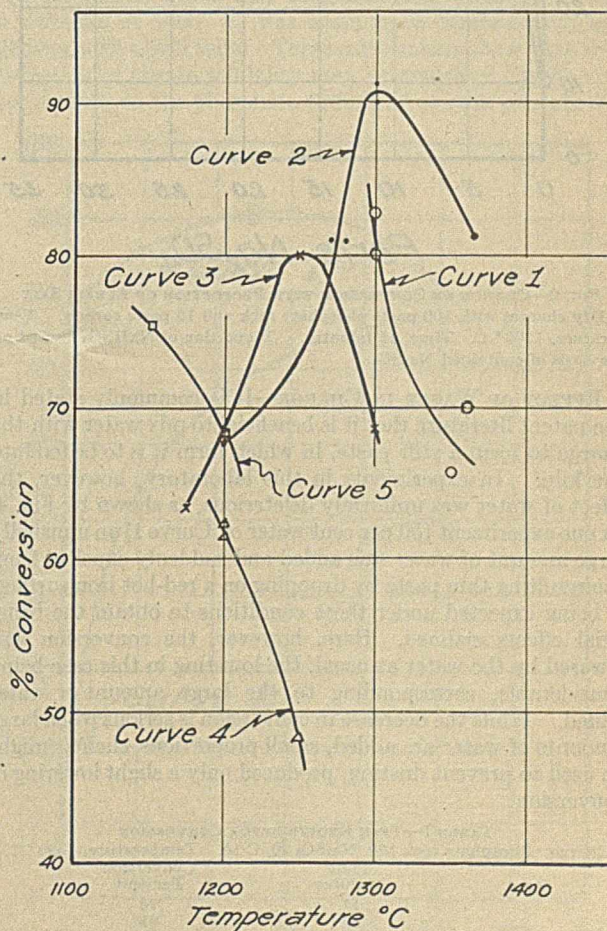
FIG. 1—CHANGE OF CONVERSION WITH TEMPERATURE IN VARIOUS CHARGES

	Phosphate Rock	Na_2SO_4	Carbon	Water
Curve 1	100	10	15	0
Curve 2	100	20	15	0
Curve 3	100	30	15	32.5
Curve 4	100	55	27	0
		Na_2CO_3		
Curve 5	100	224	0	0

very little sulfate remained in charge. It is evidently sodium oxide, and not the salt, which is the active agent in conversion. This explains the failure, reported in patent literature, to get conversion with the stable salt, sodium chloride.
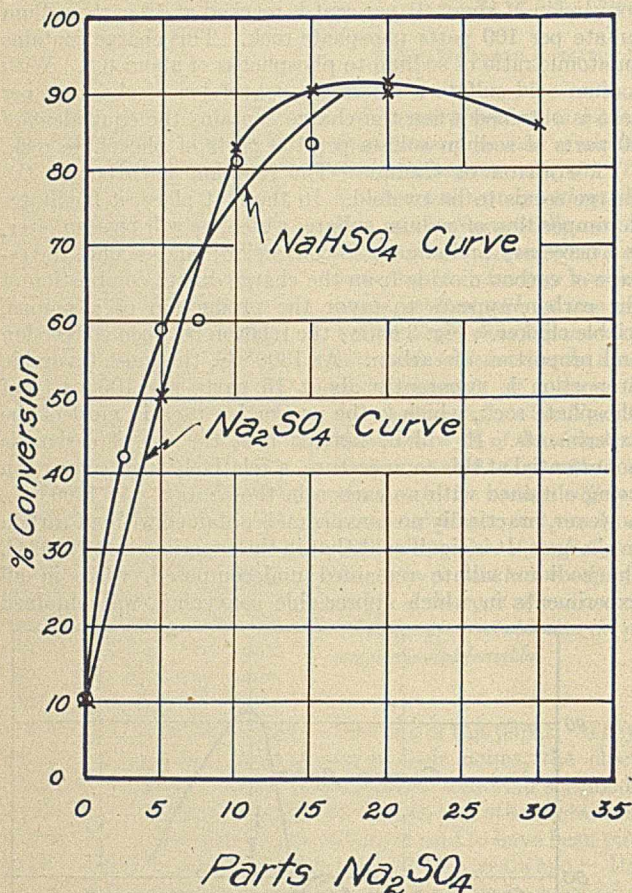

FIG. 2—CHANGE OF CONVERSION WITH PROPORTION OF ALKALI SALT
Dry charges with 100 parts phosphate rock and 15 parts carbon. Temperature, 1300° C. Time, 15 minutes. Proportion of NaHSO₄ figured on the basis of contained Na₂SO₄.

EFFECT OF WATER IN CHARGE—It is commonly stated in the patent literature that it is beneficial to mix water with the charge to form a stiff paste, in which form it is to be fed into the kiln. In experiments in this laboratory, however, the effect of water was uniformly deleterious, as shown by Fig. 4. In one experiment (50 per cent water on Curve 1) an unusually large amount of water was added and suddenly expelled from the resulting thin paste by dropping on a red-hot iron surface, it being expected under these conditions to obtain the beneficial effects claimed. Here, however, the conversion was lowered by the water as usual, the lowering in this case being considerable, corresponding to the large amount of water added. While the decrease in conversion is serious when large amounts of water are added, small proportions, such as might be used to prevent dusting, produced only a slight lowering of conversion.

TABLE I—TIME REQUIRED FOR CONVERSION
Charge: Phosphate rock 100, Na₂SO₄ 20, C 15. Temperature, 1300° C.

Expt.	Time Minutes	Conversion Per cent
1	17	76
2	25	91
3	40	88

TIME REQUIRED FOR CONVERSION—In most of the experiments described in this paper the time required for the charge to pass through the kiln was 25 to 30 minutes. A comparison of Experiments 1 and 2 of Table I shows that reducing the heating time to 17 minutes materially lowered the conversion. The 25-minute heating is apparently sufficient, however.

As shown by Experiment 3, no appreciable loss in conversion results from continuing the heating for a longer period.

AGITATION OF CHARGE—In most experiments the kiln was turned at the rate of 1.3 r. p. m. In one experiment this rate of rotation was increased to 2.4 r. p. m. to see if greater agitation would increase the rate of conversion. As seen in Table II, the change did not appreciably affect the rate.

TABLE II—EFFECT OF AGITATION ON CONVERSION RATE
Charge: Phosphate rock 100, Na₂SO₄ 20, C 15. Temperature, 1300° C. Time, 16 minutes

Expt.	Rate of Rotation of Kiln R. p. m.	Conversion Per cent
1	1.3	76.1
2	2.4	78.84

FINENESS OF GRINDING OF MATERIALS—From the mechanical analysis of the phosphate rock given under "Materials" it is seen that only 16.5 per cent passed a 200-mesh sieve. In one experiment the phosphate rock was pulverized to pass completely a 200-mesh sieve. As shown by Table III, the finer grinding did not greatly increase the rate of conversion.

TABLE III—EFFECT OF FINENESS OF PHOSPHATE ROCK
Charge: Phosphate rock 100, Na₂SO₄ 20, C 15. Temperature, 1300° C. Time, 16 minutes

Expt.	FINENESS OF PHOSPHATE ROCK	Conversion Per cent
1	Sample as received. (Mechanical analysis on p. 228)	76.1
2	All through 200 mesh	79.7

It may be further noted from Table IV that fine grinding of the alkaline salt is unnecessary. In Experiment 2 sodium acid sulfate was introduced into the charge in pea-sized lumps. The conversion was, in fact, slightly higher than in the parallel Experiment 1, in which the salt was finely ground and intimately mixed with the other constituents of the charge. The product of the experiment in which lumps were employed consisted in part of small, round, very friable balls, the centers of which had been left hollow by the decomposition of the salt and the absorption of the sodium oxide by the surrounding material.

TABLE IV—EFFECT OF FINENESS OF ALKALI SALT
Charge: Phosphate rock 100, NaHSO₄ (calcd. as Na₂SO₄) 7.5, C 15. Temperature, 1300° C. Time, 25 minutes

Expt.	FINENESS OF NaHSO₄	Conversion Per cent
1	Powdered	60.12
2	Pea-sized lumps	68.56

CONVERSION WITH MISCELLANEOUS SALTS—It was established that conversion could be obtained with practically any sodium or potassium oxy-salt. The conversions obtained are of no particular significance, since no attempt was made to determine optimum conditions except in the case of sodium sulfate and sodium acid sulfate. In all cases, however, the conversion was above 60 per cent.

CONDITIONS RECOMMENDED FOR MANUFACTURE OF CALCINED PHOSPHATE

The writers see no reason to suppose that the most favorable temperature of charge proportions should be appreciably different in a large kiln from those determined in the experimental kiln. The time required might perhaps be somewhat longer, owing to the greater depth of charge and lesser degree of agitation. By way of summing up the foregoing relation of the dependence of conversion on various factors, the most favorable conditions for the production of calcined phosphate as indicated by this investigation may now be stated. If sodium sulfate is used, the most economical charge is phosphate rock 100 parts, sodium sulfate 15 parts, powdered coal 15 parts. If necessary to prevent dusting, a small amount of water—say 15 per cent—may be added, but large proportions should be avoided. This charge should be heated by means of a direct flame, as in an internally fired rotary kiln, for 25 to 30 minutes at 1300° C. The type of burner used should be such as to permit the closest possible control, since

the optimum temperature range is narrow. Under these conditions about 90 per cent of the phosphorus of phosphate rock becomes available, according to the citrate solubility test. If sodium acid sulfate (niter cake) is to be used, the best charge is phosphate rock 100 parts, sodium acid sulfate 10 parts (calculated as sodium sulfate), powdered coal 15 parts. If this charge is heated for 25 to 30 minutes at 1300° C., a conversion above 80 per cent may be obtained. Two all-day runs, one with sodium sulfate and one with a commercial niter cake, were made in the experimental kiln under the conditions here recommended. The average conversion in the sodium sulfate experiment was 85 per cent and in the niter cake experiment 80 per cent.

Chemical and Physical Nature of Calcined Phosphate

A rather complete chemical examination was made of a large number of experimental calcined phosphates in order to gain an insight into the nature of the change of the phosphorus of phosphate rock to a citrate-soluble form and into the composition of the resulting product.

It is important to notice, first of all, that the proportion of sodium salt used is in most cases too small to permit an adequate explanation of the citrate solubility of the phosphorus of calcined phosphate, based merely on the formation of a citrate-soluble calcium sodium phosphate analogous to the citrate-soluble calcium hydrogen phosphate of acid phosphate. It will be seen that if citrate solubility were due solely to this compound, the sodium-phosphorus ratio in the citrate solution should be at least unity. This ratio was determined—analysis for sodium being made by the method of elimination—on a wide variety of calcined phosphates, and was found in many cases to be much less than unity—in one case as low as 0.277.

Since, then, no chemical change sufficient to account in full for the conversion which is obtained can be found, the feasibility of an explanation based on a change of the physical state of phosphate rock must be considered. One of the most evident effects of the calcination with alkaline salts is to break up the physical structure of the rock so that the clinker of calcined phosphate falls readily upon crushing to an extremely fine powder. Since it is well known that tricalcium phosphate which is in an extremely fine state of division, as by reprecipitation or extremely fine grinding, becomes quite soluble in ammonium citrate solution, it seems probable that the increase in citrate-soluble phosphorus during calcination is due, in large measure at least, to this breaking down of the rock into a very fine state of division.

This being granted, the manner in which this disintegration is accomplished must be determined. All the evidence at hand indicates that it is in some way brought about by the action of the sodium oxide of the various salts used.

(1) As noted above, no conversion was obtained with sodium sulfate, except under conditions such that sulfur trioxide is lost.

(2) Such stable salts as sodium chloride are useless as calcining agents.

(3) Conversion is not dependent on the volatilization of the alkali salt from within the mass of the charge at high temperature as assumed in patent literature, as in the case of sodium sulfate, at least, practically all the sodium oxide remains in the charge, only sulfur trioxide being lost.

(4) Neither is the generation of such gases as sulfur trioxide or carbon dioxide from within the charge at all essential for conversion, as was demonstrated by an experiment in which the gases of combustion from the burner passed over the sodium carbonate at 1400° C., sweeping the vapors of sodium carbonate—more or less dissociated—over phosphate rock. Here, where there was no mixing of the reactants at all, a moderately high conversion was obtained. Passing of furnace gases with no sodium carbonate in the furnace gave no conversion. That the generation of gases is not important is again shown by the fact that a high conversion could be obtained with sodium peroxide, although the evolution of gases from this compound should have ceased far below the calcination temperature.

These experiments indicate that the disintegration of the rock is brought about chiefly by the action of sodium oxide.

A variety of hypotheses might be advanced to explain the manner in which alkali oxide brings about the disintegration of the rock.

(1) The rock and alkali oxide might be assumed to form a solid solution at the calcining temperature, the crystalline structure being thereby broken down.

(2) The alkali oxide might react with impurities such as silica which are microscopically disseminated throughout the rock phosphate, resulting in the breaking down of the rock structure.

(3) The alkali oxide might react with the phosphate compound to form a compound such as, for example, $3CaO.Na_2O.P_2O_5$ or $2CaO.Na_2O.P_2O_5$. It might be supposed that the formation of a relatively small proportion of such a compound, if disseminated throughout the rock, might be sufficient to cause the disintegration of the entire rock structure and thus lead to high citrate solubility.

The first two hypotheses are discredited by the results of this investigation. If, as assumed in the first, sodium oxide merely forms a solid solution with the rock, it should be water-soluble, whereas practically all the sodium oxide is soluble only in ammonium citrate solution. As to the second hypothesis, it is entirely possible that some disintegration of phosphate rock is brought about by the action of the alkali on silica contained in the rock. The presence of silica in the rock is, however, not an essential condition for conversion, as was shown by a number of experiments in which pure calcium phosphate which had been rendered citrate-insoluble by sintering at 1500° C. was again made citrate-soluble by calcining with alkali salts. These experiments show that the production of citrate solubility may be explained by the action of alkali on the phosphate compound of rock phosphate.
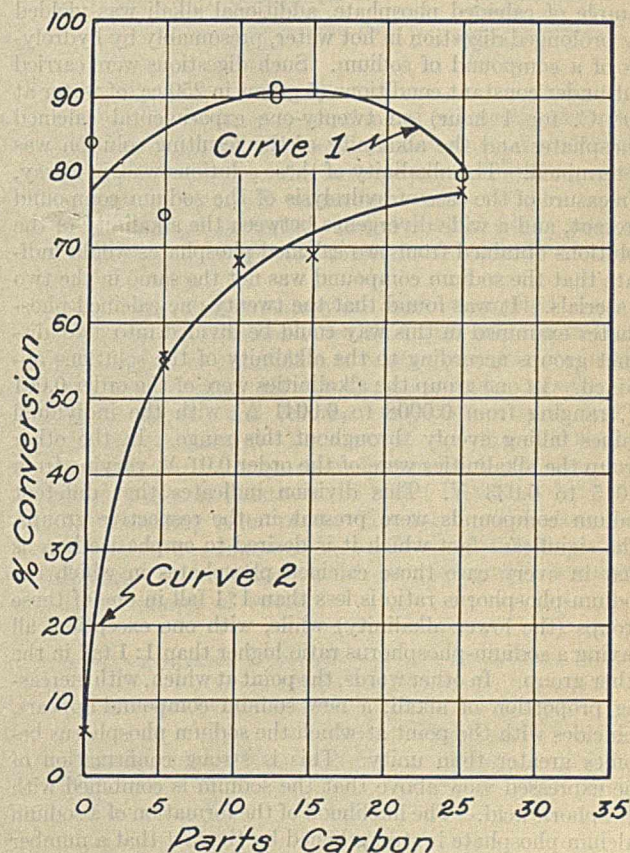

Fig. 3—Change in Conversion with Variation of Proportion of Carbon (to 100 Parts Phosphate Rock)

Curve 1. Charge: Phosphate rock 100, Na_2SO_4 20, water 0, carbon variable. Temperature, 1300° C.

Curve 2. Charge: Phosphate rock 100, Na_2SO_4 30, water 32.5, carbon variable. Temperature, 1200° C.

The third hypothesis seems to be the correct one. Additional evidence that the sodium oxide is combined with phosphoric acid is afforded by the following experiments. After washing out the small amount of free alkali from a
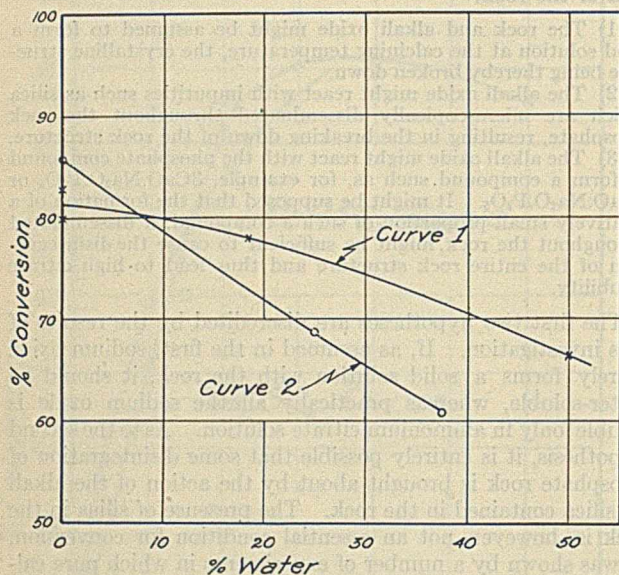

FIG. 4—CHANGE OF CONVERSION WITH ADDITION OF WATER TO CHARGE

Curve 1. Charge: Phosphate rock 100, Na_2SO_4 10, C 15. Temperature, 1300° C.

Curve 2. Charge: Phosphate rock 100, Na_2SO_4 30, C 15. Temperature, 1300° C.

sample of calcined phosphate, additional alkali was yielded by prolonged digestion in hot water, presumably by hydrolysis of a compound of sodium. Such digestions were carried out under constant conditions (5 grams in 250 cc. of water at 70° C. for 1 hour) on twenty-one experimental calcined phosphates and the alkalinity of the resulting solution was determined. The alkalinity of these solutions was, in a way, a measure of the ease of hydrolysis of the sodium compound present, and a wide divergence between the alkalinity of the solutions obtained from two calcined phosphates would indicate that the sodium compound was not the same in the two materials. It was found that the twenty-one calcined phosphates examined in this way could be divided into two distinct groups according to the alkalinity of the solutions obtained. In one group the alkalinities were of the order 0.001 N, ranging from 0.0008 to 0.0041 N, with the individual values falling evenly throughout this range. In the other group the alkalinities were of the order 0.01 N, varying from 0.015 to 0.033 N. This division indicates that different sodium compounds were present in the respective groups. The significant fact which it is desired to emphasize here is that in every case those calcined phosphates in which the sodium-phosphorus ratio is less than 1:1 fall in one of these groups (the lower alkalinity) while, with one exception, all having a sodium-phosphorus ratio higher than 1:1 fall in the other group. In other words, the point at which, with increasing proportion of alkali, a new sodium compound appears, coincides with the point at which the sodium phosphorus becomes greater than unity. This is strong confirmation of the expressed view above that the sodium is combined with phosphoric acid. The likelihood of the formation of a sodium calcium phosphate is strengthened by the fact that a number of sodium calcium phosphates, including $2CaO.Na_2O.P_2O_5$, have been prepared.[3] The exact formula of the sodium calcium phosphate formed cannot be stated. However, from the fact that the ratio total base $(CaO + Na_2O) : P_2O_5$ in the

[3] Ditte, Compt. rend., 94, 1592 (1882).

citrate-soluble portion is in some cases as low as 3:1, it seems probable that the compound formed is $CaNaPO_4$.

To sum up, it appears that production of citrate-soluble phosphorus by calcining rock phosphate with alkali salts is largely due to disintegration of the structure of the rock brought about by the action of sodium oxide, which combines with a portion of the calcium phosphate to form a double sodium calcium phosphate. At the calcining temperature the charge is semi-sintered, so that the penetration of the sodium oxide into the interior of the phosphate particles is not difficult to conceive. It is not necessary for all the phosphoric acid to be combined with sodium oxide in this way, since, presumably, the formation of a small amount of the double compound is sufficient to disintegrate the rock structure completely. This disintegration may result merely from the solid solution of the new compound in the rock, or may perhaps be brought about by the formation and decomposition, under changing conditions in the kiln, of the sodium calcium phosphate. The writers have, however, no direct evidence on this point.

COMMERCIAL CONSIDERATIONS

Since only small-scale work was done in this investigation, it is not desirable to attempt an accurate estimate of the cost of manufacture of calcined phosphate. It can only be stated that, if the small-scale results can be duplicated on a commercial scale, the material costs will be considerably lower than for acid phosphate, even using the same grade of phosphate rock. If it should be possible to use low-grade phosphate rock, as seems possible, a further saving in material costs would be realized. For example, it should certainly be possible to use phosphates that are high in iron and aluminium, although these are valueless for acid phosphate manufacture. Using figures for cement-burning costs for estimating the cost of the calcining operation, the writers are led to believe that the cost of manufacture will also compare favorably with that of acid phosphate.

The chief commercial advantage of calcined phosphate, however, will not be its lower cost, but its availability for mixing with basic materials such as calcium cyanamide.

UNITED STATES PATENTS ON CALCINED PHOSPHATE

Patent No.	Year	PATENTEE	ABSTRACT REFERENCE
345,125	1896	Dune	Am. Fertilizer, 41, 44
601,089	1898	Wiborg	
721,489	1903	Wolters	
931,846	1909	Connors	U. S. Dept. Agr., Bull. 312
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1,162,944	1915	Newberry and Barrett	U. S. Dept. Agr., Bull. 312
1,163,130	1915	Connor	C. A., 10, 366 (1916)
1,173,303	1916	Newberry and Barrett	U. S. Dept. Agr., Bull. 312
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Soluble Aluminium and the Hematoxylin Test in Filtered Waters[1]

By William D. Hatfield

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R ECENT studies[2] on the presence of soluble aluminium in mechanically filtered waters which have been coagulated with aluminium sulfate have shown that the insolubility zone for aluminium hydroxide is approximately from pH 5.7 to 7.3. When the pH value of the coagulated or filtered water is less than pH 5.7 or more than 7.3, unprecipitated aluminium is found by the gravimetric method of analysis.

If extreme care is used to remove silica[3] completely, the gravimetric method determines the amount of alumina originally present in the water plus any unprecipitated aluminium from the aluminium sulfate, thus requiring two determinations to detect the presence of an excess of aluminium in the filtered water. As these operations are not well fitted for routine work in a waterworks laboratory, it is highly desirable to have a rapid colorimetric method which is sensitive to aluminium ions, and not to the alumino complexes which are present in the raw water.

Atack's[4] method for determining aluminium with Alizarin S (red) has not given very satisfactory results in the hands of numerous investigators.

The logwood or hematoxylin color reaction with aluminium ions is so pronounced that it offers possibilities worthy of study. The most serious objections to the hematoxylin test for alum have been, first, that hematoxylin is an indicator and hence is subject to variations in color with changes in hydrogen-ion concentrations; and second, that other ions produce colors with hematoxylin which would interfere. The experimental work described below sustains these two objections to the test as it has often been made, but presents a modified hematoxylin method which overcomes these objections and is very satisfactory for routine water analysis.

EXPERIMENTAL WORK

In Table I are shown the maximum color changes which take place when an aqueous solution of hematoxylin is added to buffer solutions ranging from 2.4 to 14.0 pH units. To these buffer solutions containing hematoxylin, 0.37 p. p. m. aluminium was added and a distinct color change took place at pH 8.0 to 8.5 and at pH 14.0. The aluminium-hematoxylin color compound which is formed at pH 14.0

[1] Presented before the Division of Water, Sewage, and Sanitation at the 66th Meeting of the American Chemical Society, Milwaukee, Wis., September 10 to 14, 1923.

[2] Baylis, J. Am. Water Works Assoc., 10, 365 (1923); Daniels, Eng. News-Record, 91, 93 (1923); Hatfield, paper presented before the 43rd Annual Convention of the American Water Works Association, May, 1923; Miller, paper presented before the 43rd Annual Convention of the American Water Works Association, May, 1923.

[3] Buswell, Discussion at the 43rd Annual Convention of the American Water Works Association, May, 1923.

[4] J. Soc. Chem. Ind., 34, 936 (1915).

The minimum solubility zone for aluminium hydroxide in carbonate and bicarbonate solutions extends approximately from pH 5.7 to 7.3. Where water filtration plants use aluminium sulfate and operate so that the pH of the treated water falls near the limits of or outside of this zone, the effluent will in all probability contain soluble aluminium ("residual alum").

The gravimetric test for this aluminium is tedious and is complicated by the naturally occurring aluminosilicates. It is not suitable as a routine test for the average waterworks laboratory.

The modified hematoxylin test presented here gives results that are accurate to 0.1 p. p. m. aluminium. The modification consists in forming the hematoxylin-aluminium color compound in samples of water which have been adjusted to pH 8.2 to 8.3 and then acidifying the color solution to pH 4.5.

TABLE I

pH OF BUFFER SOLUTIONS	COLOR PRODUCED WITH HEMATOXYLIN, No Al+++ PRESENT	COLOR PRODUCED ON ADDITION OF 0.37 P. P. M. Al+++
14.0	*Lavender*	*Green*
12.0	Red	Red
11.0	Orange	Orange
9.0	Orange-yellow	Orange-yellow
8.5	*Red*	*Purple*
8.0	*Pink* (lavender tint)	*Lavender-purple*
5.5	Yellow	Yellow
2.4	Yellow	Yellow

Concentrated aqueous solutions of numerous phosphates, carbonates, oxalates, and acetates were studied to determine which buffer salt gave the best results in adjusting samples of lake water with pH values from 3.0 to 8.0 to a constant hydrogen-ion concentration, and also which buffer salts gave the best final hydrogen-ion concentration for the aluminium color formation.

The aluminium-hematoxylin color compound does not form in buffer solutions more acid than pH 6.0 unless the concentration of aluminium is relatively high. In solutions more alkaline than pH 8.5 the color fades rapidly, while between pH 6.5 and 7.5 the color formation is slow but relatively permanent. Between pH 8.0 and 8.5 the most rapid and satisfactory color formation is obtained. The data in Table II illustrate the buffer action of three of the most promising salts tried. The most satisfactory buffer and technic was found to be 1 ml. of saturated ammonium carbonate (ammonium carbonate-carbamate) solution in a 50-ml. sample of water.

fades rapidly, but the color compound formed at pH 8.0 to 8.5 is very pronounced and quite permanent. These data show very clearly that while hematoxylin is an "indicator" it also gives, at pH 8.0 to 8.5, distinctly different colors in the presence and absence of aluminium ions. Therefore, the hematoxylin test for aluminium in filtered waters must be made on samples which are buffered to a constant hydrogen-ion concentration.

TABLE II—EFFICIENCY OF BUFFER SOLUTIONS IN ADJUSTING SAMPLES TO A CONSTANT pH

(Technic: 1 ml. buffer solution to 50 ml. sample of water)

Ml. 0.2 N H2SO4 per 1000 Ml. Raw Water	pH of Treated Water (Colorimetric)	pH AFTER ADDITION OF BUFFER TO SAMPLE 10% Ammonium Acetate	Saturated Sodium Acetate	Saturated Ammonium Carbonate
0.0	8.1	6.7	7.4—	8.2—
0.5	7.5	6.7	7.4	8.2—
1.0	7.3	6.7—	7.3—	8.2—
2.0	6.9	6.6—	7.2	8.2
4.0	6.5	6.6	7.0	8.2
6.0	5.9	6.6	6.8	8.2
8.0	5.5—	6.6—	6.8	8.2
10.0	3.5	6.5—	6.5—	8.2
Hematoxylin color formation	Variable	Slow but constant	Variable	Rapid and constant

The pure aluminium-hematoxylin color, in solutions made alkaline with saturated ammonium carbonate solution, is blue, but if there is an excess of hematoxylin, which is red in this solution, the combination of red and blue produces the lavender or purple tint usually reported as characteristic of aluminium. When acid is added the excess hematoxylin turns yellow and the aluminium color compound turns purple. Combinations of these two colors give gradations of color from yellow through brown to purple.

Hematoxylin was tested for its color reaction with salt solutions which represented the ions commonly found in natural waters. The data in Table III show that the solutions of *alkaline* salts give a red color with hematoxylin, the intensity depending on the hydrogen-ion concentration, and that *neutral* and *acid* salt solutions and distilled water (pH 5.8) give a yellow color.

All these salt solutions, except those containing magnesium, ferrous, and ferric ions, turn red when made alkaline (pH 8.2) with 1 ml. of saturated ammonium carbonate solution. These solutions turn to a lavender color which is very similar to that produced by aluminium ions when treated in a similar manner.

TABLE III—COLOR REACTION OF SOME SALT SOLUTIONS WITH HEMATOXYLIN

┌──ACID AND NEUTRAL──┐		┌────────ALKALINE────────┐	
SOLUTION	COLOR	SOLUTION	COLOR
KCl	Yellow	KOH	Red
KH$_2$PO$_4$	Yellow	K$_2$HPO$_4$	Red (lavender tinge)
NaCl	Yellow	NaHCO$_3$	Red (fades)
		Na$_2$CO$_3$	Red (fades)
		NaOH	Red
NH$_4$Cl	Yellow	NH$_4$OH	Red
		(NH$_4$)$_2$CO$_3$	Red (lavender tinge)
FeSO$_4$(NH$_4$)$_2$SO$_4$	Yellow		
FeSO$_4$	Yellow		
MgSO$_4$	Yellow		
MnSO$_4$	Yellow		
CaCl$_2$	Yellow	Ca(OH)$_2$	Red
Distilled water	Yellow		

On acidification of the solution containing the magnesium color with 1 ml. of 30 per cent acetic acid, the lavender color is destroyed and does not interfere with the aluminium color formed under the same conditions. Tests with ferrous and ferric ions indicate that, in solutions buffered with ammonium carbonate, iron will interfere in concentrations greater than 0.1 to 0.2 p. p. m., but on acidifying the solution with 1 ml. 30 per cent acetic acid (resulting pH 4.5) the interference is not serious until a concentration of 1.0 p. p. m. of iron is reached.

Summarizing, small amounts of aluminium plus hematoxylin at pH values less than 6.0 do not produce readable color changes, but amounts as low as 0.05 p. p. m. aluminium, if treated with hematoxylin at pH 8.2 (more or less) and subsequently acidified, do give readable colors which are not subject to interference from other ions normally found in natural waters.

TABLE IV—EFFECT OF HYDROGEN-ION CONCENTRATION ON HEMATOXYLIN COLORS IN LAKE ST. CLAIRE WATER

Ml. 0.2 N H$_2$SO$_4$ per 1000 Ml. Water	pH of Treated Sample	1 Ml. Hematoxylin in 50-Ml. Sample	0.27 P. p. m. Aluminium plus Hematoxylin	0.27 P. p. m. Aluminium 1 Ml. (NH$_4$)$_2$CO$_3$ 1 Ml. Hematoxylin (pH 8.2)	Column 5 Acidified with 1 Ml. 30% Acetic Acid (pH 4.5)
(1)	(2)	(3)	(4)	(5)	(6)
0.0	7.8	Red	Blue	Lavender-blue	Yellowish brown
0.5	7.5	Pink	Blue	Lavender-blue	Yellowish brown
1.0	7.1	Yellow-pink	Lavender	Lavender-blue	Yellowish brown
2.0	6.8	Yellow	Faded lavender	Lavender-blue	Yellowish brown
4.0	6.5	Yellow	More faded lavender	Lavender-blue	Yellowish brown
6.0	5.9	Yellow	More faded lavender	Lavender-blue	Yellowish brown
8.0	5.8	Yellow	More faded lavender	Lavender-blue	Yellowish brown
10.0	3.5	Yellow	Yellow	Lavender-blue	Yellowish brown

The data in Table IV were obtained on acidulated samples of Lake St. Claire water and show the effect of the hydrogen-ion concentration of the water on the color formed with hematoxylin both with and without the presence of aluminium ions. The samples in Columns 4, 5, and 6 were treated with an equivalent of 0.27 p. p. m. aluminium. Column 4 shows the variation of color due to the variation in hydrogen-ion concentration, and Columns 5 and 6 show how satisfactorily the addition of buffers, according to the technic described below, brings the colors to a constant shade.

The solutions and procedure for this modified hematoxylin method for aluminium in filter plant effluents are as follows:

REAGENTS—(1) Dissolve 0.1 gram C. P. hematoxylin (white crystals) in 100 ml. of boiling distilled water. This solution is stable for 2 or 3 weeks.

(2) Saturate 500 ml. distilled water with ammonium carbonate and keep the solution in a glass-stoppered bottle in presence of an excess of crystals.

(3) Prepare a 30 per cent acetic acid solution by diluting glacial acetic acid with distilled water.

(4) Prepare a standard ammonium alum solution by dissolving 0.8366 gram of ammonium alum in distilled water and dilute to 1000 ml. One milliliter of this solution in 50 ml. of distilled water is equivalent to 1.0 p. p. m. aluminium. Use also a 1:10 dilution of this standard solution.

PROCEDURE—To 50 ml. of water (to be tested) contained in a tall-form Nessler tube add 1 ml. of a saturated solution of ammonium carbonate and 1 ml. of hematoxylin indicator solution. Mix by inverting tube twice. Let the tube stand 15 minutes for the maximum lavender color to form, and then acidify with 1 ml. of 30 per cent acetic acid.

Compare the color formed with that of standard color tubes which were prepared in exactly the same way and at the same time by using standard ammonium alum solution and distilled water to represent from 0.0 to 1.0 p. p. m. aluminium. With concentrations less than 0.15 p. p. m. aluminium the color is compared against white paper through the length of the Nessler tubes, but with higher concentrations than 0.15 p. p. m. the color is best compared through the sides of the tubes.

The color standards should be made as nearly as possible at the same time as the unknown color tube, because the color varies with time of formation. A difference of 15 minutes will make some difference in the tint, but will allow readings to 0.1 p. p. m. Color standards prepared with distilled water were satisfactory with the Great Lakes water, but if, because of interfering ions, the raw water does not compare with the zero distilled water standard, the standards should be made with raw water which has been filtered through a Berkefeld filter. In this way any naturally occurring ions which interfere with the aluminium-hematoxylin color are compensated for in the standards. Care must be taken that the Berkefeld filter does not become contaminated with alum dust from the plant.

Many comparisons of results obtained by the gravimetric method and the modified hematoxylin method have been made on filtered water samples with hydrogen-ion concentrations ranging from 3.3 to 9.0 pH units. The comparisons show that the results check very satisfactorily where the pH values of the samples were above 6.0. Samples of the filtered water with pH values below 6.0 very rapidly dissolve silica from the ordinary flint glass laboratory sample bottles. This is particularly true as the acidity increases. Unless special precautions are taken to remove all silica, the gravimetric results on these acid samples are high. The modified hematoxylin method gave very consistent results on acid samples, which compared closely with the theoretical amount of aluminium ions added. Near the two extreme ends of the aluminium hydroxide insolubility zone (pH 5.7 to 7.3) the hematoxylin method is more sensitive than the gravimetric method.

The Fixation of Nitrogen as Cyanide[1]

By Richard Franchot

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When working at a capacity of 40 million tons of pig iron, the American blast furnace is fixing nitrogen probably at the rate of 6 million tons a year and spending coke in doing it. This is double the rate at which it has been estimated that nitrogen is taken from our soil in crops. In terms of energy, the hearth of the blast furnace in the United States deve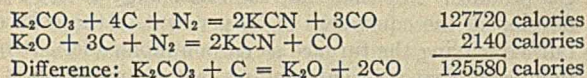lops some 12 million kilowatts, of which 25 per cent is apparently available for and absorbed in work done at 1500° C. Of this it appears that one-half is devoted to keeping in circulation as cyanide a large accumulation of alkali. There appears to be power here of the order of 2 million horsepower, not only developed and available, but actually already engaged in nitrogen fixation.

I N THE process of the solution by chemical science of the problem involved in the return to the soil of an adequate proportion of the nitrogen removed by crops (the "nitrogen cycle"), certain inherent possibilities as to low cost in the fixation of atmospheric nitrogen as cyanide appear to have been as yet somewhat neglected. In view of these possibilities, the difficulties thus far encountered would seem to be well worth surmounting; and it may be said that these difficulties do not appear to be insurmountable.
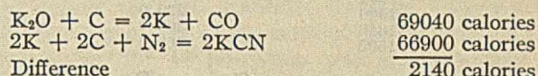
Since the discovery, about 1840, that alkali and carbon heated with nitrogen form cyanide, many attempts have been made to utilize the reaction for the commercial production of alkali cyanides. From Possoz and Boissiere[1],* in 1847 to Bucher[2] in 1917 the primary difficulty has proved to be that inherent in trying to deliver heat to the reacting materials at an adequate rate through the medium of externally heated retorts, the reaction being highly endothermic and absorbing great quantities of heat while requiring high temperatures for adequate speed. A secondary difficulty has been the loss of alkali by volatilization. Processes that involve heating by electrical means with removal of cyanide as vapor from the formation zone would not seem to be subject to these difficulties; but there is still another difficulty in that condensation with separation of the cyanide from by-product gases presents a problem of preventing the reversion of cyanide to alkali, carbon, and nitrogen which takes place in the presence of carbon monoxide at temperatures ranging below those at which cyanide formation occurs. In view of the comparatively high cost of electrical heating, the most promising method of commercializing the cyanide reaction appears to be that comprising broadly the use of mixtures of nitrogen and oxygen such as air, coupling the exothermic oxidation of carbon with the endothermic formation of cyanide. Certain patents lately issued to McElroy[3] describe processes involving the application of this principle. The promise of the method is reinforced by repeated observation of the presence of cyanides in the blast furnace, where air or producer gas contacts with carbon and accumulated alkali at temperatures ranging up to 1500° C.[4,5]

CHEMISTRY OF CYANIDE FORMATION

Typical reactions in which cyanide is formed from alkali may be written:

$$K_2CO_3 + 4C + N_2 = 2KCN + 3CO \qquad 127720 \text{ calories}$$
$$K_2O + 3C + N_2 = 2KCN + CO \qquad\qquad 2140 \text{ calories}$$

Difference: $K_2CO_3 + C = K_2O + 2CO$ 125580 calories

The chief endothermic component of the process of cyanide formation from carbonate is thus seen to be the reduction of carbonate to oxide, the further reduction to metal absorbing but little more heat than that set free in the formation of cyanide from its elements:

$$K_2O + C = 2K + CO \qquad 69040 \text{ calories}$$
$$2K + 2C + N_2 = 2KCN \qquad 66900 \text{ calories}$$

Difference   2140 calories

(The heats of formation are those given in Richards, "Metallurgical Calculations.")

In the course of an investigation of the cyanide reaction in the McElroy laboratory, it has been found that cyanide and carbonate react at about 1000° C. with evolution of alkali metal vapor. Upon heating a molten mixture of sodium carbonate and sodium cyanide in a retort, the effluent gases carry off relatively large quantities of metallic sodium as vapor. With an excess of carbonate the cyanide is completely decomposed, and with an excess of cyanide carbonate entirely disappears. So far as can be seen from the literature, this reaction has not heretofore been mentioned or described. The mechanism may include:

$$2NaCN + Na_2CO_3 = 4Na + 3CO + N_2$$
$$2NaCN + 3Na_2CO_3 = 4Na_2O + 5CO + N_2$$
$$2NaCN + 2Na_2O = 6Na + 2CO + N_2$$
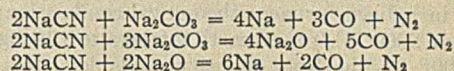
In the production of cyanide from alkali, carbon, and nitrogen, the carbon and nitrogen being in excess, cyanide itself may be made to play an important role as accelerator of the reduction of alkali and hence of cyanide formation, alkali metal formed by interaction of cyanide and alkali reacting exothermically with the excess of carbon and nitrogen to re-form cyanide with heavy increase. Systems comprising cyanide, alkali, carbon, nitrogen, and carbon monoxide come to equilibrium involving the relative concentrations of nitrogen and carbon monoxide, the temperature, and the ratio of cyanide to alkali. This equilibrium has been studied experimentally by feeding alkalized charcoal more or less continuously into an electrically heated, vertical tube through which a current of nitrogen, producer gas, or air was passed. At three different temperatures the percentages of cyanide in the total alkali were found to be as follows:

Temperature ° C.	Nitrogen Per cent	CO + 2N₂ Per cent	Air Per cent
950	96	40	38
1000	98	62	61
1050	98	93	94

The samples were taken from a point in the tube far enough from the gas inlet to insure that the material analyzed represented that which had been subjected to the noted temperatures and the stated gases for a time adequate to bring about equilibrium under the indicated conditions. Perhaps the most interesting of these results is the close agreement between the cyanide ratios for air and for producer gas. Essentially, the experiments show the result of heating alkali, carbon, and nitrogen in the presence of cyanide itself. The pronounced effect of temperature increase may be noted. These results are in fair agreement with those of Ferguson and Manning,[6] and also with those of Ingold and Wilson.[7] The figures indicate that at very slightly higher temperatures

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* Numbers in text refer to bibliography at end of article.

cyanide is entirely stable in the presence of carbon monoxide and nitrogen in relative concentrations approaching those of producer gas. The figures suggest, too, that not far above 1050° C. a critical temperature is reached at which the velocity of cyanide formation from alkali is great enough to become a direct linear function of the rate of heat supply. In this connection the vapor pressure of cyanide is pertinent, since in this temperature range cyanide becomes volatile and since in a process of producing cyanide in the vapor phase the vaporization heat becomes a factor to be taken into account.

VAPOR PRESSURES OF SODIUM CYANIDE[8]

Temperature °C.	Pressure Mm. of Mercury
1000	12.5
1050	21.4
1100	37.0
1200	90.0
1300	220.0
1350	300.0
1500	760.0

THERMODYNAMICS OF CYANIDE PRODUCTION

From the practical standpoint, the production of cyanide in any case depends upon a quantity supply of heat which must be available at cyanide-forming temperatures—that is, the temperature must be maintained against the cooling effect of cyanide formation—and in order to do this, available heat must be delivered to the reaction zone at a rate correlated with that of cyanide formation. In coupling cyanide production with the combustion of carbon with air oxygen, the heat development is limited to that of carbon monoxide formation, constituting only 30 per cent of the total combustion value of the carbon burned, 29,160 calories per mol. If recuperative principles are applied, a good proportion of this heat may be available for cyanide formation. For example, in a blast furnace (theoretical combustion temperature above 2000° C.[9]) the hearth temperature being usually about 1500° C., the heat quantity available at this temperature is about 1000 pound-calories per pound of carbon burned with air at a usual blast heat, the carbon being preheated during its descent through the shaft, thus:

	Calories
Carbon monoxide formation from 1 pound carbon	2430
1 pound carbon at 1500° C.	654
5.6 pounds air at 600° C.	840
	3924
6.6 pounds carbon monoxide and nitrogen at 1500° C.	2700
Decomposition of blast moisture—5 grains per cu. ft. = 0.05 pound	160
	2860
Heat available at 1500° C.	1064

The available heat may thus be taken as 12,760 calories per mol carbon. At 1500° C., under usual pressures, cyanide is in the vapor phase, and to 63,860 calories, the heat absorbed in formation, must be added the heat of vaporization, 37,000 calories;[8] the total heat absorbed in forming cyanide vapor from carbonate is thus 100,860 calories per mol potassium cyanide. This amount of heat comprises 62,790 calories for the reduction of carbonate to oxide and 38,070 calories for conversion of liquid oxide to cyanide vapor, these two components being in a ratio of 62 : 38 or 1 : 0.61. The heat available per mol carbon is equal to that absorbed in the formation from oxide of 0.33 mol cyanide vapor, or in the fixation as 1.78 pounds potassium cyanide vapor of 0.37 pound nitrogen per pound carbon burning wth air; and the heat so becoming latent, if set free in condensation of cyanide and its reversion to oxide, is equal to the heat required to reduce carbonate to oxide equivalent to 61 per cent of the cyanide vapor so reverting. Hence, with alkali in the furnace, for example, if about two-thirds of the cyanide vapor-laden gases produced in the hearth are caused to pass up through the shaft and one-third are withdrawn from the furnace through outlet provided in the hot zone, the latent heat of the cyanide vapor carried into the shaft becomes available for the reduction of carbonate equivalent to the cyanide with-

drawn in the hot gas. Such amount of carbonate may be charged with the fuel at the top and descend toward the hearth in countercurrent to the ascending gases. Reacting with cyanide vapor, the alkali may be largely converted to cyanide before reaching the hearth. The output of cyanide from the furnace could thus be one-third of that cyclically formed, or the equivalent of 0.12 pound nitrogen per pound carbon burning with air. Moreover, if the fraction of hot gas withdrawn from the furnace is passed through a mass of alkalized charcoal, the gas in cooling to about 1100° C. develops in cyanide condensation an amount of heat equal to that absorbed in the formation of a 50 per cent increment of liquid cyanide. The indicated ratio of nitrogen fixed is 18 per cent of the carbon burned with air, or about 4 per cent of the air nitrogen. In a modern blast furnace taking 40,000 cubic feet of air per minute and thus burning to carbon monoxide about 550 pounds carbon per minute, the availability of heat is such as to indicate a recovery of something like 100 pounds of fixed nitrogen per minute, or about 70 tons per day. The expenditure of not more than half the fuel value of about 7 pounds carbon at $10.00 per ton would suggest an energy cost of less than 2 cents per pound nitrogen.

CYANIDES IN THE BLAST FURNACE—BEARING UPON FUEL ECONOMY

It appears that in the blast furnace are to be found the exact conditions under which, as indicated by the heat relations and by experimental observation, alkali is readily converted to cyanide with utilization of the heat of oxidation of carbon to supply heat absorbed in cyanide formation. There seems to be a rational basis for a nitrogen fixation process in which carbon is gasified by air and alkali in a reaction which may be pictured thus:

$$O_2 + 3.78N_2 + 0.33K_2O + 2.99C = 2.33CO + 0.66KCN + 3.45N_2$$
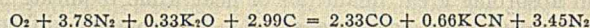
Under blast furnace conditions—that is, with carbon and alkali preheated and with air at 600° C.—the theoretical temperature of this reaction is 1500° C. With a higher blast heat, the proportions of carbon and alkali remaining unchanged, the reaction is exothermic at 1500° C. It will be noted that the reaction involves the fixation of over 8 per cent of air nitrogen as cyanide vapor in a concentration about 10 per cent by volume of the gases produced. The ratio of nitrogen to oxygen in the gases is 2.96 : 1.

That cyanide formation actually takes place in the blast furnace to a notable extent is a matter of repeated observation, the materials charged usually carrying an appreciable content of potash and soda. Moreover, there is to be found in the literature very strong evidence, amounting almost to conclusiveness, that through accumulation of alkali in the furnace cyanide vapor formation in the hearth of the blast furnace is generally of sufficient magnitude to constitute a most substantial heat absorbing factor. It is not too much to say that, although the bearing of cyanides in the furnace upon its fuel economy has not heretofore, so far as is known, been recognized, there are strong reasons for regarding cyanide vapor formation as a primary factor which accounts for the fact that the blast furnace functions very largely as a gas producer—the fact that the fuel energy is not over half developed, the equivalent of 70 per cent of the coke carbon burned leaving the furnace as carbon monoxide. It may be significant that this outstanding fact of practice has not as yet been otherwise adequately explained. The evidence that cyanides are of vital significance in the furnace economy may be summarized as follows:

The classic work of Bunsen[4] showing substantial concentrations of alkali cyanides in gases taken from near the tuyeres.
The exhaustive study of Lowthian Bell[10] on the circulation of cyanides in his furnaces, with observation of total alkali concen-

trations in the hearth gases as high as the equivalent of 0.02 pound potassium cyanide per cubic foot of gas, which is equal to 1.7 pounds potassium cyanide in 85 cubic feet of gas (under standard conditions) produced per pound of carbon gasified with air.

The very general statement in metallurgical textbooks that cyanides are found in notable quantities in the hot zone.

The phenomenon, accepted as fact and discussed by the older metallurgists, Percy, Lowthian Bell, Crooks, and others, that the ratio of the content of nitrogen to that of oxygen in the gases at the tuyere level is much smaller than the nitrogen ratio of the air as blown, and that the relative content of nitrogen *becomes greater* as the gases rise through a considerable height in the furnace. Lowthian Bell's analyses of the gases taken from one furnace at different times show the following ratios of nitrogen to oxygen (by weight).

	Air	At Tuyere Level	6 Feet above Tuyeres	11.5 Feet above Tuyeres
1	3.25	2.88	3.27	3.22
2	3.25	2.84	2.75	3.22
3	3.25	2.75	3.02	2.95
4	3.25	2.73	2.95	3.00
Average	3.25	2.80	2.99	3.10

Recent work by Perrott and Kinney, of the Bureau of Mines,[11] analyzing the gases which were sampled, by means of a tube inserted through the tuyeres, at different distances from the tuyere noses, the object being to investigate the speed of combustion. Following are the averages of the ratios of nitrogen to oxygen (by volume) calculated from the analytical figures on seven to ten different furnaces, the air ratio being 3.78 nitrogen per volume oxygen:

Distance from Tuyere Noses Inches	Volumes Nitrogen per Volume Oxygen	REMARKS
0	4.09	
4	4.34	
8	4.54	11.2 per cent free oxygen
12	4.23	
16	4.31	
20	4.38	
24	4.11	
28	4.00	
32	3.24	Free oxygen disappears
36	2.80	
40	2.87	
44	2.70	Carbon dioxide disappears
48	2.75	
54	2.66	
60	2.50	
66	2.17	
72	1.86	
78	1.91	
84	2.30	

These observations of Perrott and Kinney, being made on a straight line running from the tuyeres into the center of the hearth, are, as far as they go, in agreement with the generally observed decrease of the nitrogen-oxygen ratio in the gases formed at the tuyeres from that of the air. The variations are too great and too sharp to be explained by oxidation and reduction of the metal constituents. They are entirely in accord with what would be caused by successive decomposition and formation of cyanide in the reactions:

$$2KCN + 2(O_2 + 3.78N_2) = K_2CO_3 + CO + 8.56N_2$$
$$K_2O + 3C + N_2 = 2KCN + CO$$
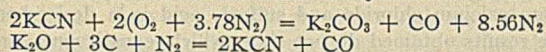
Cyanide formation takes nitrogen from the gases and puts oxygen into them; decomposition of cyanide adds nitrogen and subtracts oxygen. This explanation of the variation of ratio could be readily tested in individual furnaces by repeating Lowthian Bell's experiments, in which he found surprisingly large concentrations of cyanides and other alkali compounds, attributed to the accumulation by successive vaporization and condensation of exceedingly small proportions of alkali in the ore, coke, and limestone. The Bureau of Soils[12] has estimated an average of 0.2 per cent K_2O in the blast furnace materials used in the United States. This would indicate an input of alkali (potash and soda) to a 500-ton furnace of perhaps 5 tons daily. That the alkalies would accumulate to a concentration many times that due to the small quantity in the charge appears *a priori* probable, the usual basicity of slag tending to reduce its alkali content to a minimum.

Recently, the writer had occasion to measure the concentration of cyanide in gases issuing from the cinder notch of a large furnace smelting Mesabi ores with a relatively low coke consumption. Analysis of the ore, coke, and limestone indicated an alkali input to the furnace equivalent to about 0.016 pound potassium oxide per pound carbon burning with air. This could cause a concentration of 0.00026 pound potassium cyanide vapor per cubic foot of gas formed at the tuyeres, 85 cubic feet per pound carbon. A number of measurements gave concordant results averaging 0.009 pound potassium cyanide equivalent per cubic foot of gas. This is a concentration thirty-four times that due to the alkali input. Such an average concentration in the hearth gases would involve 0.76 pound cyanide per pound carbon burning with air.

Relying upon the statements generally made in the literature that cyanides are usually present in substantial amount, it would appear that the generally observed variations of the nitrogen-oxygen ratio in the gases of the hot zone may be concluded to be due to formation and decomposition of cyanide. If this conclusion is sound, then the variation of this ratio may be taken as measuring the cyanide concentration in the gases, and hence the extent of alkali accumulation in the furnace. On this hypothesis, Perrott and Kinney's gas analyses indicate that in American furnaces generally alkali accumulation and cyanide formation are of about the same relative order of magnitude as in Lowthian Bell's furnace, where the gas composition in the tuyere zone would be accounted for by a net fixation as cyanide in that zone of about 5 per cent of the air nitrogen, the gas carrying 1.04 pounds potassium cyanide vapor per pound of carbon burning with air or 0.012 pound per cubic foot. This is considerably less than the concentration of cyanide and carbonate observed by Bell in the gas at 12 inches from a tuyere. Perrott and Kinney's average gas composition at 8 inches from the tuyere noses in eight furnaces shows a change in relative nitrogen content from 3.78 in the air to 4.54 volumes per volume oxygen, with yet 11.2 per cent free oxygen in the gas and hence 53.5 per cent of unchanged air. This suggests a nitrogen ratio of 5.41 in 46.5 per cent of the gas. Such a change of ratio would be brought about if for each pound of carbon burning to carbon monoxide with air a minimum of 0.96 pound potassium cyanide or its equivalent is burned to potassium carbonate—that is, if the gas formed from air carries 0.011 pound potassium cyanide vapor per cubic foot. The entering air forms a flame of burning oxygen in an atmosphere of producer gas, the carbon dioxide thus formed serving as a carrier of air oxygen to the coke. The changing gas composition near the tuyeres indicates that carbo-nitrogen compounds also serve as oxygen carriers and that there is a most substantial concentration of such compounds as vapors in the gases formed. At 32 inches from the tuyeres, where the free oxygen has disappeared, carbonate vapor has apparently again taken up nitrogen and given back its oxygen to the gases, while in addition the gas has lost nitrogen or gained oxygen sufficient to change the ratio to 3.24, a decrease of 14 per cent from the air ratio. Such a change is in concordance with Lowthian Bell's observations and would seem to measure a net formation from oxide of about a pound of cyanide vapor per pound of carbon burning with air.

The formation or vaporization of such a quantity of cyanide in the hearth of the furnace absorbs more than half of the heat available in the hearth with the usual blast heat and accounts quantitatively for the fact that the furnace burns about twice as much coke to carbon monoxide with air as is needed to give the heat absorbed in the smelting process proper. This excess heat may be held responsible for the low carbon dioxide ratio. Analysis of the furnace conditions leads to the conclusion that a withdrawal of gas from the hot zone and, correlated therewith, an addition of alkali to the furnace charge will, without interfering with iron production but with positive

benefit to the furnace operation, make possible the fixation and recovery of over 1 per cent of the air nitrogen.

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Analysis of Gypsum and Gypsum Products[1]

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Samples of raw gypsum were analyzed for gypsum and anhydrite according to present recommended method of analyses (Proc. Am. Soc. Testing Materials, 1921) and checked by microscopic analysis. The method was found to be unsatisfactory, variations of from 1 to 8 per cent occurring. The present method does not distinguish between the different forms that may be present: (1) gypsum ($CaSO_4$.$2H_2O$), (2) calcined gypsum ($CaSO_4$.$^1/_2H_2O$), (3) soluble anhydrite ($CaSO_4$), and (4) natural anhydrite ($CaSO_4$). The following method is recommended which enables the chemist to determine the percentages of these constituents present in their mixtures: If gypsum, determine hygroscopic moisture by drying sample in air having a vapor pressure slightly greater than dissociation pressure of gypsum; then determine total combined water by drying at 200° C. If calcined gypsum, determine the total combined water as for gypsum and then pass air dried by 25 N sulfuric acid over sample to constant weight. From the total combined water, water taken up by sample from 25 N sulfuric acid to form $CaSO_3$.$^1/_2H_2O$, and analysis for CaO and SO_3, the amounts of gypsum, calcined gypsum, natural anhydrite, and soluble anhydrite may be calculated.

CALCIUM sulfate occurs in the natural state in two common forms, as gypsum ($CaSO_4$.$2H_2O$) and as natural anhydrite ($CaSO_4$). It is also found sometimes as a double salt in several compounds, such as syngenite ($CaSO_4$.K_2SO_4.H_2O) and polyhalite ($2CaSO_4$.$MgSO_4$.K_2SO_4.$2H_2O$). Gypsum has many uses, anhydrite very few. As some anhydrite is usually contained in the gypsum, a satisfactory method of determining quantitatively the amounts of each present is necessary.

In the gypsum industry, however, there are four well-defined crystalline forms in which calcium sulfate is found: (1) gypsum ($CaSO_4$.$2H_2O$), (2) calcined gypsum or hemihydrate ($CaSO_4$.$^1/_2H_2O$), (3) soluble anhydrite ($CaSO_4$), and (4) natural anhydrite ($CaSO_4$). Gypsum itself is used as land plaster and retarder in Portland cement. The hemihydrate, which is commonly called plaster of Paris, is made by calcining gypsum at about 140° C. This material is used in many ways, as wall plaster, molding plaster, etc. Soluble anhydrite, known as second settle stucco, is made by calcining gypsum at about 200° C., but owing to its instability it must be used immediately after calcining. This product is sometimes used in making partition tile. Natural anhydrite takes up water very slowly to form gypsum and has very few uses at present. However, it is sometimes used as a filler in paints. A product similar to natural anhydrite may be prepared by heating gypsum at about 600° C. for several hours.[2]

These different forms may be distinguished microscopically,[3] but no satisfactory method of chemical analysis has been developed that will determine how much of each form is present. The microscopic method, however, requires a knowledge of microscopic optical mineralogy which is not at the command of the ordinary chemist.

PRESENT METHOD OF ANALYSIS

The method in use at the present time for distinguishing the amounts of each constituent present is one recommended

by the American Society for Testing Materials.[4] It consists substantially in heating a thin layer of not less than 450 grams (about 1 pound) of the sample at 45° C. for 2 hours in order to drive off any hygroscopic moisture present (A. S. T. M. specifications for 1919 require that the hygroscopic moisture be driven off at 60° C.). One gram of the dried sample is then ground to pass a No. 100 sieve and heated in a covered crucible at 215° to 230° C. to constant weight in order to drive off the combined water. From the analysis of a sample for CaO, SO_3, and combined water, the amounts of gypsum and anhydrite are calculated.

The objections to this method are many:

1—From the vapor pressure curve of gypsum it will be seen that some of the combined water under some conditions would be driven off at either 45° or 60° C.[5]

2—Fine grinding of the gypsum is liable to cause serious error in the determination of combined water.[6]

3—The soluble anhydrite takes up water rapidly from air while being weighed in a crucible, and has a tendency to take up water from calcium chloride and sulfuric acid in a desiccator.

4—The results obtained do not show which constituents are present. For instance, in a mixture of gypsum, calcined gypsum, and natural anhydrite there is no way of telling in what combination the combined water is present, and accurate analyses are impossible.

SEARCH FOR IMPROVED METHOD

With these considerations in mind work was started on an improvement of the present method, or the development of a new method which would be accurate and would enable the chemist to distinguish between the four materials likely to be present. Samples of gypsum as fed to the calcining kettle were obtained from several manufacturers. These samples were screened and four different screenings obtained—on a No. 70, No. 70 to 100, No. 100 to 200, and past a No. 200 sieve. The amounts of gypsum and anhydrite present in each separated part and in the original sample were then

Table I—Percentages of Gypsum and Anhydrite Found by Different Methods
G = gypsum; A = anhydrite; O. S. = original sample before screening

Grain Size	Retained on Sieves Per cent	Chem. I		Chem. II		Chem. III		Microscopic	Flotation	New	
		G	A	G	A	G	A	A	A	G	A
Sample 1											
O. S.	..	69.7	3.5	70.2	3.5	..	..	..	..	74.3	0
On 70	6	52.0	8.0	62.9	0.0	59.3	2.5	0	..	63.0	0
70 to 100	3	55.0	8.5	65.0	1.0	..	..	..	..	64.9	0.6
100 to 200	10	54.0	8.0	68.5	0.7	64.2	4.0	0	..	66.8	1.8
Past 200	81	65.5	8.0	74.2	1.3	..	..	..	..	75.1	0.6
Sample 2											
O. S.	..	90.0	5.0	92.0	3.6	..	..	..	..	95.4	0.6
On 70	25	93.6	2.0	95.8	0.4	..	..	0	..	95.8	0.1
70 to 100	10	95.0	2.0	96.2	0.7	..	..	0	..	96.7	0.3
100 to 200	23	95.0	2.0	91.3	4.7	..	..	Trace	..	95.9	1.1
Past 200	42	91.0	4.0	97.5	3.0	..	..	0	..	96.3	0
Sample 3											
O. S.	..	63.7	8.0	67.0	5.5	..	..	7.2	..	..	..
On 70	5	74.3	12.0	73.4	13.0	..	..	..	7.0	..	..
70 to 100	6	78.4	12.0	79.4	11.0	..	..	..	5.0	81.5	6.3
100 to 200	21	63.6	9.5	69.0	5.3	..	..	7.1	7.0	85.2	6.9
Past 200	62							5.1	4.0	69.0	5.2
Sample 4											
O. S.	..	63.4	11.0	61.0	13.0	..	..	9.3	..	..	..
On 70	5	68.6	21.0	71.4	19.0	..	..	..	5.2	..	..
70 to 100	6	70.0	16.0	78.0	9.0	..	..	..	5.5	79.8	11.9
100 to 200	31	61.6	19.0	77.8	10.0	..	..	11.0	7.7	80.4	8.1
Past 200	58							8.0	7.0	75.4	8.0
Sample 5											
O. S.	..	63.8	8.6	65.2	7.5	..	..	..	..	71.4	1.8
On 70	4	36.4	2.1	34.4	3.0	..	..	..	..	37.6	1.1
70 to 100	2	48.2	2.4	46.7	3.7	..	..	0.3	..	49.9	1.1
100 to 200	8	58.5	3.9	59.3	11.0	..	..	..	2.3	60.9	2.1
Past 200	86	70.5	6.0	69.4	6.0	..	..	..	..	74.3	1.9
Sample 6											
O. S.	..	87.5	3.3	..	..	..	3.3	..	..	84.7	1.6
On 70	38	77.6	4.4	80.2	2.4	..	..	0.2	..	82.2	0
70 to 100	9	78.8	5.8	80.9	4.1	..	..	..	..	84.9	0.8
100 to 200	29	88.0	4.2	89.3	3.2	..	..	..	..	91.8	1.2
Past 200	24	81.6	4.1	79.9	5.4	..	..	..	..	84.0	2.1
Sample 7											
O. S.	..	91.0	6.0	94.8	3.0	..	..	2.0	..	97.1	1.5
On 70	21	90.1	6.8	90.2	6.7	..	..	..	..	96.5	1.8
70 to 100	9	92.4	5.6	93.5	4.7	..	..	..	..	98.7	0.6
100 to 200	23	92.2	5.6	95.7	3.0	..	..	..	..	98.3	0.8
Past 200	47	91.4	5.2	93.1	4.0	..	..	..	..	98.5	0
Sample 8											
O. S.	..	47.0	46.6	..	..	..	..	..	..	..	..
On 70	93.5	57.5	36.8	..	..	..	..	..	..	..	..
70 to 100	1.5	58.1	36.0	..	..	..	..	..	..	59.8	34.7
100 to 200	3	55.0	39.5	..	..	..	..	..	..	56.5	38.3
Past 200	2	62.1	33.5	61.2	34.3	..	..	..	..	63.8	32.3

determined according to the method of analysis at present in use. It was found that the percentage of anhydrite to gypsum was slightly greater in the coarse than in the fine material. The results of analyses are shown in Table I. Five chemists analyzed the samples and variations occur in every case.

In order to determine the accuracy of any method developed it was desirable to have some check on the results obtained. Therefore, the amount of anhydrite in each sample was determined microscopically by E. S. Larsen, of the U. S. Geological Survey. Although the analyses of different petrographers are subject to variations, the results should be quite accurate where the amount of the substance presence is quite small, as in the above case. The results of Larsen differed radically from those afforded by the chemical method described above.

Several methods for determining the amounts of gypsum and anhydrite in a sample containing only the two constituents might be suggested, one being a specific gravity method. However, this is not satisfactory, for gypsum always has impurities, such as calcium carbonate, silica, etc., incorporated with it. Determination by the relative solubilities was suggested, but was abandoned because the rates of solubility of the two materials are different,[7] and because the size and shape of the particles affect the solubility.[8]

A flotation method was used with some success, but was abandoned because of the time required. In this method the two constituents were separated by bromoform, a liquid with a specific gravity between that of gypsum and that of an-

hydrite. Fair results were obtained with coarse particles, but great difficulty was obtained in getting an accurate separation of the fine particles.

Finally, a study of van't Hoff's vapor pressure curves of gypsum forming the hemihydrate, soluble anhydrite, and natural anhydrite was made. From these curves it would appear that the order of the transition of gypsum from one form to the other was reversed from the order obtained in actual practice.[9]

Table II—Checks of Gypsum in Samples
Obtained by analysis for total combined water and percentage of gypsum calculated from hemihydrate obtained by passing over the calcined sample air-dried by 25 N H_2SO_4

Sample	Total Water Per cent	Gypsum Calculated Per cent	Water Taken up as Hemihydrate Per cent	Gypsum Calculated Per cent
1	17.64	84.4	4.45	85.1
2	17.67	84.6	4.39	84.7
3	20.10	96.0	5.2	99.4
4	20.75	96.8	5.11	97.6
5	14.80	70.8	3.77	72.1
6	10.90	52.2	2.70	52.4
7	12.85	61.5	3.30	63.5
8	13.30	63.6	3.28	62.8
9	15.95	76.3	3.92	75.3
10	18.10	86.6	4.67	89.0
11	20.20	96.0	5.01	96.3
12	12.00	57.5	2.98	57.3

The correctness of these curves, however, is questionable. Davis[10] claims that curves for transition of gypsum to soluble anhydrite, and gypsum to natural anhydrite are incorrect. The writer's results, obtained by varying the vapor pressure over calcined gypsum, seem to justify Davis' criticism.

[7] McCaleb, *Am. Chem. J.*, **11**, 31 (1889).
[8] Hulett, *Z. phys. Chem.*, **37**, 385 (1901).
[9] Van't Hoff, *Z. phys. Chem.*, **45**, 257 (1903).
[10] "The Nature of the Changes Involved in the Production and Setting of Plaster of Paris," *J. Soc. Chem. Ind.*, **26**, 727 (1907).

It would seem that any hygroscopic moisture could be eliminated by passing over gypsum air which has a vapor pressure just above that of gypsum. In order to check this, samples of gypsum were exposed to a stream of air of a vapor pressure just above the dissociation pressure of the gypsum. These samples were then dried to constant weight. Samples immersed in
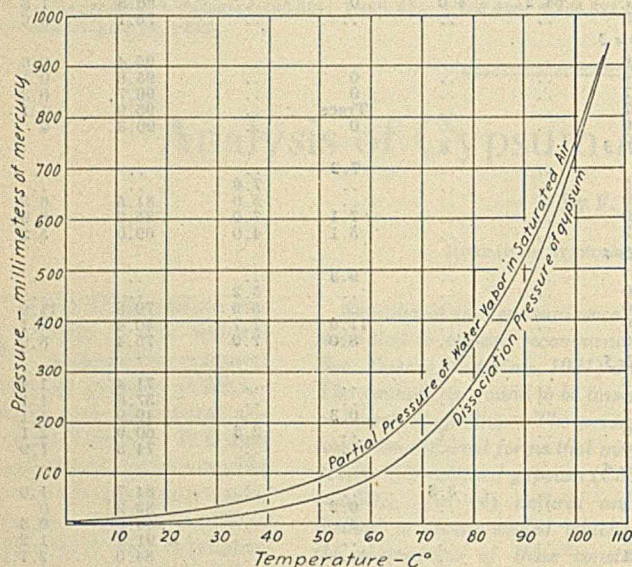

Fig. 1—Dissociation Pressure of Gypsum

water were treated in like manner. Constant results were obtained. After removal of the hygroscopic moisture the samples were heated to constant weight in a U-tube at 200° C., and air-dried by passing through phosphorus pentoxide passed over the samples at the same time. The moisture driven off was collected in a sulfuric acid bulb. The loss in weight of the U-tube and the gain in weight of the sulfuric acid bulb served as a check. The water given off was combined water, from which the amount of gypsum in the sample was calculated. Samples analyzed in this manner checked more nearly the analyses by the microscope than did previous analyses.

Van't Hoff's curve for the dissociation pressure of gypsum to hemihydrate was assumed correct in this case. Further study of the curve made it seem possible that analysis of other forms of calcium sulfate could be made by varying the vapor pressure of air passed over gypsum. In an analysis of gypsum products there are five different phases to consider:

(1)	(2)	(3)	(4)	(5)
H_2O	$CaSO_4.2H_2O$	$CaSO_4.\frac{1}{2}H_2O$	$CaSO_4$	$CaSO_4$
Hygroscopic moisture	Gypsum	Calcined gypsum	Soluble anhydrite	Natural anhydrite

The mixtures of these phases met with in practice would be: 1, 2, 5; 1, 2; 1, 5; 2, 3, 5; 2, 3; 2, 5; 3, 4, 5; 3, 4; 3, 5; 4, 5. It is not probable that any other mixture would exist except in a freshly calcined material, where gypsum, hemihydrate, and soluble anhydrite might be present. This combination is unstable and is not likely to be encountered.

As gypsum is unstable in the presence of air with a vapor pressure below that of gypsum, it is presumed that the hemihydrate is the stable form. On this assumption dehydrated samples resulting from the total water content determination as previously described were subjected to the action of a stream of air with a vapor pressure below that of the dissociation pressure of gypsum (according to van't Hoff's curve). The amount of water taken up by the soluble anhydrite should have been one-quarter of the total combined water, or about 6.6 per cent of the weight of the pure dry sample. However, such was not the case. There was a fairly rapid

rise in the amount of water taken up until 7 per cent was reached, then a more gradual rise. Van't Hoff holds that soluble anhydrite will unite with water when exposed to air to form exactly the hemihydrate (6.6 per cent H_2O). Cloez[11] and Gallo,[12] on the contrary, determined the amount of water absorbed by the anhydrite to be 8 per cent. Davis checked the work of Cloez and found that the soluble anhydrite in taking up the 8 per cent of water forms the hemihydrate and retains the excess as hygroscopic moisture. This combination is unstable and, from the hydrating property of the hemihydrate, does not seem possible.

TABLE III—Results Obtained by Suggested Method on Mixtures of $CaSO_4.2H_2O$ and $CaSO_4.\frac{1}{2}H_2O$

Total Water Per cent	Water Taken up as Hemihydrate Per cent	$CaSO_4.2H_2O$ Present Per cent	$CaSO_4.2H_2O$ Found Per cent	$CaSO_4.\frac{1}{2}H_2O$ Present Per cent	$CaSO_4.\frac{1}{2}H_2O$ Found Per cent
10.16	3.86	40.1	40.2	28.4	28.6
10.44	3.83	42.2	42.2	24.4	26.2
11.20	5.65	35.8	35.4	62.3	61.4
11.25	3.51	49.1	49.3	16.1	15.3
10.05	3.94	38.9	39.1	31.3	30.1

As it seemed logical that there must be some point exactly at which the hemihydrate would be formed, the vapor pressure of the air was decreased until a point was reached at which the amount of water taken up by the soluble anhydrite was just one-quarter of the total combined water. This was obtained by passing the air over 25 N sulfuric acid. Several samples of gypsum were then calcined and the soluble anhydrite was treated in like manner. In each case the amount

[11] Bull. soc. chim., [3] 29, 169 (1903).
[12] Ann. soc. ing. arch. Ital., 27, Nos. 21 and 22 (1914); Gazz. chim. ital., 44, I, 497 (1914).
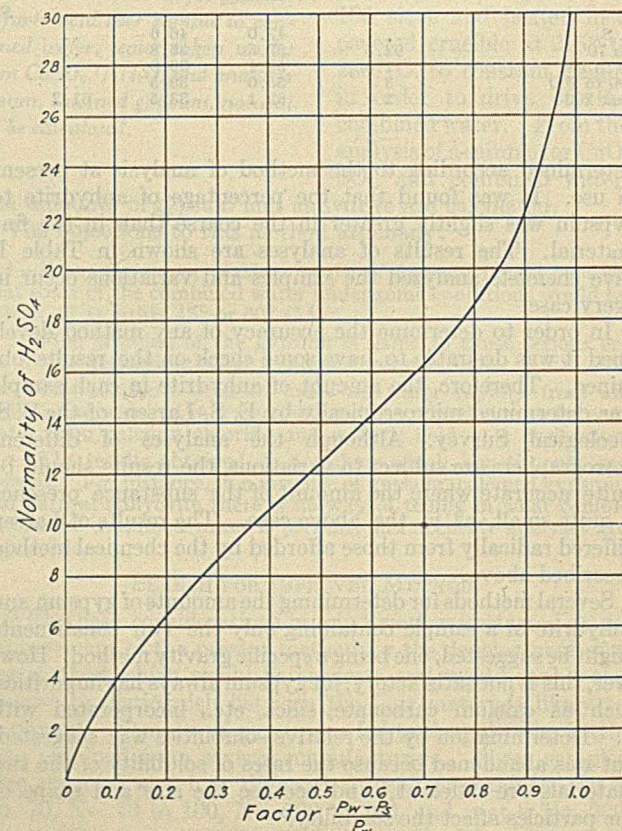

Fig. 2—Vapor Pressure of Different Aqueous Solutions. [Boswell and Cantello, Can. Chem. Met., 4, 109 (1920).] Sulfuric Acid Curve Determination at 23° C. ± 1°

$$\frac{P_w - P_s}{P_w} = \text{Relative dryness}$$

P_w = Vapor pressure of water
P_s = Vapor pressure of solution

of water taken up was one-quarter of the weight lost on calcining. To samples of the hemihydrate obtained as above known amounts of gypsum were added, the mixtures were recalcined, and the total hemihydrate was obtained again. From the total water lost and the amount taken up again in forming hemihydrate, the amounts of gypsum and calcined gypsum could be calculated. The results obtained are shown in Table III.

It has been shown that the present analytical method for determining the amounts of the different phases of calcium sulfate present in a sample is very unsatisfactory. Probably the greatest errors come from fine grinding and the tendency of soluble anhydrite to form hemihydrate. From results of the analyses by the proposed method it appears that fine grinding of material is not necessary for accurate work. Determination by the microscope is a very satisfactory method, but as a chemical method is desirable the one described below is suggested.

Proposed Method

1—After grinding the sample until it all passes a No. 48 sieve, determine gravimetrically the CaO and SO_3.

2—Decide from other evidence whether the sample is raw gypsum or calcined gypsum.

3—If raw gypsum, determine the hygroscopic moisture by drying to constant weight in a current of air having a vapor pressure slightly greater than the dissociation pressure of gypsum at the temperature of the experiment. The dissociation pressure of gypsum may be found from Fig. 1, and Fig. 2 shows the concentration of sulfuric acid necessary to give the air the desired humidity. These have been combined to make Fig. 3, which shows directly the concentration of acid required for any temperature. The loss of weight is reported as free water.
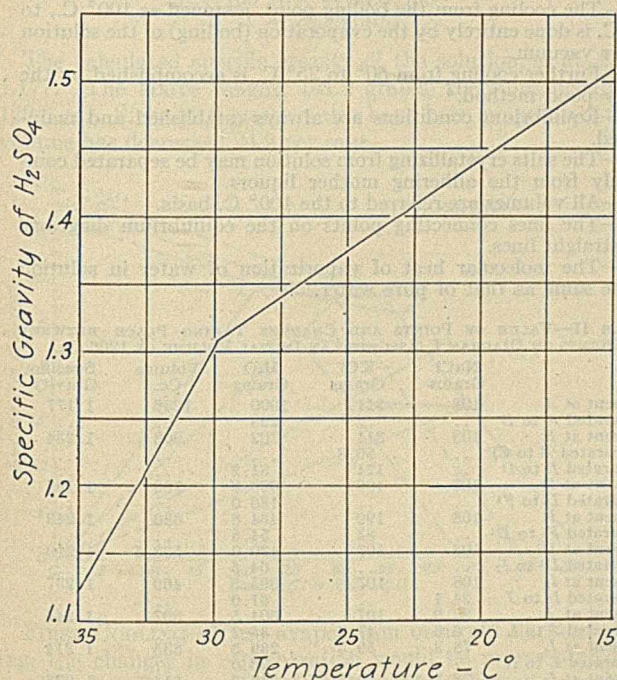

FIG. 3—CONCENTRATION OF H_2SO_4 at 23° C. $\pm$ 1°, THE VAPOR PRESSURE OF WHICH EQUALS THE DISSOCIATION PRESSURE OF GYPSUM BETWEEN 15° AND 35° C.

4—Complete the drying of the sample in a U-tube heated over a sand bath at 200° C. Pass a current of air, dried over concentrated sulfuric acid, over the sample, and absorb the water given off in concentrated sulfuric acid. Check the water thus collected against the loss in weight of the sample. This is water combined as gypsum. Multiply this weight by 172/36 (mol. wt. $CaSO_4.2H_2O$/mol. wt. $2H_2O$) and report as gypsum.

5—If the sample contains calcined gypsum, dry completely as in (4), and note the weight of water lost. Call this W. Cool the sample to room temperature and pass over it a current of air which has previously been passed over 25 N sulfuric acid. Continue this to constant weight and note the amount of water taken up. Call this w. The active part of the sample is now equivalent to calcined gypsum.

6—If $W = w$, the water lost and gained was all present in calcined gypsum. Multiply by 145/9 (mol. wt. $CaSO_4.$ $^1/_2 H_2O$/mol. wt. $^1/_2 H_2O$) and report as such.

7—If W is greater than w, the sample contained both gypsum and calcined gypsum. From the molecular weights it is found that the amount of gypsum was 172/27 ($W - w$), and the amount of calcined gypsum was 145/27 ($4w - W$).

8—If W is less than w, the sample contained both calcined gypsum and soluble anhydrite. In this case all the water lost came from the calcined gypsum, which can therefore be found by multiplying W by 145/9. ($w - W$) represents the water taken up by the soluble anhydrite when changing to the hemihydrate. The soluble anhydrite is therefore found by multiplying ($w - W$) by 136/9.

9—Any CaO and SO_3 not accounted for above should be reported as natural anhydrite with the excess of either constituent.

The samples of gypsum tested were representative samples from the leading gypsum-producing sections of the United States, with the exception that no gypsites were analyzed. The effect of impurities in gypsite on the results obtained would be questionable. However, as some of the samples tested were quite impure, it is believed results just as accurate could be obtained with gypsites.

Results

In Table I are given the amounts of gypsum and anhydrite found by the method recommended by the American Society for Testing Materials, the amount of anhydrite present according to microscopic analysis and to specific gravity separation, and the amounts of gypsum and anhydrite present according to the new method of analysis suggested. Table II gives the results obtained by analyzing at first for the water combined as gypsum and then forming the hemihydrate by passing air dried by 25 N sulfuric acid over the dried sample. Table III gives results of analyses of mixtures of gypsum and calcined gypsum.

Acknowledgment

Extensive Use of Fertilizers

Among the concrete results of extension work along agricultural lines which the Department of Agriculture has been conducting may be mentioned increased interest on the part of farmers in the work with soils and in the use of commercial fertilizers. During the year 1922, 213,000 farmers consulted their county agricultural agents in regard to the use of commercial fertilizers. In addition, farmers conducted 15,235 fertilizer and 4035 lime demonstrations.

As a result of the activities in connection with lime, 48,000 farmers used 630,000 tons according to the methods advocated by the agents. In addition to the above, 105,000 farmers modified their methods of soil management. In order to maintain and improve soil conditions, 3750 drainage systems, involving 575,000 acres, and 29,000 pieces of terracing, involving 445,000 acres, were carried out according to the methods outlined by the extension workers of the Department of Agriculture.

Potash from Kelp[1,2,3]

VIII—Certain Equilibria Used in the Manufacture of Potassium Chloride from Kelp Brines

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IN THE preceding article it has been shown how the separation of potassium and sodium chlorides may be accomplished conveniently by the alternate evaporation of the brine containing the two to the point of saturation with respect to the potassium salt and then cooling for its crystallization, the sodium salt crystallizing on evaporating after saturation with respect thereto has been attained. Thus, advantage is taken of the wide difference in their respective temperature coefficients of solubility to precipitate the one on evaporating the solution and the other on cooling it.

The apparatus employed, described in full in the preceding article, consists essentially of a preheater, an evaporator, and a vacuum crystallizer, with accessory apparatus for filtering off the crystals of precipitated salts and for transferring the brines as desired.

In practice, rectified brine is transferred from the preheater to the evaporator and there evaporated to the point of saturation with potassium chloride, that salt preponderating and saturation with respect thereto being reached before that of the sodium chloride. The solution is then transferred to the vacuum crystallizer and cooled by boiling in vacuum, whereupon the potassium salt is crystallized. The mother liquor is returned to the preheater, is brought to its original volume by the addition of a fresh portion of rectified brine, and the evaporation is repeated. The point is soon reached at which the solution is saturated with sodium chloride, and evaporation beyond this point causes that salt to crystallize. As evaporation, however, is not carried beyond the point of saturation with respect to potassium chloride, and as upon reaching that point the solution is transferred to the vacuum crystallizer, sodium chloride precipitates in the evaporator and potassium chloride in the crystallizer, a separation of the two salts thus being effected. Each combination of the three operations of preheating, evaporating, and cooling is spoken of in this discussion as a cycle.

This article supplements the preceding article of the present series in that it deals specifically with the theory on which is based the manufacture of potash salts from kelp brines as described in the former article. Herein is shown how, from an understanding of the equilibria involved, the theoretical efficiency of the method of recovering potassium chloride may be calculated.

Methods of calculating concentrations and compositions are developed and applied which enable one to determine equilibria both obtained in practice and predicted. These are employed in showing the elasticity of the system and the optimum conditions for the operation of an evaporator and vacuum crystallizer, as illustrated by three new processes.

ent discussion. The system to be discussed, accordingly, is that made up of the components potassium chloride, sodium chloride, and water.

Data for this system have been established by Blasdale,[5] and these with some extrapolations form the basis of the present discussion. The following assumptions have been made, and conditions imposed:

1—The evaporation of rectified brine takes place at atmospheric pressure.

2—The solubility data presented by Blasdale for this system at 100° C. (Table I) are the same as for the temperatures (about 106° C.) at which these solutions boil.

3—The cooling from the boiling point, assumed as 100° C., to 50° C. is done entirely by the evaporation (boiling) of the solution under vacuum.

4—Further cooling from 50° to 25° C. is accomplished by the spray pond method.[6]

5—Equilibrium conditions are always established and maintained.

6—The salts crystallizing from solution may be separated completely from the adhering mother liquors.

7—All volumes are referred to the 100° C. basis.

8—The lines connecting points on the equilibrium diagrams are straight lines.

9—The molecular heat of vaporization of water in solution is the same as that of pure water.

THEORETICAL CONSIDERATIONS

Rectified or purified kelp potash brine, it has been shown, is made up essentially of potassium and sodium chlorides, the two being present in the approximate ratio of 20 : 7. As other saline materials are present in only negligible amount, they will be disregarded entirely in the present

TABLE I—COMPOSITION OF CERTAIN SATURATED SOLUTIONS
(Grams per 100 grams water)

Temperature °C.	Saturated with	NaCl	KCl
25	KCl	..	36.96
25	NaCl	35.63	..
25	KCl and NaCl	29.88	16.28
50	KCl	..	43.12
50	NaCl	36.50	..
50	KCl and NaCl	29.09	22.03
75	KCl	..	49.70
75	NaCl	37.75	..
75	KCl and NaCl	27.87	29.06
100	KCl	..	56.20
100	NaCl	39.40	..
100	KCl and NaCl	27.39	35.16

TABLE II—VALUE OF POINTS AND CHANGES TAKING PLACE BETWEEN POINTS ON DIAGRAM I, ASSUMING AN INITIAL VOLUME OF 1206 Cc.

	NaCl Grams	KCl Grams	H₂O Grams	Volume Cc.	Specific Gravity
Present at A	108	311	1000	1206	1.177
Separated A to B	..	..	298	..	..
Present at B	108	311	702	908	1.234
(Separated B to C)	..	86.3	...	..	...
Separated B to D	..	121	81.2	..	...
Present at D	108	190	620.8	766	1.198
Separated D to F¹	..	..	136.0	..	...
Present at F	108	190	484.8	630	1.243
Separated F¹ to D¹	..	83	54.8	..	...
Present at D¹	108	107	430.0	533.5	1.210
Separated D¹ to I₂	..	..	64.5	..	...
Present at I₂	108	107	365.5	469	1.237
Separated I₂ to J	24.1	..	61.0	..	...
Present at J	83.9	107	304.5	397	1.247
Separated J to L	5.6	47.7	35.2	..	...
Present at L	78.3	59.3	269.3	335	1.214
Separated L to I₁	..	..	20.0	..	...
Present at I₁	78.3	59.3	249.3	315	1.228
Separated I₁ to J	32.1	..	80.5	..	...
Present at J	46.2	59.3	168.8	220	1.247

FIRST CYCLE

FIRST EVAPORATION—Rectified brine as delivered to the evaporating system contains 31.1 grams potassium chloride

[1] Received October 24, 1923.

[2] Published with the permission of the Secretary of Agriculture.

[3] Parts I to VII, THIS JOURNAL, **11**, 864 (1919); **12**, 682, 786 (1920); **13**, 605 (1921); **14**, 19, 441 (1922); **15**, 159 (1923).

[4] The formulas and calculations contained in this paper are for the most part the contribution of the junior author.

[5] THIS JOURNAL, **10**, 344 (1918).

[6] This discussion is introduced as an answer to the question raised as to advantages to be gained from cooling over wider ranges of temperatures.

and 10.8 grams sodium chloride per 100 grams water (141.9 grams). This composition is represented by the point A on Diagram I. When this solution is evaporated by boiling, the ratio of the salts to each other for a period does not change, while that of the salt to water does change. This change is represented by the line AB, which is a continuation of OA. At B the equilibrium curve of potassium chloride is encountered, beyond which, if evaporation is continued further, potassium chloride precipitates. The point B corresponds to a concentration of 44.3 grams potassium chloride and 15.4 grams sodium chloride in 100 grams water. Thus, from A to B there has been an increase in concentration of potassium chloride from 31.1 to 44.3 grams per 100 grams water.

TABLE III—COMPOSITION OF SOLUTIONS
(Grams per 100 grams water)

Point	NaCl	KCl
A	10.8	31.1
B	15.4	44.3
C	15.4	32.1
D	17.4	30.6
F^1	22.3	39.2
D^1	25.1	24.9
I_2	29.4	29.3
J	27.4	35.2
L	29.1	22.
I_1	31.3	23.8
K	27.9	29.1
F	25.7	36.5

The amount of water, X, which has been evaporated to effect the concentration to the point B is obtained from the relation

$$A : 100 - X = b : 100 \qquad (I)$$

in which A = grams potassium chloride (or sodium chloride) per 100 grams water initially
b = grams potassium chloride (or sodium chloride) per 100 grams water finally

Substituting the numerical values for A and b and solving for X, there follows:

$$31.1 : 100 - X = 44.3 : 100$$
$$X = 29.8 \text{ grams}$$

The calculated specific gravity of the solution, as at A, is 1.177. The above weight, 141.9 grams, therefore, occupies 120.6 cc. Since 29.8 grams water have been evaporated, the volume has decreased 24.9 per cent.
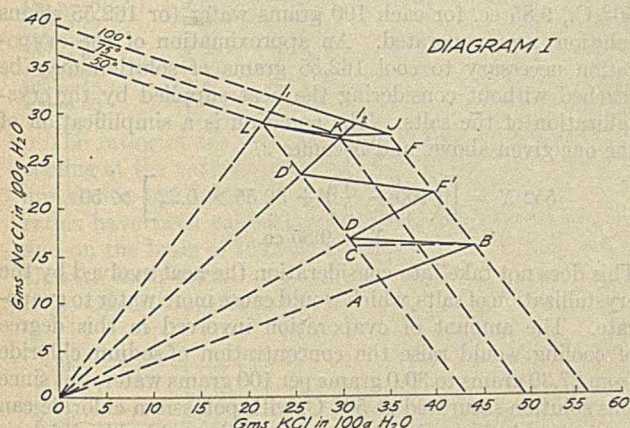
DIAGRAM I

FIRST COOLING—If no evaporation occurred during cooling, the changes in concentration would be represented by the line BC, Diagram I. No sodium chloride could precipitate because the amount present is still below that which can be held in solution at 50° C. Since no sodium chloride precipitates, and assuming there is no evaporation, the ratio of sodium chloride to water remains constant. The line BC is, therefore, parallel to the potassium chloride axis, cutting the 50° C. curve at C, which point represents a concentration of 32.1 grams potassium chloride and 15.4 grams sodium chloride per 100 grams water.

However, the condition is imposed that cooling from 100° to 50° C. shall be by evaporation. This will cause the solubility, and likewise the concentration of potassium chloride, to decrease and the concentration of sodium chloride to increase. These changes, represented by the line BD, are even greater than if cooling were done by conduction. From the slope of the 50° C. potassium chloride solubility curve it is observed that for every unit increase in the concentration of sodium chloride the solubility of potassium chloride is decreased 0.724 unit (grams per 100 grams water).

The evaporation X, necessary to effect the cooling of 159.7 grams of brine of the concentration represented by B (44.3 grams potassium chloride and 15.4 grams sodium chloride per 100 grams water), may be determined by the equation

$$LX = M + N \qquad (II)$$

in which L = average number of calories required to vaporize 1 gram water between the temperatures 100° and 50° C. = 552
X = grams water vaporized
M = calories supplied by the solution in cooling
N = calories supplied by the potassium chloride in precipitating

The amount of water in grams cooled through a range of 50 degrees (from 100° to 50° C.) is $100 - X/2$; and since the specific heat of water is 1, the heat yielded, measured in calories, is $50 (100 - X/2)$.

The total weight of the salts cooled is 59.7 grams. The specific heat of this mixture being taken as 0.22, the heat in calories yielded by the salts on cooling is $59.7 \times 0.22 \times 50$. The expression for M, then, is

$$M = 50 \left[\left(100 - \frac{X}{2} \right) + 59.7 \times 0.22 \right]$$

The amount of heat yielded by the crystallization of potassium chloride depends on the weight of potassium chloride precipitated and its molecular heat of solution. This weight is that of the salt held in the solution in 100 grams water at 100° C. minus the amount held in $(100 - X)$ grams water at 50° C. The heat of solution is -4440 calories per gram molecular weight.

Consideration must be given the change in solubility of potassium chloride at 50° C. caused by the change in the concentration of sodium chloride as well as that due to the change in temperature. The change in concentration will be $\dfrac{100 \times C_1}{100 - X} - C_1$, in which C_1 represents the initial concentration of sodium chloride, in this case 15.4 grams per 100 grams water. For every unit increase in the concentration of sodium chloride the solubility of potassium chloride decreases 0.724 unit. Therefore, this decrease, induced by the change in concentration of sodium chloride, is represented by the expression

$$\left(\frac{100 \times 15.2}{100 - X} - 15.4 \right) 0.724$$

Had the concentration of sodium chloride remained constant, the solubility of potassium chloride at 50° C. would have been 32.1 grams per 100 grams water.

The final solubility of potassium chloride, in grams per 100 grams water, becomes

$$32.1 - \left[\left(\frac{100 \times 15.4}{100 - X} - 15.4 \right) 0.724 \right]$$

The heat evolved in the precipitation of potassium chloride, then, is expressed as

$$\left\{ 44.3 - \left(32.1 - \left[\left(\frac{100 \times 15.4}{100 - X} - 15.4 \right) 0.724 \right] \right) \frac{(100 - X)}{100} \right\} \frac{4440}{74.56}$$

The final equation becomes

$$552 X = \left[\left(100 - \frac{X}{2} \right) + 59.7 \times 0.22 \right] 50 +$$
$$\left\{ \left[44.3 - \left(32.1 - \left[\left(\frac{100 \times 15.4}{100 - X} - 15.4 \right) 0.724 \right] \right) \frac{(100 - X)}{100} \right] \frac{4440}{74.56} \right\}$$
$$X = 11.6 \text{ grams}$$

Equation II becomes expanded into the general expression:

$$LX = \left\{ \left[\left(100 - \frac{X}{2}\right) + (C_1 + C_2)S \right] [T_1 - T_2] \right\} +$$

$$\left\{ \left[C_2 - \left(\frac{C_2 - \left[\left(\frac{100\,C_1}{100 - X} - C_1 \right) 0.724 \right]}{100} \right) (100 - X) \right]_H \right\}$$

which simplifies to:

$$X = \frac{2[(T_1 - T_2)[100 + (C_1 + C_2)S] + H(C_2 - C_3)]}{2L + T_1 - T_2 - 0.02M(C_2 + 0.724C_1)} \quad \text{(III)[7]}$$

in which X = grams water evaporated by vacuum cooling

C_1 = grams sodium chloride per 100 grams water at temperature T_1

C_2 = grams potassium chloride per 100 grams water at temperature T_1

C_3 = grams potassium chloride per 100 grams water at temperature T_2 if cooling were accomplished by conduction

(The value of C_3 is obtained graphically)

T_1 = temperature before cooling

T_2 = temperature after cooling

S = specific heat solid potassium and sodium chlorides = 0.22

H = heat of precipitation of 1 gram potassium chloride = 59.5 calories

L = average heat of vaporization of water between temperatures T_1 and T_2

The volume of solution B containing 100 grams water, when cooled to D, contains 88.4 grams water and 15.4 grams sodium chloride. Accordingly, the concentration of sodium chloride has increased to 17.4 grams per 100 grams water. The point on the 50° C. curve representing this concentration is D, and the line BD describes the changes which occur in the concentration of potassium chloride as the brine is cooled by evaporation from 100° to 50° C. The amount of potassium chloride precipitated, calculated from the resulting volume of water and the solubility at D, is 17.2 grams. Had the cooling been done by conduction, only 12.2 grams potassium chloride would have been precipitated. Thus, vacuum cooling affords an increased precipitation of 40 per cent.

The volume of the solution at B (containing 100 grams water), calculated from the specific gravities of the dissolved salts, is 129.2 cc. The progressive change in volume B to D is represented by the expression

$$V_1 - V_2 = W + M/S \quad \text{(IV)}$$

in which V_1 = volume of the solution at B (containing 100 grams water)

V_2 = volume of the solution at D

W = volume of water evaporated

M = weight of potassium chloride precipitated

S = specific gravity of the precipitated potassium chloride

Substituting the values derived above and solving for V_2

$$129.2 - V_2 = 11.6 + \frac{17.2}{1.99}$$

$$V_2 = 109 \text{ cc.}$$

The calculation of specific gravities instead of their experimental determination has introduced some slight errors, but, as shown by Table IV, these are so slight (at 100° C.) as to have little if any effect on the final result.

[7] It should be noted that the constant 0.724 is derived from the slope of the 50° C. potassium chloride curve and applies only when T_2 is 50° C. If another temperature than 50° C. is selected for T_2, then the constant will change somewhat.

SUCCEEDING CYCLES

ALTERNATE EVAPORATING AND COOLING—When the solution of the concentration represented by the point D, Diagram I, is evaporated at 100° C., the changes are represented by the line DF^1, for which the volume changes may be calculated as were those above for the line AB. At F^1 the solution is saturated with potassium chloride, and the changes on cooling are represented by the line F^1D^1, for which calculation may be made as for the line BD. If the solution represented by the point D^1 is again evaporated at 100° C., the composition changes until the point I_2 is reached, which is on the sodium chloride saturation curve; and if continued beyond that, sodium chloride precipitates and the changes in composition follow the line I_2J. At the point J the solution is saturated with both potassium and sodium chloride. At this point, therefore, if there is further evaporation, both salts begin to precipitate together.

DIAGRAM II
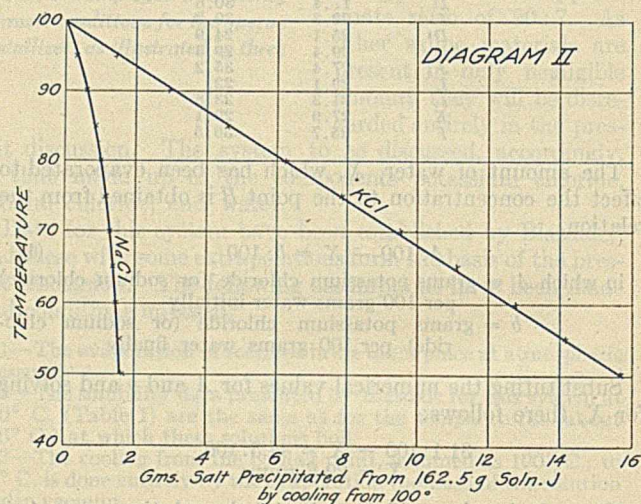
If the solution represented by the point J, whose composition is 35.16 grams potassium chloride and 27.39 grams sodium chloride in 100 grams water, is now cooled in vacuum to 50° C., 9.85 cc. for each 100 grams water (or 162.55 grams solution) are evaporated. An approximation of the evaporation necessary to cool 162.55 grams of solution may be reached without considering the heat supplied by the crystallization of the salts. The equation is a simplification of the one given above, and becomes

$$552 X = \left[\left(100 - \frac{X}{2} \right) + 62.55 \times 0.22 \right] \times 50$$

$$X = 9.85 \text{ cc.}$$

This does not take into consideration the heat evolved by the crystallization of salts, which would cause more water to evaporate. The amount of evaporation involved in this degree of cooling would raise the concentration of sodium chloride from 27.39 grams to 30.0 grams per 100 grams water, but since this solution saturated at 50° C. with potassium chloride can retain in solution only 29.09 grams sodium chloride, it is evident that there must have been a precipitation of sodium

TABLE IV—A COMPARISON OF CALCULATED AND OBSERVED SPECIFIC GRAVITIES OF TYPICAL BRINES

Temperature °C.	Grams NaCl per 100 Grams H₂O	$\frac{\text{G. NaCl}}{2.17}$ = Cc. Calcd. Cc. NaCl	Grams KCl per 100 Grams H₂O	$\frac{\text{G. KCl}}{1.99}$ = Cc. Calcd. Cc. KCl	Total Volume Solution (Calcd.) Cc.	Total Weight Solution Grams	Calcd. Specific Gravity	Observed Specific Gravity	Per cent Error
100	..	..	56.20	28.24	128.24	156.20	1.218	1.217	0.08
100	39.40	18.20	..	..	118.20	139.40	1.177	1.175	0.17
100	27.39	12.62	35.16	17.67	130.29	162.55	1.147	1.253	0.48
75	37.75	17.39	..	..	117.39	137.75	1.173	1.183	0.85
75	..	..	49.70	24.97	124.97	149.70	1.198	1.204	0.50
75	27.87	12.84	29.06	14.64	127.48	156.93	1.232	1.249	1.36
50	29.09	13.48	22.03	11.06	124.54	151.12	1.214	1.246	2.56
50	36.50	16.82	..	..	116.82	136.50	1.169	1.188	1.60
50	..	..	43.12	21.66	121.66	143.12	1.176	1.198	1.84

chloride. The significance of this is that, in cooling in vacuum from 100° to 50° C. a solution of the composition represented by J, both potassium and sodium chlorides are crystallized. The solution over this range of temperature is in equilibrium with both salts and at any given temperature has a composition represented by the intersection of the two solubility curves for this temperature. The point K is located on the 75° C. curve. The curve of the line JKL indicates that sodium chloride precipitates somewhat more rapidly at the higher temperatures of this range than at the lower.

The evaporation, X, effected in passing from points J to K is calculated in the same manner as that from B to D, except that the heat of crystallization of sodium chloride must also be considered. Thus, from Equation III,

$$544 X = \left[\left(100 - \frac{X}{2}\right) 25 + (62.55 \times 0.22 \times 25) \right] + \left[\left(35.16 - \frac{(100 - X) \, 29.06}{100}\right) \frac{4440}{74.56} \right] + \left[\left(27.39 - \frac{27.87 \, (100 - X)}{100}\right) \frac{1180}{58.46} \right]$$
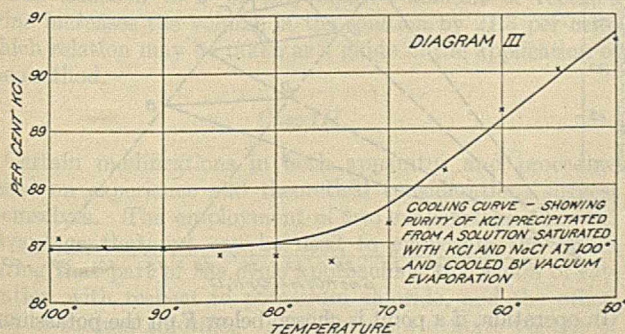$$X = 6.08 \text{ grams}$$

This value for the quantity of water evaporated, substituted in the expression for the quantity of sodium chloride precipitated, which is $27.39 - \dfrac{27.87 \, (100 - X)}{100}$, gives the values 1.214 grams sodium chloride; and similarly, the amount of potassium chloride is shown to be 7.86 grams. The salts precipitated at this 75° C. point, then, have the ratio 7.86:1.214, and the mixture is 86.6 per cent potassium chloride. Likewise, for the 50° C. point, L, the amount of water evaporated (from 162.55 grams of solution at J as before) is 11.57 grams; the amount of potassium chloride precipitated is 15.7 grams and of sodium chloride 1.67 grams; and of the total salts, 90.5 per cent is potassium chloride. In practice, however, the point K is passed over, the cooling being carried directly from J to L.

TABLE V—DATA PERTAINING TO SOLUTIONS UNDERGOING COOLING IN VACUUM CRYSTALLIZER AND PRECIPITATED SALTS

Temperature °C.	Grams H₂O Evaporated from 100 Grams H₂O at Start	Latent Heat of Evaporation	Grams NaCl Precipitated	Grams KCl Precipitated	Per cent KCl in Precipitated Salts
100 to 99.9	0.025	536	0.005	0.03	86.92
100 to 99	0.25	536	0.049	0.33	87.15
100 to 95	1.26	537.2	0.25	1.65	86.98
100 to 90	2.48	539.2	0.48	3.25	86.95
100 to 85	3.71	541	0.74	4.83	86.76
100 to 80	4.91	542.8	0.98	6.37	86.72
100 to 75	6.08	544	1.21	7.87	86.63
100 to 70	7.27	545.6	1.34	9.52	87.66
100 to 65	8.39	547.2	1.45	11.11	88.46
100 to 60	9.49	548.8	1.48	12.75	89.6
100 to 55	10.55	550.4	1.58	14.21	90.0
100 to 50	11.57	552	1.67	15.68	90.5

The ratios of the two salts being precipitated by vacuum cooling at the various temperatures between 100° and 50° C. are shown by Table III and Diagrams II and III. These ratios have been calculated by interpolations of Diagram I and on the basis of 162.5 grams of solutions saturated at 100° C. with both salts.

DIAGRAM III

COOLING CURVE – SHOWING PURITY OF KCl PRECIPITATED FROM A SOLUTION SATURATED WITH KCl AND NaCl AT 100° AND COOLED BY VACUUM EVAPORATION

METHODS OF ADDING FRESH BRINE

The details of the foregoing process have been described in full for the purpose of showing how it is possible to calculate the results which can be obtained at every stage by its use. In order that it may be operated as a continuous process with a more nearly uniform cycle of operations, provision is made for the addition of fresh quantities of brine. Three methods of accomplishing this are suggested, and the results to be obtained by them are calculated in the following paragraphs. Three cases are assumed:

Case I—The evaporation of rectified brine to saturation with respect to potassium chloride, its cooling under vacuum to 50° C., its dilution to its original volume with rectified brine in the preheater, and the repetition of the cycle, finally resulting in precipitation of sodium chloride on evaporating and of potassium chloride and some sodium chloride on cooling.

Case II—The evaporation of rectified brine to saturation with respect to potassium chloride and its cooling under vacuum to 50° C., and the continuation of the cycle to the point where the danger of precipitating sodium chloride together with potassium chloride in the crystallizer is encountered, whereupon sufficient brine A is added in the evaporator to decrease the ratio of sodium chloride so that when transferred to the crystallizer the precipitation point of that salt is not reached and only pure potassium chloride is there crystallized, resulting in the precipitation of sodium chloride on evaporating and of potassium chloride on cooling.

Case III—The evaporation of rectified brine beyond the saturation point with respect to potassium chloride, to some point, F (Diagram VI), in the first of two proposed evaporators, its cooling under vacuum to 50° C., and its evaporation in a second evaporator beyond the point of saturation with respect to sodium chloride and to that with potassium chloride. This is followed by dilution in the first evaporator with such a quantity of rectified brine that on evaporation back to F it will have the same volume as in a preceding cycle, after which the cycle is repeated. The precipitation of sodium chloride will occur in the second evaporator and of potassium chloride in the first evaporator and the crystallizer.

Case I

Of the rectified brine, solution A, 1206 liters are evaporated at 100° C. to saturation with respect to potassium chloride. (This volume is taken because it is that volume which contains 1000 liters water at A and simplifies calculations. In plant operation it is simpler to deal in kiloliters, and the values here given can be reduced thereto by using the factor 1000/1206.) The changes in composition are described by the curve AB, Diagram IV. As shown by the application of Equation I, 298 liters of water have been evaporated. This represents a decrease in volume of 24.7 per cent. The composition of the solution at B is shown in Table VI.

TABLE VI—VALUE OF POINTS AND CHANGES TAKING PLACE BETWEEN POINTS ON DIAGRAM IV—CASE I

(Initial volume of 1206 liters solution A)

	NaCl Grams	KCl Grams	H₂O Grams	Volume Cc.	Specific Gravity
Present at A	108.0	311.0	1000.0	1206.0	1.177
Separated A to B	..	..	298.0	..	..
Present at B	108.0	311.0	702.0	..	..
Separated B to D	..	121.0	81.2	..	..
Present at D	108.0	190.0	620.8	766.0	1.198
Added A to D	39.4	113.5	364.8	440.0	..
Present at X	147.4	303.5	985.6	1206.0	1.191
Separated X to Y	..	..	245.4	..	..
Present at Y	147.4	303.5	740.2	..	..
Separated Y to D_1	..	124.8	83.3	..	..
Present at D_1	147.4	178.7	656.9	815.2	1.207
Added A to D_1	35.0	100.7	324.0	390.8	..
Present at X_1	182.4	279.4	980.9	1206.0	..
Separated X_1 to Y_1	..	..	235.4	..	..
Present at Y_1	182.4	279.4	745.5	..	..
Separated Y_1 to D_2	..	125.9	83.9	..	..
Present at D_2	182.4	153.5	661.6	822.8	1.213
Added A to D_2	34.3	98.8	317.7	383.2	..
Present at X_2	216.7	252.3	979.3	1206.0	..
Separated X_2 to Z	..	..	211.8	..	..
Present at Z	216.7	252.3	767.5	..	..
Separated Z to J	19.9	..	50.2	..	..
Present at J	196.8	252.3	717.3	934.8	1.247
Separated J to L	12.0	112.6	83.2	..	..
Present at L	184.8	139.7	634.1	789.5	1.214
Added A to L	37.3	107.4	345.4	416.5	..
Present at X^{111}	222.1	247.1	979.5	1206.0	..
Separated X^{111} to Z^1	..	..	203.0	..	..
Present at Z^1	222.1	247.1	776.5	..	..
Separated Z^1 to J	29.7	..	74.0	..	..
Present at J	192.4	247.1	702.5	915.3	1.247

On cooling in vacuum to 50° C., as shown by Equation III, there is an evaporation of 81.2 liters water, and 121 kg. (or 60.8 liters) potassium chloride are precipitated, representing a total decrease in volume from B of 15.5 per cent. During this period the composition has followed the line BD and the point D represents the composition of the solution at the end of that period.
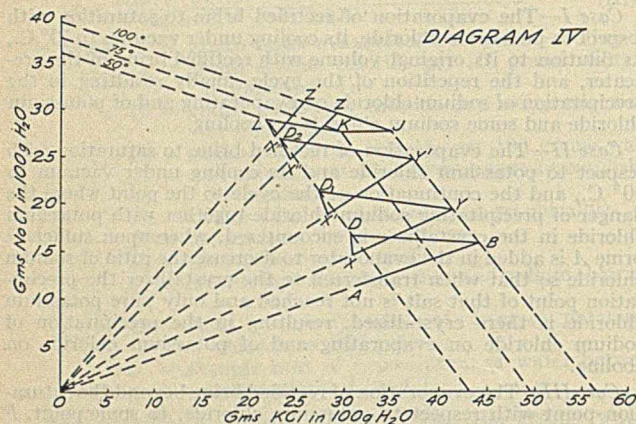
DIAGRAM IV

The residual solution, now reduced to 766 liters, is transferred to the preheater, where its volume is again brought to 1206 liters through the addition of 440 liters of rectified brine. The composition is represented on the diagram by the point X. This is transferred to the evaporator and again evaporated to the point of saturation with respect to potassium chloride represented by point Y, during which the composition has followed the curve XY, with the evaporation of 245.4 liters water. At this point it is again saturated with potassium chloride. On cooling to 50° C. (point D^1), 83.3 liters water are evaporated and 128.8 kg. (or 62.7 liters) potassium chloride crystallized. The solution is then consecutively diluted to X^1 with 390.8 liters rectified brine, evaporated to Y^1, with the loss of 235.4 liters water, cooled to D_2, with the loss of 83.9 liters water and 125.9 kg. potassium chloride, diluted to X_2, and eventually evaporated to Z, at which point sodium chloride begins to crystallize, and through Z to J, at which point the solution is saturated with both potassium and sodium chlorides. During this period from X^{11} to J, 262 liters water and 19.9 kg. sodium chloride have been removed, as calculated by Equation I. On cooling the solution represented by J the composition follows the curve passing through K to L, where the volume is restored with the addition of 416.5 liters as at X^{111}, and the solution evaporated, following the curve $X^{111} Z^1$ to J, from which point the cycle repeats itself. (This is not strictly correct, as the volume of J the first time around is approximately 2 per cent greater than the second. Each additional cycle will reduce this difference. If the cycle is to be repeated indefinitely with a constant volume at X^{111}, for every 100 volumes of L there must be added 55.2 volumes of A. The point X^{111} will have the composition 22.45 grams sodium chloride and 25.32 grams potassium chloride per 100 grams water.) The points B, Y, Y^1, and J are on the line of saturation, at 100° C., with potassium chloride; X, X^1, X^{11}, and X^{111}, arrived at through adding rectified brine A to the solutions represented by D, D_1, D_2, and L, are situated on curves, respectively, intersecting these points and the point A. Points D, D_1, D_2, and L are situated on the 50° C. potassium chloride saturation curve.

Case II

In order to prevent the precipitation of sodium chloride with potassium chloride during cooling in vacuum, the composition of the solution represented by the point J

(which is saturated at 100° C. with both sodium and potassium chlorides) may be altered by the addition of rectified brine and evaporation, so that at the point from which cooling is started it is saturated with potassium chloride but so far removed from saturation with sodium chloride that none of this crystallizes during cooling. This makes possible the crystallization of potassium chloride in the pure state during cooling and of sodium chloride in the pure state during evaporation.

TABLE VII—VALUE OF POINTS AND CHANGES TAKING PLACE BETWEEN POINTS ON DIAGRAM V—CASE II

	NaCl Grams	KCl Grams	H$_2$O Grams	Volumes Cc.	Specific Gravity
Present at A	108	311	1000.0	1206	1.177
Separated A to B	..	..	298	..	..
Present at B	108	311	702	908	1.234
Separated B to D	..	121	81.2	..	..
Present at D	108	190	620.8	766	1.198
Separated D to F_1	..	..	136.0	..	..
Present at F_1	108	190	484.8	630	1.243
Separated F_1 to D^1	..	83	54.8	..	..
Present at D^1	108	107	430.0	533.5	1.210
Separated D^1 through I_2 to J	24.1	..	125.5	..	..
Present at J	83.9	107	304.5	397.0	1.247
Added A to J	7.6	21.9	70.3	84.8	..
Present at N	91.5	128.9	374.8	481.8	..
Separated N to F	..	..	23.4	23.4	..
Present at F	91.5	128.9	351.6	458.4	1.245
Separated F to L	..	59.8	40.8	..	..
Present at L	91.5	69.1	310.8	..	..
Separated L to I^1	..	..	22.3	..	..
Present at I^1	91.5	69.1	288.5	..	..
Separated I^1 to J	38.2	..	94.0	..	..
Present at J	53.3	69.1	194.5	253.7	1.247

The point F (Diagram V), as determined by the following formula derived from Equation III, designates the lowest ratio of sodium chloride to potassium chloride permissible in a solution from which no sodium chloride is to precipitate on cooling in vacuum.

$$552 X = \left(100 - \frac{X}{2}\right) 50 + (56.20 - ZY + Y) 0.22 \times 50 + \left[(56.20 - ZY) - \frac{(100 - X) 22.03}{100} \right] \frac{4440}{74.56}$$

in which X = grams water evaporated from F to L

$Y = \dfrac{29.09(100 - X)}{100}$ = grams sodium chloride per 100 grams of water at F

Z = decrease in the solubility of the potassium chloride per unit increase in the concentration of the sodium chloride along the line $BF(0.7682)$

Solving this equation,

$$X = 11.6 \text{ grams water}$$

The point F therefore represents a concentration of 25.71 grams sodium chloride and 36.45 grams potassium chloride per 100 grams water.

DIAGRAM V
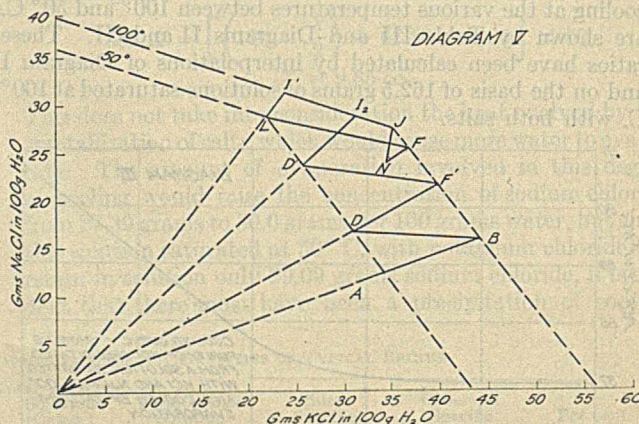
In operation, if a point is chosen below F on the potassium chloride curve, the probability of sodium chloride precipitating because of faulty operation will be lessened. This adjustment can be accomplished by increasing the ratio of brine added to solution J.

Since the composition of rectified brine is represented by point A, the addition to solution J of any quantity of this solution will cause a variation in concentration along the line JA (Diagram V). Sufficient should be added to bring the composition of the solution to that represented by the point N, which is the intersection of the lines JA and OF, since upon the evaporation of this solution the composition will follow the line NF.

To calculate the volume Z of rectified brine A which must be added to the solution represented by J to bring its composition to that represented by N, the following formula may be employed:

$$Z = \frac{i-n}{n-a} \times \frac{\text{specific gravity } J}{\text{specific gravity } A} \times \frac{Ta}{Tj} \qquad \text{(V)}$$

in which j = grams potassium chloride per 100 grams water of solution as at J = 35.16 grams

n = grams potassium chloride per 100 grams water of solution as at N = 34.4 grams

a = grams potassium chloride per 100 grams water of rectified brine as at A = 31.1 grams

Ta = total weight in grams of that quantity of solution A which contains 100 grams water = 100 grams + total weight both salts, or 141.9 grams

Tj = total weight in grams of that quantity of solution as at J which contains 100 grams water = 100 + 35.16 + 27.39 = 162.55 grams

Specific gravity solution J = 1.247, solution A = 1.177

Substituting these values and solving the equation, it is found that to bring the composition of the solution to that represented by N, to each volume of solution J must be added 0.2137 volume of rectified brine A.

In applying this principle, 1206 liters of rectified brine A are evaporated to B and cooled to D, during which time changes take place as derived under Case I. The brine is then evaporated again to saturation with potassium chloride at F^1, during which process from D to F^1 136 liters of water have been evaporated. Cooling from F^1 to D^1 results in the evaporation of 54.8 liters of water and the crystallization of 83 kg. potassium chloride. From D^1 the evaporation is carried through I_2 to J, with the elimination of 125.5 liters of water and the crystallization of 24.1 kg. sodium chloride. At this point, to the volume of 397 liters solution J remaining are added 84.8 liters of rectified brine A as derived from Equation V, which causes the composition to proceed along the line JA to the point N. The mixture is evaporated to F with the loss of 23.3 liters of water, at which point it has become saturated again with potassium chloride, and is then cooled to L, with the evaporation of 40.8 liters of water and the precipitation of 59.8 kg. potassium chloride. After evaporation through LI^1J the cycle is repeated.

The addition to J of the required amount of rectified brine increases the volume of the solution by 21.3 per cent, which relation may be taken as a guide in the application of the method.

Case III

Certain modifications in both apparatus and procedure based on experience and theoretical considerations suggest themselves. The employment of two evaporators offers the advantage that one can be used to evaporate the brines during that part of the cycle approaching the region of saturation with respect to potassium chloride, and the other, that of sodium chloride. Thus, in one a definite volume of rectified brine is evaporated to the composition corresponding to the point F (Diagram VI), and is then transferred with or without its precipitated potassium chloride to the vacuum crystallizer. After cooling and the further precipitation

and elimination of potassium chloride, it is transferred to the preheater and thence to the other evaporator, where sodium chloride is deposited and the composition is brought to that represented by the point J. It is then transferred to the first evaporator, fresh portions of rectified brine are added to bring the composition of the solution to that of the point R, and the whole is evaporated, whereupon the composition becomes that represented by S and then F. At this point the cycle begins anew. The point R is so chosen that subsequent evaporation to F will yield exactly the same volume as in a preceding cycle.

DIAGRAM VI
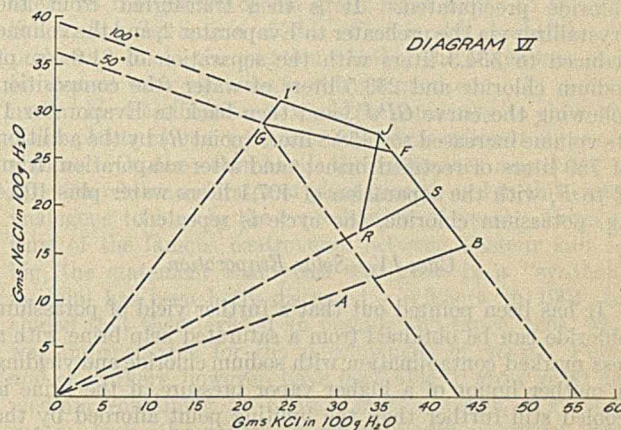
With the three parts of the apparatus operating at a fixed rate, the first evaporator yields a definite volume of brine F for the crystallizer, which in turn delivers a fixed volume of brine G for the second evaporator, and it in turn a fixed volume of brine J to the first evaporator, there to be mixed with a fixed volume of rectified brine A. As long as the composition of the rectified brine remains constant, these relations are maintained constant through automatic, mutual adjustment, and control analyses and laboratory supervision are reduced to a minimum. Thus the cycle, instead of following the curves A to B, B to D, D to X, and X back to Y, as in Case I (Diagram IV), follows the course A to B to F (Diagram VI), undergoing evaporation the while; and from B to F it deposits potassium chloride. At F the brine is transferred to the crystallizer and therein cooled to 50° C. to G, precipitating more potassium chloride. At G it is transferred to the second evaporator, concentrated to I^1, at which point sodium chloride begins to crystallize, and thence is concentrated to J. At J it is returned to the first evaporator, where rectified brine is added to bring the composition to R, is evaporated again through S to F, and the cycle repeated.

TABLE VIII—DATA FOR CASE III

	NaCl Grams	KCl Grams	H₂O Grams	Volume Cc.	Specific Gravity
Present at A at start	197.4	568.6	1828.3	2205.5	1.177
Separated A to F (Evaporator 1)	..	288.3	1060.3	1205.5	..
Present at F (cycle start)	197.4	280.3	768.0	1000.0	1.245
Separated F to G (vacuum crystallizer)	..	130.7	89.1	..	..
Present at G	197.4	149.6	678.9	..	..
Separated G to J (Evaporator 2)	81.0	..	253.5	290.8	..
Present at J	116.4	149.6	425.4	554.3	1.247
Added to J (Evaporator 1)	81.0	233.2	750.0	904.5	1.177
Present at R	197.4	382.8	1175.4	1458.8	1.204
Separated R to F (Evaporator 1)	..	102.4	407.1	458.6	..
Present at F (end of cycle)	197.4	280.4	768.3	1000.2	1.245
Total separation $RFGJ$	81.0	233.1	749.7	904.3	..
A added, J to R	81.0	233.2	750.0	904.5	..

In order to determine just what changes in volumes, concentrations, and degree of crystallization take place in this proposed cycle, it is necessary to start with rectified brine A.

To apply these relations to the operation of the evaporator the condition is imposed that 1000 liters of solution F are to

be produced. To yield this amount, the quantity X of rectified brine required is determined by the ratio

$$120.6 : 54.68 = X : 1000; \text{ or } X = 2205.5$$

The manipulation of this volume in accordance with Case III is illustrated by Table VIII.

In practice, then, 2205.5 liters of rectified brine A are reduced in Evaporator 1 to a volume of 1000 liters, with the loss of 1060.3 liters of water and the precipitation of 288.3 kg. potassium chloride. The brine is then cooled to 50° C., when 89.1 liters of water are evaporated and 130.7 kg. potassium chloride precipitated. It is then transferred from the crystallizer via the preheater to Evaporator 2, and the volume reduced to 554.3 liters with the separation of 81.0 kg. of sodium chloride and 253.5 liters of water (the composition following the curve GI^1J), and then back to Evaporator 1, its volume increased to 1458.8 liters (point R) by the addition of 750 liters of rectified brine; and after evaporation, from R to F, with the separation of 407.1 liters water plus 102.4 kg. potassium chloride, the cycle is repeated.

Case IV—Solar Evaporation

It has been pointed out that a further yield of potassium chloride can be obtained from a saturated kelp brine with a less marked contamination with sodium chloride and yielding a mother liquor of a higher vapor pressure, if the brine is cooled still further than the limiting point afforded by the vacuum crystallizer. Cooling below 50° C. cannot be accomplished by boiling in vacuum. Cooling by conduction is suggested, but serious difficulties are encountered here in the invariable caking of the cooling surfaces with masses of crystalline potassium chloride, immediately retarding and soon entirely stopping the transfer of heat. Cooling coils or refrigerating-brine-jacketing should be adopted only after careful consideration. For further cooling, the spray pond suggests itself as a possibly advantageous instrument, inasmuch as it makes possible the effectual prevention of insulating deposits of crystals forming over the cooling surfaces. The cooling surface, being the aggregate of the surfaces of all the innumerable droplets constituting the spray, is relatively enormous. Cooling by conduction and without evaporation is desirable, since the purpose is to secure potassium chloride in as pure a state as possible. Without evaporation no sodium chloride precipitates, and the proportion that does crystallize is determined by the amount of evaporation. However, it has been shown in Case II that a brine saturated at 100° C. with potassium chloride, but so far removed from saturation with sodium chloride that considerable further evaporation of water is possible, permits a further cooling of the solution by evaporation and the consequent precipitation of potassium chloride, without the crystallization of sodium chloride. Such a solution may quite properly be cooled in a spray pond.

The effect of spray cooling depends on the temperature and degree of humidity of the air. Under normal conditions there is always some evaporation, the maximum being that theoretically required to effect the cooling observed, assuming that no heat is absorbed from outside sources. Accordingly, the curve representing the further cooling of the brine of the composition of that at D (50° C.) (Diagram VII[s]) is properly the approximate projection of the curve BD.

The application of this modification to the system of operating as described under Case I introduces the change that the cooling curve BD is prolonged to E^1, which is on the 25° C. solubility curve of potassium chloride.

The application of the spray pond to Case II introduces the modification that the solution represented by E^{111} on evapo-

ration undergoes changes described by $E^{111}I_{11}J$, indicating the precipitation of sodium chloride over a wider range. This and the precipitation of potassium chloride over a wider range and of a higher degree of purity, yielding both in larger quantity per cycle, are the advantages of this modification. As the solution on each cycle is brought back to the composition of point F, the changes effected are only in that part of the field bounded by $F^1E^{111}I_{11}J$.

DIAGRAM VII
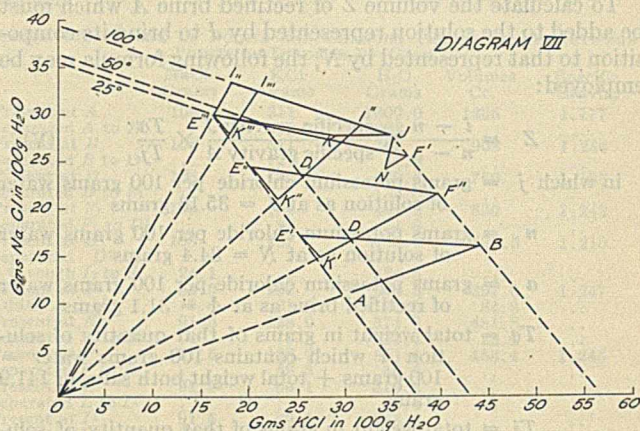
Likewise, in its application to Case III; inasmuch as the solution in each cycle is brought to a definite composition F^1 before being cooled, the changes induced are in the field $F^1E^{111}I_{11}J$ and exhibit themselves as a larger precipitation of both salts, a somewhat purer grade of potassium chloride, solutions of higher vapor pressures, and an increased degree of evaporation per cycle.

The use of a spray pond offers certain advantages. Its cost of operation is represented mainly by that of running a pump to maintain the sprays and to return the cooled brine to the preheater. It acts as a storage reservoir for a large volume of brine of high concentration and purity, thus reducing fluctuation in composition and the effects of faulty operation. On the other hand, its use leads to the production of potassium chloride at a point considerably removed from that at which the bulk of the potash is being produced, thus introducing a certain complication in the manipulation of the salts. Air cooling connotes air circulation; unless this is carefully regulated there will be heavy losses through the blowing away of the finest spray. On the other extreme there is the possibility of cooling entirely by the spray pond method with the elimination of the vacuum crystallizer.

Conquering the Earth

"Conquering the Earth" is the title of a brochure recently issued by the Hercules Powder Company in which is assembled a unique collection of information on a variety of subjects. While calling special attention to historical facts upon which certain advertisements have been based, the text, which is well illustrated, offers in convenient form a number of facts not easily accessible to the average reader. These facts have to do principally with certain industrial operations throughout the world's history, including the mining of copper in the Stone Age, building the pyramids, the Chinese wall, the Roman tunnels, ancient coal operations, and the like. This book may be obtained without charge by addressing the advertising department of the Hercules Powder Company, Wilmington, Del.

[s] Based on *a priori* and not experimental data.

The Soil Organic Matter and Growth-Promoting Accessory Substances[1]

By Norman Ashwell Clark

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THE action of the organic matter in the soil in relation to the plant has been investigated from two viewpoints—the direct and the indirect effects on the growth of the plant. The indirect effect has received the greatest attention, and the influence of organic matter on the soil texture and water-holding capacity, on soil temperature, and on the reaction and composition of the soil solution, has been studied by many investigators. The direct effects, which may be nutritional, toxic, or of an "accessory" nature, are more difficult to examine, but may prove to be of even greater importance to the plant.

The nutritional value of the organic matter in the soil was the subject of a spirited controversy in the early nineteenth century. At that time humus was regarded as the food of plants, but the work of de Saussure and Senebier, with Liebig's famous address to the British Association in 1840, served to kill the humus theory. At the present time there is no doubt that the nutritional requirements of the plant for carbon can be supplied solely by the carbon dioxide of the air, although Grandeau in France, about forty years ago, indicated the possibility of organic substances contributing occasionally to the supply of carbon. Grandeau's suggestion found little acceptance, however, until modern work showed that under certain circumstances these substances could be absorbed by plants and might prove either toxic or beneficial.

Among those who studied the effect of organic matter on the plant were Schreiner and Shorey, of the Bureau of Soils, who in 1910–1912 made a systematic investigation of the organic matter of the soil and isolated a number of pure compounds. Some of these—e. g., picoline carboxylic acid—they found to be distinctly toxic to wheat when placed in a nutritive solution; others, such as arginine and histidine, were beneficial; while a few were harmless and had no effect on plant growth. Knudson, at Cornell, showed that sugar could be assimilated by maize and peas, and Livingston pointed out the efficacy of small quantities of organic matter added to nutritive solutions in increasing growth of wheat.

The possibility of the presence in the organic matter of the soil of growth-promoting accessory substances for the green plant was brought into prominence by Bottomley, in England. He came to the conclusion that the addition to inorganic nutrients of small quantities of certain organic substances was absolutely essential for growth and reproduction of green plants, and that these substances must be obtained from the organic matter of the soil.

To these accessory factors Bottomley gave the name "auximones," from the Greek word meaning "growth-promoting." He considered that they were analogous to vitamins, the growth-promoting substances which are essential for the health and reproduction of animals. He found that extracts from soil and from peat, especially from peat which had been first treated with bacteria and then extracted, had a remarkable effect on the growth of plants, not only in water cultures, but also when added to the soil. Several patents were secured for the manufacturing of the "bacterized peat" extract, and the product was tried on flowers, bulbs, lawns, and in market garden work.

That small quantities of organic matter have a decided effect on the growth of the green plant seems to be established, but the nature of this effect is still doubtful. The problem is dual—the question whether the auximones are to be classed with vitamins is still an open one. In order to make this classification it would be necessary to show that green plants cannot grow and reproduce without these substances. On the other hand, the auximones may have the function of an accelerator of plant growth and in this case be analogous to bios in the reproduction of yeast. From the time of the famous controversy between Pasteur and Liebig, the statement that yeast can grow in a "synthetic" medium has been hotly discussed. Wildiers, in 1901, concluded that there existed an organic substance, bios, which was indispensable for the development of yeast. Fulmer and co-workers, however, have been able to grow yeast on a medium containing no organic matter except a synthetic sugar; bios—the nature of which is still unknown—must therefore have an accelerating action rather than be an essential factor. The first part of the problem—the comparison between auximones and vitamins—has been studied in this laboratory and the same plants were used as were grown by Bottomley.

When the endosperm was removed from the seed, Bottomley[2] found that the seedling responded very quickly to organic materials; from this he argued that the seed contained auximones, which were needed for the growth of the plant. In order to avoid introducing the auximones in this way, he used *Lemna major* and *Lemna minor* of the duckweeds, both of which are water plants and reproduce by forming buds that grow to the size of the mother frond and then separate. These plants grew well in water containing soil, but when tested with Detmer's solution composed only of inorganic salts, they soon failed to attain normal size and the speed of reproduction became very slow. On the addition to this medium of extracts from substances containing organic matter, such as soil, manure, etc., the health of the plants was much improved and the rate of budding accelerated. A solution containing Knop's salts gave even poorer growth than Detmer's, but also produced normal plants when organic extracts were added.

From the fact that no systematic attempts had been made to obtain a nutritive solution especially suited for the *Lemna*, it seemed to the author that the reason for the poor growth of the plants in Detmer's and Knop's salts might be the unsuitability of the media, and that further testing might give solutions in which the health of the plants could be maintained without organic additions. Success in the growth of cuttings in mineral solutions has been recorded in many instances, and in a genetic study at Cornell, Mendiola reported growth of *Lemna minor* in a modified Pfeffer's medium which contained no organic matter.

The three salts first suggested by Livingston[3]—monocalcium phosphate, potassium nitrate, and magnesium sulfate, with iron supplied as ferric phosphate made up as described

[1] Received November 23, 1923.

[2] *Ann. Botany*, **28**, 531 (1914); *Proc. Roy. Soc. (London)*, **89B**, 481 (1917); *Ann. Botany*, **34**, 345 (1920).

[3] "Plan for Coöperative Research on the Salt Requirements of Representative Agricultural Plants," Johns Hopkins University, 1919.

in the National Research Council's bulletin—were used as the basis for media in which to grow *Lemna major*. The plant was found to be very sensitive to light and to the reaction of the medium, but concentrations of the three salts were found in which the plant would reproduce at a regular rate, and in which there was no loss of health or decrease in size. For nearly five months, representing about thirty generations, the rate of growth has kept approximately constant, and the *Lemna* are as large and as healthy as the controls grown in water containing soil, although the rate of reproduction of the plants in the mineral solutions is rather slower than in the soil mixtures.

As these green plants will maintain their health and reproduce without the aid of organic matter, the auximones cannot be regarded as *essentials* for growth of green plants in the same way, as vitamins are essentials for the growth of animals. It is probable, therefore, that their function is of the same nature as the function of bios in the reproduction of yeast and this point is being further investigated in this laboratory.

The Value of Sulfur in Soil Improvement and Crop Production[1,2]

By J. G. Lipman

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Sulfur lends itself to numerous uses in agriculture, among them the supplying of the element sulfur as a plant food where this may not be made available in sufficient amounts in the soil, and the creating of acid conditions that would check the development of certain fungi, particularly the organisms causing scab of potatoes, scurf, and soil rot of sweet potatoes. Sulfur may similarly be used for correcting undesirable conditions in alkali soil, for suppressing or eliminating soil-infesting insects and nematodes, for eradicating weeds, and for use as an ingredient in mineral mixtures fed to livestock and poultry. Sulfur has also been used successfully for making soluble phosphates and potassium compounds.

Data are presented to show that commercial flour sulfur ground to pass 200, 80, and 20-mesh sieves, respectively, is effective, in the order given, in controlling potato scab.

Commercial fertilizer in which the nitrogen was derived from ammonium sulfate and sodium nitrate, respectively, was used together with sulfur. Better control of potato scab was obtained where the nitrogen was derived from ammonium sulfate. Sulfur diluted with an equal quantity of ground phosphate rock seems to give better control of potato scab than the same quantity of sulfur without the admixture of the ground phosphate rock. There are indications that, under some conditions, sulfur may exert a stimulating effect on the growth of potatoes, sweet potatoes, and probably also other crops.

SULFUR and sulfur compounds are being made the subject of study and discussion to a constantly increasing extent. The explanation lies in the fact that at this time sulfur has a wide range of interest to workers in the field of agriculture. The plant physiologist, plant pathologist, veterinarian, entomologist, agronomist, and soil and fertilizer chemist are finding the different reactions of sulfur full of possibilities as to their application.

The plant physiologist is interested in the functions of sulfur in so far as they affect growth, fruit formation, and the composition of plants. To him the changes in reaction produced by sulfur are of more than timely interest, for they play a role in the metabolism of the plant and its resistance to disease. He is primarily interested in the control of diseases that may affect the underground portion of the plant or its foliage and fruit. He is concerned with the study of the fundamental relations involved in the incidence and spread of plant diseases. He knows that the hydrogen-ion concentration of the soil solution may be such as to stimulate or depress the development of certain fungi. Such diseases as potato scab and sweet potato scurf lend themselves readily to control through a modification of the hydrogen-ion concentration in the soil solution. In the control of foliage and fruit diseases different reactions and different sulfur compounds may be involved. Hence a study of the parasites, of the resistance of the host under varying conditions, of the chemical changes undergone by sulfur in the soil or on the surface of the plants, as well as the changes occurring in the soil, are matters of direct consequence in the study of disease control by means of sulfur applications.

The veterinarian and animal pathologist are giving more or less attention to the study of sulfur in its relation to animal production. The stimulus for these studies has apparently come from the farmers, who have been using sulfur in an empirical way for many years. It has long been the custom among progressive hog raisers to include sulfur in the mineral mixtures supplied to the animals. More recently, poultrymen have been inquiring concerning the possible value of sulfur for controlling chickenpox and intestinal parasites of poultry. Hence, the veterinarian is inclined to consider in an experimental way the study of the relation of sulfur to the general tone of the animal system and to pathogenic organisms and parasites which are a source of more or less serious loss to the owners of livestock. Among other things, it is recognized by the veterinarian that internal parasites of poultry, hogs, and sheep cause increasing destruction as the runs, pastures, and range become more and more infested. Theoretically, sulfur together with other materials may be used for creating conditions in the soil that would prevent the survival of the parasites in it. The soil may then cease to be a source of infection.

The entomologist is thinking of sulfur as a promising material for the control of soil-infesting insects and of nematodes. Insects, like wire worms and white grubs, are causing much damage. If the soil can be made unsuitable for the survival of these enemies, this source of damage to crops can be eliminated. Theoretically, then, the oxidation of sulfur in the soil may be utilized, under suitable conditions, for developing a sufficient quantity of acid to discourage the activities of certain insects as well as of certain fungi. No permanent injury need be done to the soil, since excessive acidity may be readily neutralized by the use of lime. In a word, then, the modification of soil reaction by means of sulfur suggests itself as a method for the control of soil-infesting insects.

The agronomist is interested in sulfur from a different point of view. He knows that sulfur is one of the essential elements in plant growth. In so far as the supply of this element is adequate, no reduction in yields need arise if the other conditions for plant growth are favorable. The question at once occurs in this connection as to the adequacy of the supply of sulfur in the soil. Analyses of representative samples of soil may serve for establishing a satisfactory inventory as to sulfur supplies; but, since soils are dynamic rather than static in their character, it is not safe to assume that a supply of sulfur now adequate will not need replenishing ten or twenty years hence. The agronomist, therefore, is inclined to study the sulfur problem from the point of view of the age and the nature of the soil, the gains of sulfur derived from atmospheric sources, the losses of sulfur due to leaching and the removal of crops, as well as the gains due to applications of fertilizers and manures. This phase of the sulfur problem is certain to receive much attention with the increasing age of our cultivated soils.

To the soil chemist sulfur makes an appeal from still another point of view. He knows that plant food is not available to crops except as it may readily become a part of the soil solution. Since the soil reaction has much to do with the concentration of and changes in the soil solution, the influence of sulfur on soil reaction becomes a matter of direct interest to him. Variations in the hydrogen-ion concentration in the soil will lead to variations in the rate at which phosphorus, potassium, calcium, magnesium, and other plant food constituents may become soluble. The soil chemist is also interested in sulfur because of its effect on the texture and structure of soils. The readiness with which sulfur oxidizes in soils suggests various possibilities for the reclamation of black alkali soils and for correcting conditions of excessive soil basicity so far as the need for such correction may exist. The soil chemist is similarly interested in the biological factors involved in sulfur oxidation—that is, the sulfur-oxidizing bacteria themselves and other bacteria and fungi which may modify the processes of sulfur oxidation and may themselves be modified by them.

The fertilizer chemist has been told that acid phosphate may be manufactured biologically in mixtures of ground sulfur and ground phosphate rock kept under suitable conditions. He has also been told that a similar method may be employed for making potassium sulfate from greensand marl. There is a question in his mind whether, under existing economic conditions, soluble phosphates and potassium sulfate may be thus manufactured biologically at a cost low enough to offer serious competition to the methods now in vogue. The last word has not been said on this subject, and further study may indicate that, under some conditions at least, acid phosphate might be made cheaply enough by the biological process to warrant its adoption in a commercial way. The fertilizer chemist is interested in sulfur because it is one of the essential plant foods commonly supplied by commercial fertilizers. As to the adequacy of the supply of this ingredient for all crops and soils, there is a question which apparently calls for further study. It is not improbable that additions of small quantities of ground sulfur to some of the brands of our commercial fertilizers may give them an increased effectiveness, especially on some areas and for some crops. Something may be said, also, about the direct use of mixtures of sulfur and ground phosphate rock as a substitute for acid phosphate, and possibly about mixtures of acid phosphate, ground phosphate rock, and sulfur. Some evidence is already at hand to show that, in some soils at least, mixtures of sulfur and ground phosphate rock are as effective as equivalent quantities of acid phosphate. In other cases the action of the acid phosphate is distinctly more favorable.

Effect of Fineness of Division on Scab Control

It is not the purpose of the writer to discuss at greater length most of the topics already referred to. It might be worth while to refer to certain data gathered at the New Jersey Experiment Station, especially by its plant pathologist, W. H. Martin, and its associate soil chemist, A. W. Blair. The data in question have to do with the fineness of division of sulfur as related to its effectiveness for the control of potato scab. As is shown in Table I, sulfur ground fine enough to pass 20, 80, and 200-mesh sieves, respectively, was employed in a series of experiments conducted in South Jersey on a number of farms during the growing season of 1923. The applications of sulfur were made at the rate of 500 pounds per acre. In each case check plots to which no sulfur at all was added were included in the test. Potato fertilizer mixtures commonly used by the potato growers were applied at the rate of 1500 to 2000 pounds per acre. The growing season was not a favorable one for the production of large crops of potatoes. There was a serious shortage of rain, and, as is well known, under such conditions the control of potato scab by means of sulfur becomes more difficult. When the potatoes were being harvested the crop from each plot was carefully sorted into three lots—namely, those entirely free from scab, those scabby but salable, and those so scabby as to be unsalable.

TABLE I—FINENESS OF DIVISION AS A FACTOR IN SCAB CONTROL

SULFUR	Clean Per cent	Salable Per cent	Unsalable Per cent
	Soil 1		
None	0.4	17.4	82.2
20 mesh	4.5	34.7	60.4
80 mesh	9.5	46.0	44.5
200 mesh	18.5	47.9	33.6
	Soil 2		
None	14.6	71.9	13.5
20 mesh	18.5	71.2	10.3
80 mesh	20.8	71.1	8.1
200 mesh	31.5	62.2	6.3

It will be observed that the data obtained from Soils 1 and 2, located in different potato sections, are in general agreement. The 200-mesh sulfur was decidedly more effective for the control of potato scab than was the 80-mesh sulfur; the latter in its turn was more effective than the 20-mesh material. In the case of Soil 1 the check plot, receiving no application of sulfur, had less than 0.5 per cent of clean tubers and as much as 82 per cent of unsalable tubers. There was a progressive increase in the proportion of clean tubers from the 20 to the 200-mesh sulfur plots and a progressive decrease in the proportion of unsalable, scabby potatoes. In spite of the unfavorable seasonal conditions 18.5 per cent of the potatoes from the 200-mesh sulfur plot were clean and only about 33.5 per cent unsalable. In the case of Soil 2 the control of scab was much better. The check plot contained 14.6 per cent of clean potatoes as against 18.5 per cent for the 20-mesh sulfur plot, 20.8 per cent for the 80-mesh sulfur plot, and 31.5 per cent for the 200-mesh sulfur plot. The proportion of unsalable potatoes was decreased from 13.5 to 6.3 per cent.

Experiments in progress at the New Jersey Station for a number of years have demonstrated that the effectiveness of sulfur for the control of potato scab is influenced, not only by the method of applying the sulfur, but also by the nature and composition of the fertilizer used. It has been shown conclusively that it is best to broadcast the sulfur and thoroughly distribute it in the surface soil rather than to mix it with a commercial fertilizer and apply it in the row. It has also been shown that ammonium sulfate, because of its tendency to increase the hydrogen-ion concentration of the soil solution, can be used to better advantage than nitrate of soda as a source of nitrogen for potatoes wherever scab control methods become important.

Other Factors Influencing Scab Control by Sulfur

Table II contains certain data gathered in a series of fertilizer experiments with potatoes conducted at Elmer, N. J., for the past six or seven years. The various treatments include, among others, the use of sulfur without fertilizer. The application of sulfur on land receiving additions of 1600 pounds of a 4:8:3 fertilizer in which all the nitrogen is derived from nitrate of soda, and a like application of sulfur on land receiving additions of 1600 pounds of a 4:8:3 fertilizer in which all the nitrogen is derived from sulfate of ammonia. The first application of sulfur was made in 1920 and the rate of application was 450 pounds per acre. An additional quantity of sulfur was supplied in 1922 at the rate of 400 pounds per acre. The data presented in Table II have to do with the yields of 1923.

TABLE II—Scab Control by Sulfur and the Influence of Other Factors

	Clean Per cent	Salable Per cent	Unsalable Per cent
	No fertilizer		
No sulfur	21.2	60.4	18.4
Sulfur	86.3	13.7	0
	Fertilizer, nitrogen as nitrate		
No sulfur	0	12.5	87.5
Sulfur	38.5	48.1	12.4
	Fertilizer, nitrogen as ammonium sulfate		
No sulfur	54.4	44.1	1.5
Sulfur	92.1	7.9	0

It will be noted that where no fertilizer has been applied there were only 21.2 per cent of clean potatoes from the no-sulfur plot and 86.3 per cent of clean potatoes from the sulfur plot. On the no-sulfur plot there were 18.4 per cent of unsalable potatoes, whereas on the sulfur plot all the potatoes were salable. Where fertilizer was used and all the nitrogen was derived from nitrate of soda, the no-sulfur plot contained no clean potatoes and 87.5 per cent of unsalable potatoes. Where sulfur was used, 38.5 per cent of the crop was clean and only 12.4 per cent was unsalable. Where fertilizer was used and all the nitrogen was derived from sulfate of ammonia, 54.4 per cent of the potatoes were clean on the no-sulfur plot and 92.1 per cent on the sulfur plot. The amount of unsalable potatoes was practically negligible on the no-sulfur plot, while all the potatoes were clean on the sulfur plot. It is obvious, therefore, that where the soil is more or less acid to begin with the constant use of ammonium sulfate as the sole, or at least the most important, source of nitrogen in the fertilizer may be quite effective in keeping down the losses due to potato scab. It is obvious, at the same time, that ammonium sulfate used together with sulfur is more effective for controlling potato scab. Here again it should be remembered that the reaction of the soil is constantly changing and that soil acidity may increase to a point where a serious depression in plant growth develops. In fact, the use of sulfur for the control of potato scab, or of other diseases for the control of which sulfur may be used, should be subject to constant scrutiny. An application of 200 pounds of sulfur per acre may be quite sufficient for one soil, while for another soil 600 to 800 pounds per acre may not be too much.

The effect of the treatment on the following crops must also be considered. Often good catches of clover and alfalfa are readily secured after an application of 500 or 600 pounds of sulfur per acre. In other instances applications of 300 pounds per acre may interfere more or less with the securing of a good stand of clover or alfalfa. Determinations of the hydrogen-ion concentration of the soil solution become in this case a valuable aid. Through its intelligent use the interests of the farmer may be safeguarded. Having established fairly satisfactory scab control with the aid of sulfur, and preferably of inoculated sulfur, the potato-grower should aim to maintain a fairly constant hydrogen-ion concentration of the soil solution. This may be accomplished most readily by the careful use of lime or by suitable proportions of sulfate of ammonia and nitrate of soda in the potato fertilizer.

Effect of Dilution with Ground Phosphate Rock

Because of the fineness of commercial flour sulfur, its even distribution is not always a simple matter. Some farmers do not own fertilizer drills sufficiently effective to provide for the even distribution of 200 to 300 pounds of commercial flour sulfur per acre. As a rule the distribution is either quite uneven with excessive amounts in some spots and inadequate amounts in others, or the application may actually be at the rate of 600 to 800 pounds per acre instead of the smaller quantity. The practical significance of this question has led the writer to suggest that ground phosphate rock might be a suitable material for diluting the sulfur used for potato scab control. The ground phosphate rock has a twofold advantage in that it may not only serve to dilute the sulfur, but also to exert some buffer effect and retard the accumulation of excessive acidity in the soil. Moreover, the tricalcic phosphate in the rock would tend to become soluble and thus serve as a source of available phosphorus. In accordance with this thought W. H. Martin, of the New Jersey Station, was led to carry out certain tests during the growing season of 1923. Applications of commercial flour sulfur at the rate of 500 pounds per acre were compared with 200, 400, and 600 pounds of sulfur, respectively, diluted with equal quantities of ground phosphate rock.

TABLE III—The Effectiveness of Sulfur as Modified by Dilution with Ground Phosphate Rock

Sulfur Pounds	Phosphate Rock Pounds	Clean Per cent	Salable Per cent	Unsalable Per cent
500	...	18.5	47.9	33.6
200	200	10.8	49.7	39.5
400	400	18.2	52.9	28.9
600	600	27.5	50.0	22.5
None	...	0.4	17.4	82.2

It is shown in Table III that 500 pounds of inoculated sulfur reduced the proportion of unsalable potatoes from 82.2 to 33.6 per cent. Two hundred pounds of inoculated sulfur mixed with 200 pounds of ground phosphate rock reduced the proportion of unsalable potatoes to 39.5 per cent and a like mixture of 400 pounds of sulfur and ground phosphate rock reduced it to 28.9 per cent. Where the mixture consisted of 600 pounds each of the inoculated sulfur and ground phosphate rock, the proportion of unsalable potatoes was reduced from 82.2 to 22.5 per cent. While it would not do to attempt to draw definite conclusions from one season's trials, there is an indication, at least, that the dilution of sulfur with ground phosphate rock is of advantage in that better uniformity of distribution, and apparently also a better control of potato scab, is secured.

Conclusion

Among other facts brought out by the experiments of the writer and his associates through a period of several years is the more or less definite tendency toward increased yields of potatoes and sweet potatoes where sulfur is used for the control of potato scab and sweet potato scurf, respectively. It is possible that we must reckon here with a stimulating effect after due allowance is made for increased production due to the suppression or elimination of the injury done by the disease. The fact just noted, together with results secured in the growing of tomatoes and other crops, quite justifies the conclusion that the effect of sulfur may be the result of the correlation of two or more factors. Thus, in some experiments the sulfur applied, together with standard mixtures of commercial fertilizers, increased the yields of tomatoes and of sweet potatoes. In this connection it might be pointed out that soil microbiological activities, particularly the formation of nitrates and perhaps the fixation of atmospheric nitrogen, may have something to do with the effects exerted by applications of sulfur on some soils and for some crops.

Removal of Naphthalene from Gas by Oil Scrubbing[1,2]

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In one case the naphthalene content of the gas was reduced by more than 50 per cent by merely transforming the arrangement of the existing scrubbers from a batch system to a 2-stage countercurrent system.

Interpretation of the data with the mathematics of the scrubbing of a gas with a liquid indicates that the best system to employ is a five-stage countercurrent system, which is substantially equivalent to a true countercurrent flow of oil with reference to the gas. In each stage the oil should have a very great rate of circulation in comparison with the net flow of oil through the system in order to supply the necessary surface of contact of gas and oil. In the case described the rate of circulation of the oil in each stage is one hundred and twenty times as great as the net advance of oil through the system.

In being recirculated, the oil should not pass into open sumps, but should remain enclosed within the scrubbing system. If this precaution is observed and only sufficient net oil is used to remove the naphthalene, there will be practically no loss of heating value from the gas, no matter how active the recirculation within the scrubber.

The scrubbing temperature should not exceed 70° F., but if it is not possible to keep the temperature as low as this by the usual means of water scrubbing, it will still be possible, within reasonable limits, to reduce the naphthalene content of the clean gas to the desired point by proper choice of the amount of net oil and the scrubber volume.

No definite limit can be set for the safe naphthalene content of the clean gas. This will vary with prevailing temperatures and with the rapidity of temperature changes.

Aside from price there are two principal criteria for choice of scrubbing oils:

(a) The naphthalene vapor pressure characteristic of the oil at constant temperature. Other things being equal, that oil is the best which, at the temperature prevailing in the scrubber, gives the lowest vapor pressure of naphthalene from a given amount of naphthalene in solution.

(b) Viscosity. Other things being equal, that oil is the best which, at the scrubbing temperature, has the lowest viscosity.

If, in examining petroleum scrubbing oils, the viscosity is made the sole criterion, the naphthalene vapor pressure characteristic will, to a considerable extent, take care of itself; at any rate, a considerable variation in this characteristic can be allowed for by simply adjusting the amount of net oil so as to keep p, the vapor pressure of naphthalene from the foul oil, within required limits.

SEVERAL years ago the Pacific Gas & Electric Company installed new oil gas generators at its Potrero, San Francisco, plant, and since that time, owing probably to higher temperatures employed in the gas-making process in these new generators, stoppages in service pipes resulting from naphthalene have been on the increase. Accordingly, an investigation was undertaken by the writers with a view to designing or selecting the best available means for removal of naphthalene from the gas before leaving the works.

About 80 per cent of the city gas for San Francisco is made at the Potrero plant, the balance being made at the Metropolitan plant. As naphthalene conditions at the latter were not corrected during the period under observation, the reduction of naphthalene complaints for the entire city noted below is to be credited entirely to the improved conditions at Potrero. The gas manufactured is oil gas made from California residuum fuel oil of about 16.5° Bé. in the improved Jones generators. The temperature carried in the checkers of these generators is relatively high, leading to a rather prolific production of naphthalene,[3] which has led to many complaints by customers on account of stopped-up service connections during summer months when sudden lowering of temperatures are frequently brought about by ocean fogs. The nominal capacity of the Potrero plant is 20,000,000 cubic feet 550 B. t. u. gas daily.

Former Scrubbing Practice

Before the changes noted below, scrubbing was conducted under the so-called "batch system." Two pairs of oil scrubbers are used, the gas being split into two streams and each stream being run through three water scrubbers, two oil scrubbers, and one water scrubber. The scrubbers are steel towers 12 feet 7 inches diameter by 39 feet high. They are partly filled with wooden trays of grids made of 1×6 inches surfaced

pine, spaced 2.5 inches on centers, and the separate trays are piled with the grids at right angles to each other. The oil is delivered into a spray chamber at the top of each scrubber and thence trickles down through the grids. The sprays are pointed vertically downwards.

In the batch system of scrubbing the fresh oil was put into service in lots of 5000 to 6000 gallons, and recirculated through the sprays and scrubbers for a period of 10 days to 2 weeks until saturated with naphthalene, when it was removed and a fresh batch substituted.

The oil used for scrubbing is a special California crude oil purchased for the purpose, known as Shamrock crude. There follows a distillation test of this oil as received and after using for 10 days.

Table I—Distillation Tests of Shamrock Crude Oil Used for Batch Scrubbing as Received and after Use for Ten Days

As Received		After Use	
Gravity at 60° F.		Gravity at 60° F.	
18.8° Bé. = 0.9409 specific gravity		14.2° Bé. = 0.9709 specific gravity	
Distillation		Distillation	
	Per cent		Per cent
Light oils { 150° F.	3.0	Light oils, 250° F.	27.0
200° F.	5.2	Heavy oils, 370° F.	45.5
250° F.	9.5	Water	13.0
Medium oils { 300° F.	11.6	Naphthalene	4.5
350° F.	16.9	Residue	9.0
Heavy oils { 396° F.	45.1	Loss	1.0
Residue	8.7		

Improved Scrubbing Practice

The improvements which were inaugurated in this practice were principally to convert it over to a 2-stage countercurrent system. The layout of the new plant is shown in Fig. 1. Practically no change was made in the net amount of oil used per thousand cubic feet of gas compared with batch scrubbing. The same kind of oil and the same method of passing the gas through the two lines of scrubbers were continued in use. The No. 4 and No. 5 scrubbers shown in Fig. 1 are oil scrubbers, and the No. 6's are water scrubbers. The gas enters the system through the No. 4 scrubbers and leaves from the No. 6's. No change was made in the internal arrangement of the scrubbers except to place one layer of 14-mesh wire screen over the top wooden tray. This serves

[1] Received June 25, 1923.

[2] Abstracted from a report on an investigation of the removal of naphthalene from gas at the Potrero, San Francisco, works of the Pacific Gas & Electric Company.

[3] Egloff and Twomey, J. Phys. Chem., 20, 121 (1916).

COUNTER CURRENT SYSTEM.
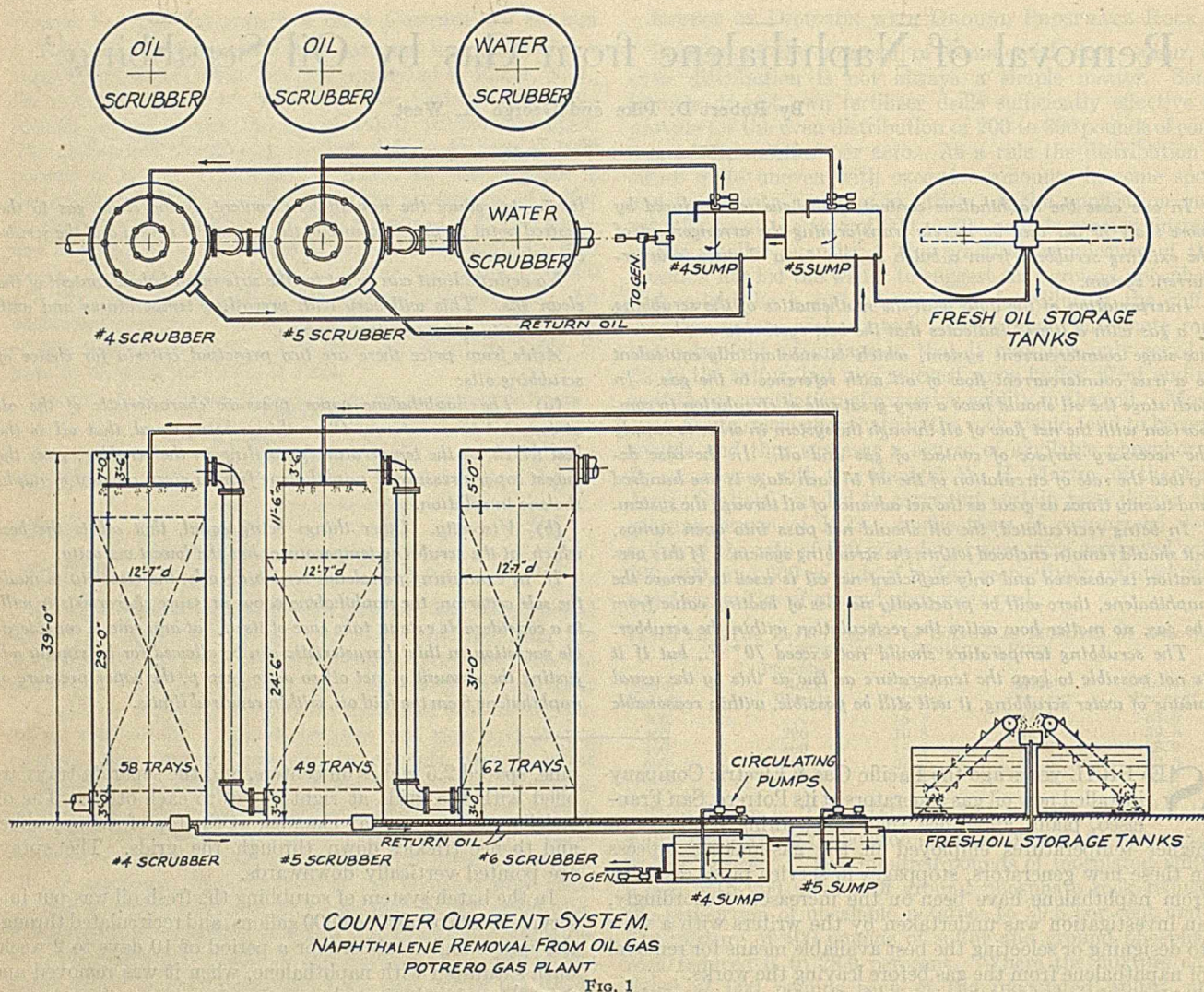NAPHTHALENE REMOVAL FROM OIL GAS
POTRERO GAS PLANT

FIG. 1

to make a better distribution of the oil and a more uniform contact of gas with oil at this level.

The oil is supplied in a small, continuous and accurately regulated stream by a "flotation feeder" mounted in the oil storage tank (Fig. 2). This oil is delivered to the sump of the No. 5 scrubbers and is circulated through the scrubber at the rate of about 6 gallons per thousand cubic feet of gas. The overflow from sump No. 5 passes to sump No. 4, whence it is circulated through scrubbers No. 4 at about the same rate, and the overflow from sump No. 4 is mixed with the oil to the gas generators.

This establishes in effect a 2-stage countercurrent system for scrubbing the gas with the oil. The system is by no

means so good as it might be, either theoretically or practically, but it had a remarkable effect on the naphthalene content of the gas leaving the works and upon the naphthalene complaints as shown in Table II.

The countercurrent system began to be effective in July, 1922, and during the balance of the year effected a great reduction in naphthalene content, with the same kind and net quantity of scrubbing oil. Naphthalene complaints took a decided drop, and it is expected that after a year or so of turning out a gas with a maximum content of 2 grains of naphthalene per 100 cubic feet (see later), thus giving the system a chance to be entirely cleared of naphthalene, the complaints arising from naphthalene deposits will have been entirely eliminated.

Table III covers some other important operating and derived data during the period July to November, 1922, when countercurrent oil scrubbing was in effect. During the period covered by these observations this average daily output was about 13,000,000 cubic feet.

VAPOR PRESSURE OF NAPHTHALENE FROM OIL

In order to calculate the "driving force" defined above under the conditions existing in the scrubber, it is necessary to determine the naphthalene content of gas which will be in equilibrium with the oil for various naphthalene contents of the latter. It is very necessary that this determination be made at the temperature that will prevail in the scrubber, because the vapor pressure of naphthalene from the oil increases very rapidly with the temperature.

TABLE II—TWO-STAGE COUNTERCURRENT SCRUBBING *vs.* BATCH SCRUBBING

	BATCH SCRUBBING DURING 1921		2-STAGE COUNTERCURRENT SCRUBBING DURING JULY–DEC., 1922[a]	
	Naphthalene Content of Gas Leaving Works		Naphthalene Content of Gas Leaving Works	
MONTH	Grains per 100 Cu. Ft.	Naphthalene Complaints	Grains per 100 Cu. Ft.	Naphthalene Complaints
January	6.5	4500	5.0	4800
February	5.0	4000	7.0	3800
March	5.0	4300	5.5	4400
April	6.0	7000	5.0	4000
May	9.5	7400	5.5	5800
June	10.0	11200	5.5	6500
July	9.5	14300	4.5	9700
August	6.5	15800	3.0	10000
September	6.0	11500	1.7	6200
October	5.0	7000	2.3	5100
November	5.5	6000	2.0	6200
December	6.0	5200	2.7	3500

[a] Because plant arrangements make it necessary to bring in extra generators during the winter months of peak load, it is not possible to use countercurrent scrubbing during this period.

This relation for Shamrock crude oil at 65° F. is shown in the curve of Fig. 3. It will be noted that the curve is not a straight line, which would be necessary to meet the requirements of Henry's law.

The method employed in getting the data for curve of Fig. 3, which we may term the "naphthalene vapor pressure characteristic of the oil at constant temperature," was as follows:

The naphthalene content of some of the used scrubber oil was determined. Naphthalene-free gas was then passed through it and the naphthalene picked up by the gas determined. The train consisted of a pressure regulator on the high-pressure gas line, two picric acid wash bottles to remove any traces of naphthalene in this gas, two wash bottles filled with the oil to be tested, two picric acid wash bottles to pick up the naphthalene carried over by the gas, and a laboratory wet-type gas meter to measure the gas passed. The high-pressure gas was found to be practically naphthalene-free. The oil frothed a great deal, increasing the surface of contact and permitting a more rapid current of gas than would otherwise be the case.

Thomas[4] found that in saturating gas with solid naphthalene he could use a volume of 0.1 cubic foot per hour. The writers have been able to obtain close checks at twice that rate from oil. This method depends on the fact that the quantity of naphthalene removed from the oil is such that it changes the concentration in the oil by only an infinitesimal amount.

The experiments were carried on in a room having a temperature varying not over two degrees from 65° F., and no attempts were made to regulate the temperature more closely. A water bath would be advisable, if it were desired to maintain a temperature differing from room temperature.

TABLE III—OPERATING AND DERIVED DATA ON TWO-STAGE COUNTER-CURRENT SCRUBBING

		Degrees F.
1	Average temperature gas	63
2	Maximum temperature gas	68
3	Minimum temperature gas	56
4	Average temperature scrubbing oil	64.5
5	Maximum temperature scrubbing oil	68
6	Minimum temperature scrubbing oil	58
		Saybolt Seconds
7	Viscosity of scrubbing oil at 65° F.	1160
7a	Viscosity after use in scrubber No. 5	582
7b	Viscosity after use in scrubber No. 4[a]	353
		Grains per 100 Cu. Ft.
8	Total naphthalene content of gas entering No. 4 scrubbers (foul gas)	28.4
9	Same contained in tar mist in gas	12.7
10	Same contained in gas as vapor	15.7
11	Total naphthalene content of gas leaving last oil scrubber No. 5 (clean gas)	3.81
12	Same contained in tar mist in gas	2.14
13	Same contained in vapor in gas	1.67
14	Total naphthalene content of gas leaving water scrubber No. 6	4.60
15	Same contained in tar mist in gas	2.96
16	Same contained as vapor in gas	1.64
17	Total naphthalene content of gas leaving works all contained in gas as vapor	1.58
		Gals./M Feet of Gas
18	Gallons of net scrubbing oil used per M feet of gas	0.05
19	Rate of circulation of scrubbing oil in No. 4 scrubbers	6
20	Rate of circulation of scrubbing oil in No. 5 scrubbers	6
21	Gross scrubber volume per M feet of gas treated per day	1.53
22	Scrubber constant K[b] for No. 4 scrubbers	0.0534
23	Scrubber constant K for No. 5 scrubbers	0.0619
24	Naphthalene balance:	Per cent
	⎧ by No. 4 scrubbers	59.1
	Removed from gas ⎨ by No. 5 scrubbers	27.4
	⎩ in tar from centrifugal exhauster	7.9
	Sent out of works	5.6

[a] The viscosity of the oil is reduced by taking lighter hydrocarbons into solution.
[b] The scrubber constant K referred to above is defined as the quantity of naphthalene transferred from gas to oil per minute per cubic feet of net scrubbing volume per unit of driving force, which latter unit is defined as the unit difference in concentration, expressed as pounds of naphthalene per pound of gas, between the actual gas being scrubbed and a gas which would have a naphthalene concentration in equilibrium with the naphthalene content of the scrubbing oil. The volume of any scrubber under like conditions will vary inversely as K; hence this number when known is of great value in comparing the relative values of different scrubber types. There are two types of scrubbing volume in each tower—i. e., spray chamber and wooden tray packing—and the K here given is the average for the entire tower. It would be desirable to determine K separately for both the spray chamber and the tower packing, but the experimental data would be difficult to obtain.

[4] Gas World, 63, 644 (1915); J. Gas Lighting, 132, 701 (1915); J. Soc. Chem. Ind., 35, 506 (1916).

REMOVAL OF HEATING VALUE FROM GAS IN SCRUBBING

Because of difficulty of sampling, it has not been possible to determine accurately the loss of B. t. u. of the gas through the oil scrubbers, but the following points seem to be well established from the writers' observations.

1—If the amount of net scrubbing oil used is that given in Table III—namely, 0.05 gallon per thousand cubic feet of gas—the amount of benzene or other of the heavier hydrocarbons present in the gas which is required to saturate this oil under the conditions existing in the scrubber is negligible compared with the total amount present, and B. t. u. losses from this loss are therefore negligible.

2—The rate of oil in circulation in each scrubber is more than one hundred times as great as the amount of net oil advanced through the scrubbers, and if this circulating oil passes through an open sump an excellent opportunity is offered for evaporation of the heavier hydrocarbons and also of the methane in solution in the oil.

3—If the advance of net oil through the system is made only great enough to remove the naphthalene and if the entire system is enclosed, the B. t. u. losses will be negligible no matter how active the circulation of oil within the system.

VAPOR PRESSURE OF NAPHTHALENE

The determinations of the vapor pressure of naphthalene are quite numerous. The results of Schlumberger,[5] Thomas,[6] Gensee,[7] and Barker,[8] have been compared in the curve of Fig. 4.
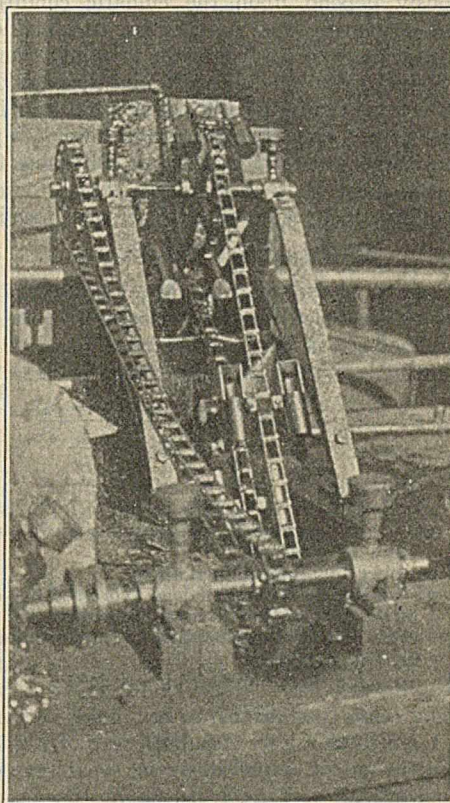
FIG. 2—OIL-FEEDING MECHANISM

In this curve the ordinates are the reciprocals of temperatures in degrees centigrade absolute and the abscissas are log P, P being the vapor pressure of naphthalene in millimeters of mercury. The curve is a straight line, as predicted by the Clausius-Clapeyron equation, and shows a good agreement among the different points. For everyday use it is more serviceable to plot the curve with direct

[5] J. Gasbel., 55, 1251 (1912).
[6] J. Soc. Chem. Ind., 35, 506 (1916).
[7] Soc. tech. de. l'industrie des gaz, 1912; abstracted in Gas World, 56, 906 (1912), and Génie civil, 61, 183 (1912).
[8] Z. physik. Chem., 21, 235 (1910).

coördinates, as is done in Fig. 5, the ordinates being grains of naphthalene per 100 cubic feet, and the abscissas temperature in degrees Fahrenheit. This curve shows that at the freezing point of water the gas will carry 2 grains of naphthalene per 100 cubic feet.

FIGURE 3
VAPOR PRESSURE
OF
NAPHTHALENE FROM SCRUBBER OIL
EQUATION OF CURVE $p = \frac{.000086\,C}{.13 - C}$
AT 65° FAHRENHEIT

PIKE & WEST
CONSULTING CHEMICAL ENGINEERS
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C · Concentration of Naphthalene in lbs per lb of original oil

P· Concentration of Naphthalene in lbs per lb of Gas

The decision as to the safe limit for naphthalene content will obviously depend upon the climatic conditions. In San Francisco during the summer months sudden chills to 50° F. are to be expected from fogs, at which point the gas will carry 6 grains per 100 cubic feet, and these sudden chills are more effective in causing naphthalene deposition in service connections than a steadily maintained lower temperature. The writers have chosen 2 grains per 100 cubic feet as a tentative safe limit for San Francisco, but a much lower limit would have to be adopted in some other localities.

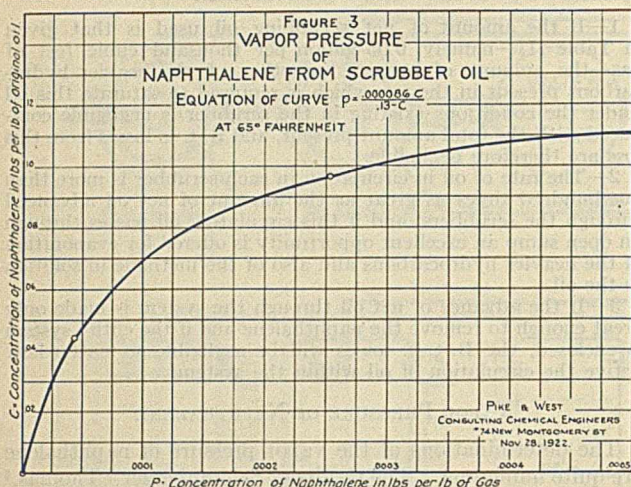### MATHEMATICAL TREATMENT

It is necessary to derive an analytical expression connecting the several variables in order to evaluate K, the scrubber constant defined above from the observed data.[9,10,11]

The following is the general formula applicable to this case:

$$U(P - P_0) = K V \frac{(P - p) - (P_0 - p_0)}{2.3 \log \dfrac{P - p}{P_0 - p_0}} \qquad (1)$$

U = pounds of gas to be scrubbed per minute
P = pounds of naphthalene per pound of foul gas
P_0 = pounds of naphthalene per pound of clean gas
V = volume of scrubber
K = scrubber constant defined above
p = concentration of naphthalene expressed as pounds per pound of gas that is in equilibrium with the vapor pressure of the naphthalene in the scrubbing oil leaving the scrubber (foul oil)
p_0 = same for clean oil entering scrubber

The assumption that Henry's law holds is implicit in Equation 1, but if this were true the curve of Fig. 3 plotted with concentration of naphthalene in the oil as ordinates against concentration of naphthalene in the gas in equilibrium with the oil as abscissas would be a straight line—which, in fact, it is not. However, in considering each of the scrubbers No. 4 and No. 5 individually, the circulation of oil compared with the net advance of oil is so rapid that the concentration of naphthalene in the oil is constant throughout the entire volume of each scrubber. Hence, for each individual scrubber

$$p = p_0 = \text{constant} \qquad (2)$$

the error implicit in Equation 1 when p is a variable, arising from the assumption that Henry's law holds, is elimi-

[9] Lewis, THIS JOURNAL, **8**, 825 (1916).
[10] Whitman and Keats, *Ibid.*, **14**, 186 (1922).
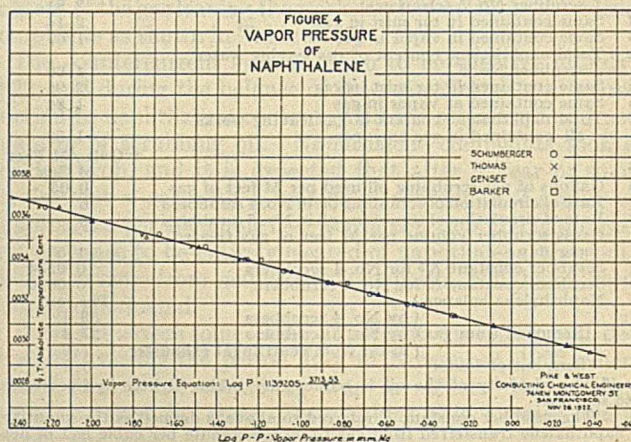[11] Lewis, *Mech. Eng.*, **44**, 445 (1922).

nated; but it must not be inferred on this account that Equation 1 then becomes a rigorously correct statement of a relation connecting all the variables that influence the scrubbing operation. It is probably impossible to derive a rigorously correct solution of these variables, but Equation 1 will serve as an approximately correct basis for the calculation of rational designs.

All the factors in Equation 1 are known from the observed data except the scrubber constant, K, which is solved for with the results given in Table III.

The scrubbing system which has been described (Fig. 1), considered ideally, is a true countercurrent system, clean oil entering at one end and foul gas entering at the other, the two passing countercurrent, the clean gas leaving in contact with the clean oil and foul oil leaving in contact with the foul gas. But the oil in its passage through the system is divided into two stages, in each of which the circulation is over one hundred times in excess of the true, net, or countercurrent flow, and in consequence there are only two oils of fixed naphthalene content in contact with the gas, so that the clean gas does not actually come into contact with a clean oil, but with one containing considerable naphthalene. The gas, of course, passes through the scrubbers without recirculation. As the number of stages of scrubbing is increased above two, reflection shows that, with each increase, the oil in the first oil stage or last gas stage more nearly approaches clean oil in composition, until, if the system is pictured as made up of an infinitely large number of infinitely small stages, it will have become a true countercurrent system with clean gas leaving in contact with clean oil.

In a true countercurrent system less scrubbing volume will be required, other things being equal, than in the two-stage countercurrent system described; but the writers' calculations indicate that if five stages are provided for the oil, in each of which the circulation of the oil is very rapid compared with the net advance, true countercurrent conditions will have been practically attained.

To calculate the volume for the five-stage, or substantially true, countercurrent system, Equation 1 is again used, it being asumed that the value of the scrubber constant, K, for the type of scrubber under consideration is known. In this case $p_0 = 0$.

FIGURE 4
VAPOR PRESSURE
OF
NAPHTHALENE

SCHUMBERGER ○
THOMAS ×
GENSEE △
BARKER □

T · Absolute Temperature in Cent.

Vapor Pressure Equation: Log P = 1139205 - $\frac{303.53}{}$

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Log P · P · Vapor Pressure in mm Hg

To get the value of p, a curve must be experimentally determined similar to that of Fig. 3 for the scrubbing oil which is to be used and the same temperature which is to exist in the scrubber. A convenient concentration, C, of naphthalene in the foul oil is then chosen, giving the value of p from the curve, and the value of V, the net scrubber volume for true countercurrent conditions, is immediately obtained by solving Equation 1. To this volume should be added about 20 per cent as a safety allowance.

Effect of Temperature

No observations have been made on oil scrubbing for naphthalene where temperatures were different from 65° F., but in the method of design described above this factor is taken care of by the rule that the naphthalene vapor pressure characteristic of the oil must be determined at the temperature which is to be actually employed in scrubbing. The calculation of V will therefore be correct for this temperature, provided K does not vary with temperature, but if the temperature is reduced much below 65° F., which might otherwise seem desirable, K would be made less because the viscosity of the oil would be increased.

Ott[12] states that when the temperature of the gas was reduced from 35° C. (95° F.) to 20°-25° C. (68°-77° F.), the amount of naphthalene removed was doubled, but that there is no advantage in cooling further.

Pannertz[13] describes a large-scale test in a 6-chamber washer, and states that the temperature should not be above 20° C. (68° F.). Experiments on a small scale showed that oil at 40° C. (104° F.) let pass about nine times the amount of naphthalene as oil at 17°-18° C. (62.6°-64.4° F.).

If it is possible, the gas should be cooled to from 60°-70° F. before oil scrubbing, and the oil should be at about this same temperature; but if it is not possible to cool the gas to this point by the usual means of water washing, it is simply necessary to so proportion the volume of scrubber with reference to the amount of net scrubbing oil advanced through the scrubber, in accordance with the foregoing procedure, as to obtain the desired content of naphthalene in the clean gas.

Choice of Oils

The procedure outlined above enables one to adopt in a rational way a wide range of scrubbing oils to the needs of naphthalene scrubbing. A lower vapor pressure of naphthalene corresponding to a given amount in solution in the oil means less net oil through system, and this is desirable because the smaller the amount of net oil per thousand cubic feet of gas the less amount of the other soluble constituents will be removed. The basis of comparison of scrubbing oils will, therefore, be by means of their naphthalene vapor pressure characteristic curves at constant temperature, as shown in Fig. 3.

Another important property of the oil is its viscosity, and, other things being equal, that oil which has the lowest viscosity at the working temperature is the best. This is because a low viscosity will permit free flow of the oil throughout the scrubber volume, thus favorably affecting the scrubber constant, K.
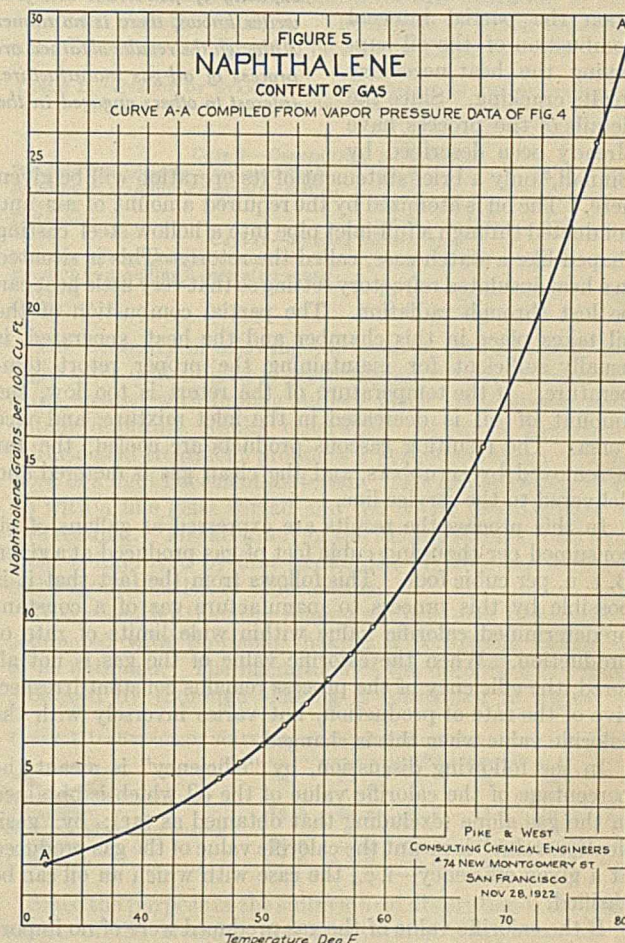
Tar Mist

As shown in Table III, 45 per cent of the total naphthalene content of the foul gas is contained in tar, which occurs as a mist in the gas, but in the application of Equation 1 it has been assumed that the total naphthalene content of both foul and clean gas exists in the form of a true vapor. This is necessary for simplicity of mathematical treatment. No doubt the total volume of oil scrubbers could be somewhat reduced if the tar mist were removed from the foul gas before oil scrubbing, and in some cases it has been found desirable to do this; but it is the writers' opinion that the tar mist can be effectively removed by the oil scrubbers, if not present in too large amounts. An exception to this statement would, of course, occur if the scrubbing oil were stripped of naphthalene or other components and then returned to the scrubber. In such case all the tar would have to be removed before oil scrubbing, otherwise the scrubbing oil would quickly become foul with tar.

12 *J. Gasbel.*, **53**, 784 (1910).
13 *Ibid.*, **54**, 912 (1911).

Determination of Naphthalene

The naphthalene vapor in the gas was determined by the well-known Colman-Smith[14] method of absorption in picric acid after the tar had been removed on cotton filters. The precipitate of naphthalene picrate was filtered off, washed with dilute picric acid, and titrated with sodium thiosulfate after mixing with a potassium iodide-iodate solution. This combination of methods was evolved from the papers of Knublauch[15] and Schlumberger,[16] from which details may be obtained.

FIGURE 5
NAPHTHALENE
CONTENT OF GAS
CURVE A-A COMPILED FROM VAPOR PRESSURE DATA OF FIG 4

Naphthalene Grains per 100 Cu. Ft.

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Temperature Deg F.

For the determination of naphthalene in tar and oil a digestion was made with an alcoholic solution of picric acid, as recommended by Knublauch. An alternative method was the digestion of the oil with a water solution of picric acid under reduced pressure. Either was satisfactory for tar or oil with over 4 per cent naphthalene, but neither was very satisfactory for a naphthalene content less than 1 per cent. More work needs to be done to get a really reliable method for low concentrations of naphthalene in oil and tar.

Acknowledgment

An earlier bibliography by White and Ball[17] was available, and since this work was done one prepared by O. L. Kawalke and A. W. Pesch was presented at the 21st Annual Convention of the Wisconsin Gas Association, March 22 to 24, 1922.

Acknowledgment is due to the assistance rendered throughout this work by the technical and operating staff at the Potrero Plant of the Pacific Gas & Electric Company.

14 *Gas J.*, **144**, 231 (1918).
15 *J. Gasbel.*, **59**, 525, 540 (1916); *Gas J.*, **137**, 64 (1917); *J. Gasbel.*, **61**, 134, 145 (1918); *J. Soc. Chem. Ind.*, **37**, 4584 (1918).
16 *J. Gasbel.*, **55**, 1257 (1912).
17 *Am. Gas Light J.*, **81**, 605 (1904); **88**, 326 (1911).

The Testing of Petroleum Oils for Gasification[1]

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The following discussion is a summary of an investigation conducted to establish the possibility of determining the gasification capacity of petroleum oils from laboratory tests. So far as the writer knows, there is no numerical relation expressing this factor. Although the results obtained are of direct application to the Dayton process of oil-gas manufacture, it is believed that they will be of interest to others engaged in the gasification of petroleum oils.

THE Dayton process for manufacturing oil gas is dependent upon the partial internal combustion of the oil supplying the heat necessary for its cracking. Since the details of the process have already been described by Binnall,[2] only a brief statement of its operation will be given here. The oil is atomized by the required amount of air and conducted through a full-inlet pipe into a hollow steel casting shaped like a watch case, called the retort. This is situated in a heat-insulated refractory setting so that very little heat can be lost through radiation. The partial combustion of the oil takes place in this chamber and the heat generated is usually sufficient for maintaining the proper retort temperature. If the temperature of the retort is too low, the amount of oil is decreased in the inlet mixture, and vice versa. The resulting gaseous products are cooled, the tar is removed by scrubbers, and the clean gas is metered and delivered to the service line.

In this process the results are expressed as gallons of oil consumed per thousand cubic feet of gas produced at a given B. t. u. per cubic foot. This follows from the fact that it is possible by this process to manufacture gas of a constant predetermined calorific value within wide limits of rate of production. When the calorific value of the gas is not altered, the efficiency of the process remains constant irrespective of the rate of production, but varies inversely with the calorific value when this is changed.

In the following discussion, by "efficiency" is meant the percentage of the calorific value of the oil which is obtained in the gas alone (excluding that obtained as tar); by "gasification value" is meant the calorific value of the gas produced at a given efficiency—i. e., the ease with which an oil can be gasified.

If the calorific value of the gas produced were of no importance, all oils could be gasified at very high efficiencies, but for practical purposes this calorific value is limited. Consequently, the gasification values of oils become of prime importance. In order to be of practical value, the tests used to determine the gasification value should be simple and easily carried out. It was with this object in view that this investigation was made and the more interesting and important results are given herein.

It was early recognized that experimental information supplied by the specific gravity, sulfur content, iodine value, and average boiling point was not complete, although quite valuable. Therefore, efforts have been made to determine the character of the constituents of the oil and, if possible, to separate them so as to be able to forecast more accurately the suitability of an oil for gasification. In this way, the formolite value and the acid absorption, particularly sulfuric acid, have been applied.

Standard methods were applied to determine the specific gravity, iodine value, and sulfur content of an oil.[3] The average boiling point was calculated from the data obtained by distilling the oil in a 200-cc. Barrett flask and noting the percentages coming over for each 50° C. from the first drop to the highest temperature attained, and at dryness.

Formolite Value

In order to determine the influence of the aromatic constituents, the formolite value was determined on several oils. This well-known reaction, first applied by Nastjukoff,[4] consists in the condensation of the aromatic bodies with formaldehyde in the presence of sulfuric acid. The modifications that have been proposed to carry out this reaction may be divided into two divisions—viz., those which use formalin and those which use solid p-formaldehyde. The use of a neutral solvent for diluting the oil is dependent upon the cleanliness and boiling point of the sample. Before attempting to decide which of the foregoing procedures is the better, a few of the observations already made on this reaction should be briefly reviewed.

Nastjukoff has found that the best proportions for the oil, sulfuric acid, and formaldehyde are 1:1:1.5, respectively, when the formolite obtained is less than 50 per cent of the oil; if the amount obtained is greater these proportions become 1:1:2. If a smaller amount of sulfuric acid than recommended is used, the product varies in character from the usual amorphous, insoluble solid through soluble solid products to soluble liquid products.[5] This reaction should be carried out at about 0° C. to obtain the best results and highest yields.[6] Marcusson[7] dilutes the oil with "normal benzene" free from unsaturated and aromatic compounds before applying the formolite reaction of Nastjukoff.

The use of trioxymethylene instead of formalin was early proposed by Richardson[8] who also suggested that the recovered oil be used since it gives more concordant results than the precipitate. Upon investigating the Nastjukoff treatment, Tausz[9] claims that the diolefins containing conjugate double linkings also respond to this reaction, and that in order to remove the aromatic compounds completely the operation should be repeated. Before the formolite reaction can take place, at least one hydrogen atom must be attached directly to the benzene nucleus. To overcome the necessity of the double treatment, Tausz advocates the use of trioxymethylene.

In order to obtain some insight into the relative merits of these suggestions, several tests were carried out. The results in Table I may be considered as typical.

It will be noticed that the results obtained following the procedure outlined by Richardson are incomplete. This is due to the nature of the product obtained, which was very gummy, insoluble in concentrated ammonium sulfate solutions, but readily soluble in water. The second precipitation

[1] Received April 23, 1923.
[2] This Journal, **13**, 242 (1921).
[3] *Bur. Standards, Tech. Paper* **117** (1920); *Tech. Paper* **37** (1914); *Cir.* **57** (1916).
[4] *J. Russ. Phys.-Chem. Soc.*, **36**, 881 (1904).
[5] Nastjukoff, *Petroleum*, **4**, 1336 (1909).
[6] *Ibid.*, **7**, 239 (1911).
[7] *Chem. Ztg.*, **35**, 729 (1911).
[8] This Journal, **8**, 319 (1916).
[9] *J. prakt. Chem.*, **99**, 276 (1919).

TABLE I—RESULTS ON FORMOLITE REACTION
(Temperature, 5° C.)

METHOD	Oil Taken Grams	Normal Benzene Cc.	Concd. H₂SO₄ Cc.	CH₂O Cc.	1st Precipitation Ppt. Grams	Oil Grams	2nd Precipitation Ppt. Grams	Oil Grams	Total Precipitate Obtained Grams	Per cent	Oil Recovered Grams	Per cent
Nastjukoff	17.46	0	20	10^a	4.32	14.00	1.59	12.03	5.91	33.8	12.02	68.9
Marcusson	17.46	35	20	10^a	5.41	15.52	0.79	13.53	5.93	33.9	13.53	77.7
Tausz	17.46	100	40	12^b	3.40	16.82	..	12.31	3.40	19.5	12.31	70.5
Richardson	17.46	100	100	8.5^b	..	8.29	..	..	..	..	..	..

a Cc. formalin.　b Grams trioxymethylene.

of the oil recovered by the procedure of Tausz gave a similar product. These experiments were repeated several times, with always the same characteristic results, so that one is forced to conclude that the use of trioxymethylene with large amounts of sulfuric acid should be avoided. Complete precipitation by one application of the formolite reaction was attained in no case, so a double precipitation is always necessary.

As originally proposed by Nastjukoff, the volume of oil entering into the precipitate is equivalent to 0.8 of the weight of the formolite expressed as grams per 100 cc. This has been found to hold true for his procedure, but when applying the method of Marcusson to a large number of experiments this factor is not constant, but averages about 0.5. (The latter method always yields too high values for the recovered oil.)

For the oils investigated, the iodine value of the recovered oil was about 78 per cent of that of the original oil.

The results given above show that none of the suggested modifications has been an improvement upon the procedure outlined by Nastjukoff. No attempt was made to establish or confirm the actual accuracy of this treatment, since, as will be shown later, the results obtained were sufficient to indicate their value for the purpose under consideration. It has been stated, however, that the Nastjukoff treatment is not only a delicate qualitative test for aromatic compounds, but also yields quantitative results.[10]

SULFURIC ACID TREATMENT

Many treatments have been proposed for the absorption of the aromatic and unsaturated compounds in petroleum, such as with nitric acid,[11] liquid sulfur dioxide,[12] mercuric acetate,[13] bacteria,[14] dimethyl sulfate, sulfuric acid, etc. Preliminary study showed that the treatment with sulfuric acid was best adapted for this work.

The use of sulfuric acid for the quantitative removal of aromatic and unsaturated compound has been extensively applied to oils. The concentration of the acid used varies from 98 per cent for the lower boiling fractions[15] up to 20 to 30 per cent for oleum.[16]

The treatment of the oils with sulfuric acid, as applied by the writers, is carried out in 10-cc. Babcock bottles graduated into 100 divisions on the neck and centrifuging at 1000 r. p. m.

For concentrated sulfuric acid absorption, pipet 10 cc. of the oil into the bottle, add 25 cc. of concentrated acid and shake thoroughly for several minutes; let settle a short time and then add more concentrated acid to bring the top of the oil layer to the upper mark of the bottle; centrifuge for 5 minutes.

For fuming acid absorption, pipet 10 cc. of the oil into the bottle, add 5 cc. of fuming sulfuric acid (15 per cent free SO₃), and shake vigorously until all action has ceased, neglecting the temperature rise; repeat with 5 cc. more of the fuming acid and then again with 10 cc. of the fuming acid, shaking thoroughly in each case until all action has ceased and no further evolution of sulfur dioxide can be induced; let stand

a short time, and bring the top of the oil layer to the upper mark of the bottle with concentrated acid and centrifuge.

In spite of the centrifuge it is necessary to allow the bottles to stand at least over night after this operation in order to obtain uniform readings. The degree to which the results are affected on standing can be seen in Table II.

TABLE II—EFFECT OF STANDING ON THE VALUE OF THE SULFURIC ACID ABSORPTION

	A₂	B₂	C₂	D₂
Case I—Concentrated sulfuric acid				
Reading immediately after centrifuging	92.8	71.8	86.4	94.2
Reading on standing 2 days after centrifuging	90.8	70.4	85.0	92.6
Difference	−2.0	−1.4	−1.4	−1.6
Case II—Fuming sulfuric acid				
Reading immediately after centrifuging	71.2	35.2	69.4	16.6
Reading on standing 2 days after centrifuging	75.2	32.4	68.6	23.6
Difference	+5.0	−2.8	−0.8	+7.0

The necessity of allowing the tests to stand at least over night after centrifuging is especially important in the case of those treated with fuming sulfuric acid. It is impossible to obtain duplicate results otherwise. At times the fuming sulfuric acid treatment produces a pseudo-emulsion of a network of a light flocculent material. This can be easily broken up with a fine glass thread and the bottle recentrifuged before reading. The accuracy of the fuming sulfuric acid treatment is improved by first freeing the oil from asphaltic material by distillation or other means.

It is essential that the fuming sulfuric acid treatment be conducted with thorough shaking if consistent results are to be obtained. The magnitude of the difference in reading produced by thorough shaking is illustrated in Table III.

TABLE III—EFFECT OF SHAKING ON FUMING SULFURIC ACID ABSORPTION

	A₃	B₃	C₃	D₃	E₃	F₃
Reading not thoroughly shaken	76.2	49.2	68.6	23.6	79.2	75.2
Reading after thoroughly shaken	68.6	46.2	62.6	17.0	75.0	71.4
Difference	−7.6	−3.0	−6.0	−6.6	−4.2	−3.8

Since the purpose of the sulfuric acid absorption is the elimination of the aromatic and unsaturated compounds in the oil, it may be of interest to see how this takes place with varying concentration of the acid—whether the aromatic or the unsaturated compounds are destroyed the most rapidly. Some of the results obtained to determine these facts are given in Table IV.

The aromatic compounds are much less difficult to remove, requiring only 100 per cent acid for the most difficult case, whereas the unsaturated compounds need the application of fuming sulfuric acid to effect their complete removal. It should be noted that the small iodine value obtained on the fuming acid treatment is due to a small amount of sulfur dioxide, since the oil residues were not washed. The apparent increase in the formolite residue with the fuming acid treatment was due to the formation of a white precipitate, which was not formolite but probably a sulfone. It is possible that an acid containing less than 15 per cent free SO₃ can be satisfactorily used for removing the unsaturated compounds. No attempt was made to establish this point. It should be mentioned that Marcusson[17] found that it was necessary to apply fuming sulfuric acid before all the olefins could be removed.

10 Severin, *Petroleum*, **6**, 2245 (1911).
11 Marcusson, *Chem. Rev. Fett-Harz-Ind.*, **17** (1910).
12 Edeleau, *Petroleum*, **9**, 862 (1914).
13 Tausz, *Z. angew. Chem.*, **32**, 1, 233 (1919).
14 *Cent. Bakt. Parasitenk*, **2**, Abt. **49**, 477 (1919).
15 Tholle, *J. Soc. Chem. Ind.*, **38**, 49 (1919).
16 Zaloziechi and Hausmann. *Z. angew. Chem.*, **21**, 1761 (1908).

17 *Chem. Ztg.*, **37**, 550 (1913).

TABLE IV—ELIMINATION OF AROMATIC AND UNSATURATED COMPOUNDS BY SULFURIC ACID

Per cent H$_2$SO$_4$	Sample A$_4$			Sample B$_4$			Sample C$_4$		
	Iodine Value	Formolite Value	Specific Gravity	Iodine Value	Formolite Value	Specific Gravity	Iodine Value	Formolite Value	Specific Gravity
Original oil	35.9	20.5	0.842	21.2	18.9	0.834	27.8	9.0	0.875
85	...	...	...	21.2	7.6	0.834	25.1	7.2	0.875
90	27.7	9.9	0.839	19.4	4.8	0.833	22.5	0.9	0.874
95	20.7	1.2	0.830	12.2	0.4	0.822	15.1	0.9	0.867
100	6.0	0.3	0.821	5.7	0.9	0.815	8.7	0.6	0.860
15 (fuming)	0.3	0.4	0.811	0.3	3.5	0.815	1.3	3.7	0.855

TABLE V—OIL ANALYSIS AND QUALITATIVE GASIFICATION

Sample	Type of Oil	Specific Gravity	Average Boiling Point °C.	Sulfur Per cent	Iodine Value	Formolite Value	Sulfuric Acid Treatment			Qualitative Gasification
							Cond. Acid Residue Per cent	Fuming Acid Residue Per cent	Fuming Acid Residue Specific Gravity	
A$_5$	Gas	0.837	293	0.92	21.7	18.9	90.3	68.6	0.824	Excellent
B$_5$	Fuel	0.885	316	0.46	32.2	31.4	70.4	37.0	0.841	Poor
C$_5$	Fuel	0.930	376	2.80	51.1	49.2	59.6	33.4	0.845	Fair
D$_5$	Fuel	0.862	272	...	37.4	35.8	85.0	56.0	0.812	High temperatures required
E$_5$	Fuel	0.885	...	1.78	47.8	56.5	66.6	46.2	0.826	Fair
F$_5$	Diesel distillate	0.881	278	0.23	28.5	9.0	88.0	62.6	0.867	Poor
G$_5$	Gas	0.825	301	0.67	30.4	2.5	93.0	71.4	0.812	Excellent
H$_5$	Gas	0.914	325	0.35	31.4	33.3	64.6	0.0	...	Practically worthless
I$_5$	Gas	0.853	317	0.19	23.1	16.6	92.6	75.0	0.835	Good
J$_5$	Gas	0.858	293	2.11	47.6	14.5	76.0	50.8	0.810	Fair
K$_5$	Oil gas tar	0.935	248	...	57.2	46.1	33.2	17.0	0.811	Scarcely gasified

GASIFICATION VALUES OF OILS

Many efforts have been made to connect chemical analysis of a petroleum oil with its gasification value, the results of which have been excellently stated by Downing and Pohlman[18] as follows: Color, odor, refractive index, surface tension, viscosity, flash and burning points, heating value, sulfur content, and bromination value are worthless, but sulfonation and formolite values furnish an approximate valuation of the oil for gasification by indicating the amount of the paraffin, unsaturated, and aromatic constituents. Inferior oils are rich in aromatic compounds. The distillation is very important information, because high boiling oils are usually of good quality. For oils of a given boiling point their value increases with the decrease in specific gravity.

It is also stated[19] that the paraffins and naphthenes are the most important constituents in the oil for gas-making.

Table V contains results obtained on gasifying a number of oils in regular plant operation for comparison with the statements outlined above.

These results confirm the findings of Downing and Pohlman, the most important features of which are that for oils of a given boiling point they improve with the lowering of the specific gravity, for a given specific gravity they improve with the boiling point, and the gasification qualities are nearly proportional to the amount of the fuming sulfuric acid residue and inversely proportional to its specific gravity.

A distillation of the fuming sulfuric acid residue yields no apparent additional useful information for determining the gasification qualities of an oil.

From these results it can be seen that the gasification value of an oil should be expressed in a general way as

$$E = \frac{KTR}{G} \qquad (1)$$

where E is the gasification, T the average boiling point in degrees centigrade, R the fuming sulfuric acid residue, G the specific gravity of the original oil, and K a constant.

The significance of the quantity T/G as a measure of the gasification value of a petroleum product can be better perceived by taking known substances with approximately identical boiling points representing the four types of compounds occurring in gas oils, and comparing their specific gravities. These results are given in Table VI.

There is a decrease in the value of T/G in passing from the paraffin to the aromatic compounds, and it is proposed to utilize this variation as a measure of the gasification value of oils.

[18] *Am. Gas Light J.*, **105**, 318 (1916).
[19] Downing, *J. Gas Lighting*, **135**, 160 (1916).

TABLE VI—VALUES OF T/G FOR DIFFERENT TYPES OF SUBSTANCES

Type Substance	Paraffin	Olefin	Naphthene	Aromatic
Substance	Decane	Decylene	Cyclononane	Pseudo-cumol
Boiling point, °C.	173	172	171	170
Specific gravity	0.232	0.228	0.221	0.192
T/G	746	753	774	885

The total gasification value of an oil is evidently the sum of the gasification values of the separate constituents. The separation of an oil into the several classes of compounds present is extremely difficult, so it was thought that separation into the fuming sulfuric acid–insoluble compounds, the paraffins and naphthenes, and those absorbed by the fuming acid, the unsaturated and aromatic compounds, would offer a practical solution. The gasification values of these two components, the fuming sulfuric acid–insoluble and soluble, would then produce the total gasification value of the oil, and can be expressed as follows:

$$E_{70} = K_{70}\left[\left(\frac{T}{G_2}\right)^a R + \left(\frac{T(1-R)}{G_1 - RG_2}\right)^b (1-R)\right]$$

where E_{70} is gasification value as 70 per cent efficiency, T the average boiling point in degrees centigrade, G and G_2 the specific gravities of the original oil and the fuming sulfuric acid residue, respectively, R the fuming sulfuric acid residue, a and b constants, and K_{70} a constant based on the gasification value at 70 per cent efficiency—this having been found to be most suitable for the process herein described.

It is impossible to obtain gas oils of a predetermined definite composition so as to permit of a direct solution of the constants in the proposed expression, so these must be determined by trial. In order to make K_{70} a constant, the values for a and b have been found to be $3/2$ and 1, respectively. The data supporting these values are given in Table VII.

These results confirm the belief that the accuracy of the chosen values for a and b is sufficient for practical purposes, thus making the final expression for the gasification value.

$$E_{70} = 0.0124\left[\left(\frac{T}{G_2}\right)^{3/2} R + \left(\frac{T(1-R)}{G_1 - RG_2}\right)(1-R)\right]$$

Since the gasification value of that portion of the oil not attacked by fuming sulfuric acid is equal to that so attacked raised to the $3/2$ power, and also since the average value of T/G for these two constituents is about 325, the gasification value of the unattacked portion is then about eighteen times that of absorbed constituents for the same value of T/G.

On applying this expression to E_{75}, or the gasification value of 75 per cent efficiency, it is only necessary to change the constant K to 0.0109, showing that for an increase in 5 per cent in heat efficiency the calorific value of the gas decreases 12 per cent.

Table VII—Relative Gasification Values of Petroleum Oils

Sample	B. t. u. Obtained per Gallon of Oil	G_1	T	R	G_2	$\dfrac{T}{G_2}$	$\dfrac{G_1-RG_2}{1-R}$	$\dfrac{T(1-R)}{G_1-RG_2}$	E_{70} Obtained	E_{70} Calcd.	Relative Gasification Value Obtained	Relative Gasification Value Calcd.	Diff.	K_{70}
A_5[a]	95,450	0.837	293	0.696	0.824	356	0.865	339	580	599	1.00	1.00	0.00	0.0122
P_6	94,100	0.820	283	0.785	0.805	352	0.855	331	665	653	1.15	1.09	0.06	0.0126
D_5	97,510	0.862	272	0.562	0.812	335	0.925	294	430	442	0.74	0.74	0.00	0.0120
M_5	96,720	0.852	276	0.556	0.812	340	0.892	309	445	451	0.77	0.75	0.02	0.0121
N_5	97,130	0.857	283	0.614	0.814	348	0.904	313	418	510	0.72	0.85	0.13	0.0102[b]
O_5	96,920	0.855	280	0.414	0.812	345	0.885	316	360	352	0.62	0.59	0.03	0.0126
F_6	99,110	0.881	278	0.626	0.867	321	0.904	308	455	463	0.78	0.77	0.01	0.0122
L_5	99,110	0.881	273	0.418	0.860	317	0.896	304	382	316	0.66	0.53	0.13	0.0151[b]
E_5	99,960	0.885	296	0.462	0.826	358	0.939	315	410	410	0.71	0.69	0.02	0.0124
											Average......		0.063	0.0124

[a] Sample A_5 has been given a value of unity for both the obtained and calculated relative gasification values, because this oil has been chosen as a standard for the comparison of other oils.
[b] Results from very short runs and consequently E_{70} not thoroughly established.

The B. t. u. obtained per gallon of oil have been included in Table VII for comparison. Since these values are dependent upon efficiency and the calorific value of the oil alone, it is evident that they are not a measure of gasification value, which indicates the ease with which an oil can be decomposed into gaseous products.

In order to convert the calorific value of the gas produced by the Dayton process into the equivalent of oil gas produced by other processes, the foregoing calorific values should be increased 2.5 times, inasmuch as Dayton gas is approximately 60 per cent inert.

Conclusion

It is believed that four factors only—the residue from the fuming sulfuric acid treatment, the average boiling point, and the specific gravities of the original oil, and the fuming sulfuric acid residue—are necessary for the calculation of the gasification value of petroleum oils.

The four factors are combined into the relation

$$E = K \left[\left(\frac{T}{G_2} \right)^{3/2} R + \left(\frac{T(1-R)}{G_1-RG_2} \right)(1-R) \right]$$

The gasification value of that portion of the oil not attacked by fuming sulfuric acid is eighteen times as great as the part so attacked for those oils usually classed as gas oils.

Acknowledgment

The writer desires to express his great appreciation to H. G. Fischer, formerly of the General Oil Gas Corporation, under whose direction this investigation was undertaken and to whose enthusiasm its success is largely due.

Acidity of Vegetable Tan Liquors[1]

By Erwin J. Kern and J. W. Koenig

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

IN vegetable tanning it is of importance to know the total titrable acidity of the tan liquors, even though the activity of the liquors is determined by the hydrogen-ion concentration. Apparently, very few tannery laboratories are equipped to make hydrogen-ion measurements, many relying upon the Procter limewater method for determining total acidity. In an earlier paper[2] it was pointed out that solutions of quebracho extract begin to precipitate when the pH value is raised to about 7.2 by the addition of limewater. The proximity of this value to the true neutral point seemed to indicate a fair degree of accuracy for the Procter method, and it was decided to determine the extent to which this would hold true for other common tanning extracts.

Tan liquors were prepared as indicated in Table I. In one series of tests the pH value of each liquor was determined by means of the hydrogen electrode and then standard sodium hydroxide solution was added to an aliquot until the pH value was raised to exactly 7.0, giving the total concentration of titrable acidity. This value was also obtained by Procter's method, in which standard calcium hydroxide solution was added to 10 cc. of filtered tan liquor, with stirring, until a slight, permanent turbidity appeared, which was taken as the end point, the solution then being transferred immediately to the hydrogen electrode and the pH value determined. The comparative results are given in Table I.

The results obtained by Procter's method may be considered very satisfactory for oak bark, wattle bark, and quebracho. It gives no end point whatever for pure solutions of larch bark and gambier extracts. In the case of the larch, it is interesting to note that an end point is obtained where 0.10 mol

per liter of lactic acid has been added and that the result is then quite accurate. No end point could be obtained with gambier—a fact appreciated by Procter, who advised the addition of some extract which would give a precipitate with lime and allowing for the acid present in the added extract. The results for the gambier-quebracho mixture show that high results are obtained by this procedure, but that the results become more nearly correct as more acid is added.

Procter's method is admirably suited for routine control work, but should be relied upon only where it has been previously demonstrated that it will check hydrogen-ion measurements.

Table I
Gram Equivalents Acid per Liter Found by

Added Lactic Acid Mols per Liter	pH Value of Tan Liquor	Titration to pH = 7.0 with NaOH	Limewater Method	pH Value at End Point of Limewater Method
Oak bark—18.0 grams solid matter per liter				
None	4.16	0.016	0.017	7.02
0.01	3.41	0.025	0.025	7.05
0.10	2.62	0.114	0.114	7.06
Wattle bark—14.0 grams solid matter per liter				
None	4.16	0.016	0.013	6.95
0.01	3.42	0.020	0.020	7.07
0.10	2.57	0.112	0.109	7.10
Larch bark—18.0 grams solid matter per liter				
None	4.07	0.018	∞	..
0.01	3.46	0.028	∞	..
0.10	2.67	0.112	0.110	6.99
Quebracho—12.0 grams solid matter per liter				
None	4.48	0.009	0.017	7.42
0.01	3.08	0.018	0.018	7.12
0.10	2.43	0.105	0.111	7.10
Gambier—19.4 grams solid matter per liter				
None	4.92	0.004	∞	..
0.01	3.83	0.014	∞	..
0.10	2.68	0.102	∞	..
Quebracho-gambier mixture—15.6 grams solid matter per liter				
None	4.23	0.010	0.032	8.64
0.01	3.48	0.034	0.046	7.45
0.10	2.59	0.124	0.132	7.18

[1] Presented before the Division of Leather Chemistry at the 66th Meeting of the American Chemical Society, Milwaukee, Wis., September 10 to 14, 1923.
[2] Wilson and Kern, This Journal, 14, 1128 (1922).

Standard Atmospheric Conditions for Paper Testing[1]

By E. O. Reed[2]

GOVERNMENT PRINTING OFFICE, WASHINGTON, D. C.

ANY atmospheric change, whether in temperature or relative humidity, which affects the moisture content of paper, and thus the physical properties of the cellulose, sizing, or other constituents of the paper, will consequently affect the physical properties of the paper as a whole. Yet, although it is fully appreciated that these atmospheric changes, either of temperature or relative humidity, produce marked changes in paper, careful consideration has never been given to the selection of a standard condition for testing. Paper testing has been conducted for a number of years at 70° F. and 65 per cent relative humidity by the very few laboratories that have taken any steps whatever to test under uniform conditions. In fact, the T. A. P. P. I., recognizing the need of standard uniform conditions, has recommended a relative humidity of 65 per cent and temperature of 70° F.

It is doubtful if there can be found a logical reason for the selection of such a high relative humidity as 65 per cent. It must be borne in mind that in determining upon uniform standard atmospheric conditions for testing paper or any other material, a careful study should be made of the actual use and service required and under what atmospheric conditions the material must be satisfactory. In the selection of a 65 per cent relative humidity, however, this fact was undoubtedly not taken into consideration. The selection of 65 per cent relative humidity as a standard testing condition was due to the fact that it had been adopted by the German Imperial Institute for testing materials at Gross-Lichterfelde in about 1890.[3] The only explanation that can be found for their selection of this humidity is that since the average outdoor relative humidity is more than 65 per cent and the indoor humidity much lower it is easier to maintain a high relative humidity.

This surely cannot be considered a sound argument for the adoption of a standard relative humidity of 65 per cent, if we consider at all the actual indoor conditions under which paper is used. Paper or any other material should be tested under conditions where a direct comparison may be made between the tests obtained and the actual serviceability. These conditions must be set so as not to favor the material, but to place it under average conditions, or possibly even under more severe atmospheric conditions than it must be exposed to and under which it must be handled.

The average outdoor relative humidity in most localities in the United States is approximately 70 per cent. Wilson[4] states that during the winter months the normal outdoor relative humidity over the more populous portions of the United States, especially east of the Missouri and north of the Ohio River, is 72 per cent, and that the average diurnal range is from 60 to 85 per cent. He determined the indoor relative humidity in heated buildings in several widely separated parts of the country, on the coast and in the interior, and states that it varies from 24 to 33 per cent, and that during that portion of the year when artificial heat is required in the United States it is lower than that of the driest climate known.

Personal observations on indoor atmospheric conditions extending over several years, at Washington, D. C., and other points, very definitely show that the indoor relative humidity, especially in the winter months, is much lower than the outdoor relative humidity, and that, although the mean annual outdoor relative humidity at the points covered in this investigation was about 70 per cent, the mean annual indoor relative humidity was between 35 and 45 per cent.

During the greater part of the year—October through May—when artificial heat is required, the average monthly relative humidity indoors is not over 40 per cent, and during the five colder months averages less than 35 per cent. Frequently in winter the relative humidity is as low as 15 or 20 per cent, averaging approximately 30 per cent for December, January, and February. During June, July, August, and September the average indoor relative humidity is higher than 40 per cent, and may go as high as 70 or 75 per cent for a few days at a time, and sometimes, but only for very short intervals, even somewhat higher than this. The averages noted for the month of June, however, were between 44 and 49 per cent, for July between 44 and 58 per cent, for August between 49 and 60 per cent, and for September between 55 and 65 per cent. In no month did the average indoor relative humidity equal the existing average outdoor relative humidity, but averaged from 15 to 40 per cent less. The highest indoor relative humidity noted occurred in August and September. The colder the climate the lower was the average indoor relative humidity, owing to the longer requirement for artificial heat, and the warmer the climate the higher was the average relative humidity indoors.

The largest quantities of paper are used indoors, where the average living and working conditions mentioned above are maintained throughout the year. It must be assumed, therefore, that a humidity approximating 45 per cent, and not one of 65 per cent, is more in harmony with the actual conditions under which paper is used and under which it should be tested.

Giving careful consideration to these facts, the Government Printing Office has adopted a standard testing condition of 50 per cent relative humidity and a temperature of 70° to 75° F. For maintenance of these conditions a testing room designed by the chief of tests, which automatically operates day and night, was constructed about two years ago, and has continuously maintained a relative humidity of 50 per cent and a temperature of 70° to 75° F. This installation has been found entirely commercial and not unreasonable in cost.

With the maintenance of any humidity for testing, it is also necessary to control the temperature within a certain range of from 70° to 75° F., and the cooling system necessary for this control will also be sufficient to de-humidify during the few short periods of the year when this is necessary. From information obtained from engineering companies it has been found that the cost of maintaining a 50 per cent relative humidity and 70° F. temperature is the same or less than that of maintaining 65 per cent at this temperature. This is contrary to statements heretofore made in defense of 65 per cent relative humidity.

It is a well-known fact that papers in actual service do not stand up in direct proportion to laboratory test values at 65 per cent relative humidity. This is especially marked in

[1] Received December 20, 1923.
[2] Chief of Tests.
[3] Mitt. kgl. tech. Versuchungsanstalten, **7**, 2 (1889); **8**, 8 (1890).
[4] "Atmospheric Moisture and Artificial Heating," Proceedings of the Convention of Weather Bureau Officers, **1898**.

regard to folding quality, which, when considered with the other tests, is most indicative of the serviceability, durability, and quality of paper. All papers exhibit a better folding quality at 65 per cent relative humidity, very few being unsatisfactory at this unusual condition. Yet some papers that are satisfactory at 65 per cent relative humidity are brittle and even unserviceable at normal indoor conditions. It is paramount, therefore, that a testing condition be selected which will give results most indicative of the real properties of the paper when in use.

From a wide experience with paper testing, especially as to folding quality, whether obtained by a folding endurance tester or by hand, it has been very definitely found that the effect of relative humidity or of temperature is not the same on all kinds of paper, or even on papers of the same grade or manufacture. This fact has been shown by other investigations to be true also of other physical tests. Hence, no factor can be used in calculating any physical test from results at one condition to equivalents at another or a standard condition, and comparative ratings of papers at one atmospheric condition will not be the same at another condition.

In the report of the technical committee[5] appointed by the Bureau of Standards in connection with the standardization of paper, the following statement was made:

This Committee does not recommend a particular relative humidity at which paper should be tested, but it does recommend that this subject be considered and that some rather narrow limits of relative humidity be adopted, taking into consideration the average indoor relative humidity and the cost of maintaining constant humidity conditions in the testing laboratory.

As stated, the Government Printing Office Testing Section has selected 50 per cent relative humidity and 70° to 75° F. temperature as a fair testing condition, and under these conditions our papers tested have shown the very properties in service that were brought out by laboratory tests. It is recommended, therefore, that full consideration be given to the acceptance of these conditions as standard for paper testing.

[5] *Paper Trade J.*, **75**, 38 (1922).

Composition of Natural Gas Gasoline[1]

By R. P. Anderson and A. M. Erskine

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THE lower boiling constituents of crude petroleum have been carefully separated and identified by Young[2] and his co-workers, but, as far as can be learned, the exact nature of the compounds present in the gasoline from natural gas has not been determined. The purpose of the work described in this article was to study the chemical composition of natural gas gasoline by separating the constituents by fractional distillation in a sufficiently pure state to make possible their identification.

A sample of natural gas gasoline was separated by five fractionations into four portions with a boiling point range of about 20° C. each, in the neighborhood of the normal paraffin hydrocarbons pentane, hexane, heptane, and octane. Three fractionations of the pentane portion with a regulated temperature stillhead resulted in the isolation of isopentane (27.8° to 28.3° C.) and normal pentane (35.5° to 36.0° C.). From the hexane portion by a series of four fractionations with the same apparatus isohexane, 2-methylpentane (60.0° to 61.0° C.), and normal hexane (68.0° to 69.0° C.) were isolated. Isoheptane, 2-methylhexane (90.0° to 91.0° C.), and normal heptane (98.0° to 99.0° C.) were separated in a fairly pure state from the heptane portion in twelve fractionations, the last two with the regulated temperature stillhead.

The approximate quantitative composition of this gasoline is: Propane and butanes 20 per cent (by volume), isopentane 13 per cent, n-pentane 17 per cent, isohexane 9 per cent, n-hexane 15 per cent, isoheptane 8 per cent, n-heptane 12 per cent, octane 4 per cent, and absorption oil 2 per cent.

The specific gravity–boiling point relations indicated the presence of traces of benzene and toluene.

columns, followed by two fractionations with a regulated temperature stillhead.

PRELIMINARY FRACTIONATIONS—In Preliminary Fractionation I a short Hempel column of 2.2 cm. (⁷/₈ inch) internal diameter filled with perforated glass beads to a depth of 13.3 cm. (5¼ inches) was used. In the second fractionation a long Hempel column with a diameter of 1.9 cm. (³/₄ inch) and a 51 cm. (20 inch) depth of beads was used below 150° C., while above this temperature the Hempel was replaced by a Vigreux column of 1.9 cm. diameter and with indentations for 22.9 cm. (9 inches) of its length. In the other three preliminary fractionations this change of columns was made at 85° C.

A copper tube condenser of the standard type for oil distillations was used with the Hempel columns, while a glass Liebig condenser in the vertical position and cooled in the usual way was used with the Vigreux column. The copper tube condenser was cooled by cracked ice for fractions below 85° C. and by running tap water for fractions above 85° C. Ordinary glass graduates fitted to the end of the condenser by a cork were used as receivers. These were surrounded by ice when the latter was used for condensation. The distilling flasks were the round-bottom, short-necked type, of capacities adjusted to the size of the fraction being distilled. High-grade Anschütz thermometers totally immersed in the vapor were used for the measurement of all vapor (distillation) temperatures.

EXPERIMENTAL

The material used was a sample of absorption gasoline taken July 3, 1922, at the Strong gasoline plant of The Mars Company. A series of five preliminary fractionations was made, which resulted in a fairly satisfactory separation of the gasoline into four distinct portions, each with a boiling point range of about 20° C. in the regions of the normal paraffin hydrocarbons pentane, hexane, heptane, and octane. The fractions in the pentane region were then treated separately in a series of three fractionations, using a regulated temperature stillhead of high efficiency similar to that employed by Young. A similar series of four fractionations was carried out on the fractions in the hexane region, using this same type of apparatus. The fractions in the heptane range were treated in ten fractionations using ordinary distilling

The original sample, with a volume of 3000 cc. and a specific gravity of 0.6667 (15.5°/15.5° C.), was distilled and

[1] Received October 1, 1923.

[2] Young and Thomas, *J. Chem. Soc.* (*London*), **71**, 440 (1897); Young, *Ibid.*, **73**, 905 (1898); Francis and Young, *Ibid.*, **73**, 920 (1898); Fortey, *Ibid.*, **73**, 932 (1898).

the distillate collected in fractions of five degrees each, this constituting the first fractionation. In the succeeding systematic fractionations each fraction was added in turn to the flask and distilled, cuts being made at previously determined points up to the final temperature which that fraction had in the preceding fractionation. The residue was left in the flask and the next fraction from the preceding fractionation was added to it. Distillation was begun again and cuts were made at all the temperatures where distillates came over, this procedure being continued up to the original final temperature of the fraction. All cuts in the same range were added to the same bottle, the total volume going to make up that of the fraction of that range.[3]

Beginning in Preliminary Fractionation II, the standard procedure was adopted of measuring the total volume of each fraction immediately before its next distillation and using this volume as the final figure for the data of the fractionation in which it was collected. This resulted in the inclusion of losses incident to handling and standing between fractionations in the fractionation in which the fractions were collected.

On all fractions that were large enough, Baumé gravity determinations were made immediately after the final volume measurement. These readings were converted to specific gravity at the observed temperature, which, multiplied by the volume, gave the weight, Δw, of each fraction. In the cases of fractions too small for gravity determinations, values which seemed reasonable for this purpose were assumed.

With the exception of Preliminary Fractionations I and II, cuts were made at such observed temperatures that the corrected "final temperature at 760 mm." would have the desired value. The values of the latter as given in the tables are therefore corrected for barometric pressure but not for thermometric errors.

PENTANE FRACTIONATIONS—In the pentane fractionations a long Hempel column of 2.2 cm. ($^{7}/_{8}$ inch) internal diameter and filled with glass beads to a depth of 54.6 cm. ($21^{1}/_{2}$ inches) was used. Between the side tube of the Hempel, which was of larger bore than usual and bent upwards, and the inlet of the condenser a regulated temperature stillhead similar in design to that used by Young[4] and by Washburn[5] was used. It consisted of a coil of 0.63 cm. ($^{1}/_{4}$ inch) copper tubing, approximately 13 cm. (5 inches) in diameter and with a total length of tube of about 118 cm. (47 inches), fitted in a cubical galvanized iron tank, 25.4 cm. (10 inches) on a side, containing water. The coil was arranged so that refluxing could take place in it readily, and the lower end was inserted in the side tube of the Hempel column by means of a cork. The upper part ended in a copper cup surrounded by asbestos cement, into which was fitted a cork carrying a glass tube with a side arm, the latter being connected with the copper tube condenser. Cracked ice was used to cool the condenser and the receivers. An Anschütz thermometer for reading the temperature of the vapor leaving the stillhead was inserted in the top of the glass tube. There was a thermometer at the top of the Hempel column, and another was placed in the constant temperature bath. The bath was heated by a Bunsen burner, which was controlled by a gas thermoregulator of the Ostwald type, consisting of a 500-cc. air bulb inside the copper coil communicating with the usual type of mercury U-tube gas-controlling device. Agitation of the bath was obtained by a stream of air. It was possible with this regulator to keep the temperature of the bath constant within 0.1° to 0.2° C.

The starting material for these fractionations consisted of Fractions 1 to 5 up to 40° C. (corrected) from Pre-

liminary Fractionation V. Each of these was distilled in turn following the same general fractionating procedure as described above. A vigorous boiling was maintained in the flask and the stillhead bath was set at the desired temperature. The distillate from the stillhead was collected until it had practically ceased coming over at that setting, when the next higher setting was made and a new fraction collected. It was found that when vapor was passing steadily out of the stillhead its temperature was within 0.1° C. of that of the bath. Consequently, the procedure was adopted of setting the thermoregulator to maintain the desired temperature in the bath and using this temperature as the "final temperature" of the fraction. The volume and gravity determinations were made as in the preliminary fractionations.

HEXANE FRACTIONATIONS—The four fractionations on the hexanes were made with the same stillhead and apparatus arrangement, a mineral seal oil with an initial boiling point of about 250° C. being substituted for the water as heating medium.

Fractions 9 to 12, inclusive, of Preliminary Fractionation V, covering the range from 55° to 75° C. (corrected), were taken for the separation of any isomers in this region. The distillations and collection of fractions were carried out in the same manner as in the case of the pentane fractionations. The volume and gravity determinations were made in the usual way in Fractionations I to III, but in IV an interval of three months elapsed from the final distillation until these measurements were made.

HEPTANE FRACTIONATIONS—In the Heptane Fractionations I to III the Vigreux column mentioned above was used, while in Fractionations IV to X the long Hempel column was employed. A glass condenser cooled by water was used and the receivers were not cooled. A regulated temperature stillhead of the same design and dimensions as described above was used for Fractionations XI to XII. The preliminary fractionating column was of the Hempel type made of Pyrex glass, inside diameter of main tube 2.54 cm. (1 inch) and of side arm 1.59 cm. ($^{5}/_{8}$ inch), and was wrapped with a double layer of heavy asbestos cord. It was filled with Raschig rings about 0.63 cm. ($^{1}/_{4}$ inch) long to a depth of 55.9 cm. (22 inches). Mineral seal oil was used in the bath and temperature regulation was maintained to within 0.1° to 0.2° C. by a gas thermoregulator. A secondary burner was necessary because of the high temperature used. Agitation was obtained by the use of a glass propeller driven by a water turbine, and an ordinary glass condenser was used for the final condensation. Anschütz thermometers were used in both the Hempel column and the stillhead outlet, and an accurate 105° C. thermometer was used in the oil bath. All thermometers were carefully compared with each other.

The starting material for this part of the work consisted of Fractions 15 to 18 from Preliminary Fractionation V covering the range from 85° to 105° C. The first ten fractionations using simple distilling columns were carried out by the same system as in the preliminary fractionations. Fractionations XI and XII with the regulated temperature stillhead followed the same general procedure as in the case of the pentane and hexane work with this apparatus. Instead of the weights of the fractions being determined from the volumes and specific gravities, however, they were obtained immediately after each fractionation by direct weighing in glass-stoppered weighing bottles. After collection in the receiving graduate each portion was poured into the weighing bottle and reserved until the entire fraction was obtained.

RESULTS AND CONCLUSIONS

PRELIMINARY FRACTIONATIONS—Table I gives the results obtained in a typical preliminary fractionation. The values listed under "Specific Gravity 15.5°/15.5° C." were obtained

[3] For further details on this method of systematic fraction see Young, "Distillation Principles and Processes," 1922, p. 98.
[4] Young and Thomas, loc. cit.
[5] Bur. Standards, Tech. Paper 140.

by converting the observed Baumé gravities to values at 60° F. and changing the latter to specific gravity by means of the tables in *Circular* 57 of the Bureau of Standards. The ratio $\Delta w/\Delta t$ served as a useful indication of the course of a fractionation—the higher its value the purer the fraction, and vice versa. The percentage weight of the fractions was based upon the weight of the original sample (2000 grams).
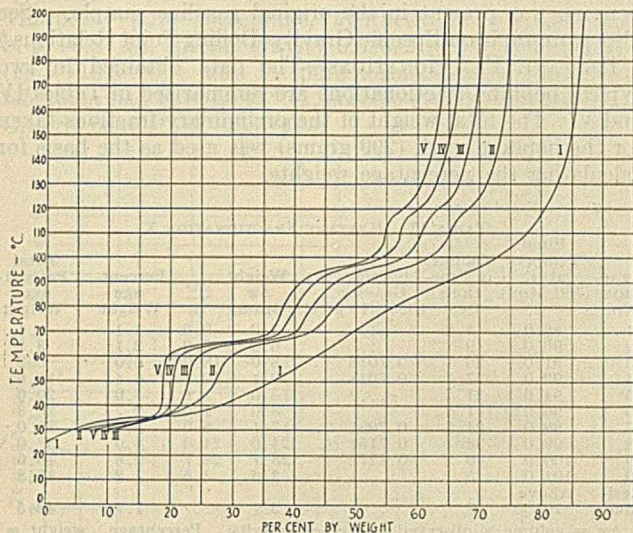

FIG. 1—PRELIMINARY FRACTIONATIONS

TABLE I—PRELIMINARY FRACTIONATION V

FRAC-TION No.	Final Temperature (760 Mm.) °C.	Volumes of Fractions Cc.	Specific Gravity 15.5°/15.5° C.	Weight Δw Grams	$\dfrac{\Delta w}{\Delta t}$	Percentage Weight	Total Percentage Weight
1+2	30	243	0.6111	152.1	..	7.6	7.6
3	35	267	0.6292	171.7	34.3	8.6	16.2
4	36	40	0.6326	25.8	25.8	1.3	17.5
5	40	35	0.6355	22.7	5.7	1.1	18.6
6	45	4	...	2.6	0.5	0.1	18.7
7	50	4	...	2.6	0.5	0.1	18.8
8	55	3	...	1.9	0.4	0.1	18.9
9	60	22.5	...	14.7	2.9	0.7	19.6
10	65	201	0.6657	132.7	26.5	6.6	26.2
11	70	297	0.6753	199.0	39.8	10.0	36.2
12	75	32.5	0.6962	22.4	4.5	1.1	37.3
13	80	24.5	0.7136	17.3	3.5	0.9	38.2
14	85	30.5	0.7161	21.6	4.3	1.1	39.3
15	90	48.5	0.7117	34.2	6.8	1.7	41.0
16	95	120	0.7081	84.1	16.8	4.2	45.2
17	100	196	0.7187	139.7	27.9	7.0	52.2
18	105	56	0.7380	41.0	8.2	2.1	54.3
19	115	30	0.7392	22.0	2.2	1.1	55.4
20	125	114	0.7292	82.4	8.2	4.1	59.5
21	135	43.5	0.7415	32.0	3.2	1.6	61.1
22	155	55.5	0.7551	41.6	2.1	2.1	63.2
23	170	20	...	15.2	1.0	0.8	64.0
24	200	14	...	10.8	0.4	0.5	64.5
Residue	Above 200	3	...	2.5	..	0.1	64.6

Δw = volume $\times$ observed specific gravity. Percentage weight = $\Delta w/2000 \times 100$.

The curves in Fig. 1 were drawn by plotting the total percentage weight of each fraction against its final temperature. In the preliminary fractionations no determination of the initial temperature could be made, since the first vapor that distilled over unquestionably had a boiling point below room temperature. The first point on each curve is therefore the final temperature of the first fraction. The five curves show an increasing tendency to flatten out in the four regions corresponding roughly to the normal paraffin hydrocarbons from pentane to octane. The curve of Fractionation V in comparison with IV showed that the limit of separation had about been reached using 5-degree cuts and that further separation would require shorter temperature intervals and more efficient fractionating apparatus. This led to the fractionating of the first three ranges separately, the amount of material in the octane region not being sufficient for similar treatment.

PENTANE FRACTIONATIONS—Table II gives a summary of the data obtained in the last pentane fractionation. The percentage weight in these fractionations was based upon the total weight of the fractions taken at the beginning of the pentane work (372 grams), and the curves in Fig. 2 were plotted on this basis. The initial temperature in Fractionation I could not be determined, but in II and III the lower part of the curve was obtained by making cuts at several points below room temperature by the use of ice water in the constant temperature bath.

TABLE II—PENTANE FRACTIONATION III

FRAC-TION No.	Final Temperature (760 Mm.) °C.	Volumes of Fractions Cc.	Specific Gravity 15.5°/15.5° C.	Weight Δw Grams	$\dfrac{\Delta w}{\Delta t}$	Percentage Weight	Total Percentage Weight
1	3.0	0a	...	0	0	0	0
2	26.0b	4	...	2.5	0.1	0.7	0.7
3	27.8	6	...	3.8	2.1	1.0	1.7
4	28.3	66	0.6247	42.2	84.4	11.3	13.0
5	28.8	26	0.6258	16.6	33.2	4.5	17.5
6	30.0	16	...	10.2	8.5	2.7	20.2
7	31.0	10	...	6.4	6.4	1.7	21.9
8	32.0	5	...	3.2	3.2	0.9	22.8
9	34.0	11	...	7.1	3.6	1.9	24.7
10	35.0	11.5	...	7.4	7.4	2.0	26.7
11	35.5	10	...	6.5	13.0	1.8	28.5
12	36.0	116	0.6309	74.8	149.6	20.1	48.6
13	37.0	8	...	5.2	5.2	1.4	50.0
..	38.0	0	...	0	...	0	50.0
Residue	Above 38.0	11	...	7.1	...	1.9	51.9

a 2 cc. were collected at this temperature but escaped through cork in bottle before final measurement.

b Constant temperature bath set at 10°, 20°, and 24° C., but no distillate obtained.

Δw = volume $\times$ observed specific gravity. Percentage weight = $\Delta w/372 \times 100$.
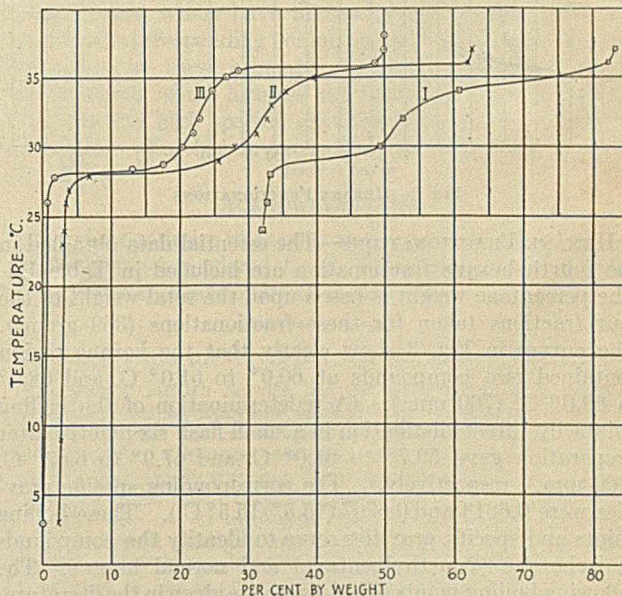

FIG. 2—PENTANE FRACTIONATIONS

The regulated temperature stillhead gave a rapid separation of the pentane fractions into two compounds, isopentane (2-methylbutane) and normal pentane, shown by the flat portions of the curves (Fig. 2), with boiling points of 27.8° to 28.3° C. and 35.5° to 36.0° C. (760 mm.), respectively. The most carefully determined values by Young[4,6] for the boiling points of these compounds are 27.95° and 36.3° C., respectively, at 760 mm. The specific gravity of the isopentane was redetermined with two different hydrometers at ice temperature and room temperature, with the following results: 0.6246, 0.6248, and 0.6251, average 0.6248 (15.5°/15.5° C.). Young's values[7] for the specific gravity are 0.63930 (0° C.), 0.63927 (0°/4° C.), and 0.62514 (14.4° C.),

6 *J. Chem. Soc.* (London), **71**, 446 (1897).

7 See also *Trans. Roy. Soc. Dublin*, **12**, 374 (1910).

which, recalculated[8] to the same basis, are 0.62482, 0.62478, and 0.62462 (15.5°/15.5° C.), respectively, average 0.62474 (15.5°/15.5° C.). Timmermans[9] gives 0.63939 to 0.63945 (0°/4° C.), or 0.62490 to 0.62497 (15.5°/15.5° C.), for isopentane. Three similar redeterminations of the specific gravity of the normal pentane fraction gave 0.6304, 0.6307, and 0.6315, average 0.6309 (15.5°/15.5° C.). Young gives the values 0.6454 (0°/4° C.) and 0.6331 (12.9° C.), which are equal to 0.63107 and 0.63115 (15.5°/15.5° C.).

TABLE III—HEXANE FRACTIONATION IV

Fraction No.	Final Temperature (760 Mm.) °C.	Volumes of Fractions Cc.	Specific Gravity 15.5°/15.5° C.	Weight Δw Grams	$\frac{\Delta w}{\Delta t}$	Percentage Weight	Total Percentage Weight
1	60.0	21.5	...	14.1	2.8	3.9	3.9
2	61.0	37.5	0.6613	24.6	24.6	6.7	10.6
3	62.0	18	...	11.8	11.8	3.2	13.8
4	63	5	...	3.3	3.3	1.0	14.8
5	64.0	0[a]	...				
6	65.0	3.5	...	2.3	2.3	0.6	15.4
7	66.0	1.5	...	1.0	1.0	0.3	15.7
8	67.0	10.5	...	7.0	7.0	1.9	17.6
9	68.0	13	...	8.7	8.7	2.4	20.0
10	69.0	83	0.6767	55.6	55.6	15.1	35.1
11	70.0	10	...	6.7	6.7	1.8	36.9
Residue	Above 70.0	7.5	...	5.1	..	1.4	38.3

[a] 3 cc. were collected at 63° to 64° C. but were lost by evaporation before final measurement.
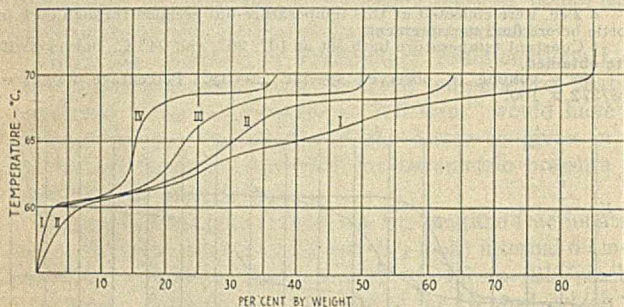Δw = volume × observed specific gravity. Percentage weight = $\Delta w/369 \times 100$.

FIG. 3—HEXANE FRACTIONATIONS

HEXANE FRACTIONATIONS—The essential data obtained in the fourth hexane fractionation are included in Table III. The percentage weight is based upon the total weight of the four fractions taken for these fractionations (369 grams). The curves in Fig. 3 show clearly that the hexane region contained two compounds at 60.0° to 61.0° C. and 68.0° to 69.0° C. (760 mm.). (A redetermination of the boiling points by direct distillation in a small flask six months after preparation gave 59.7° to 61.0° C. and 67.9° to 69.2° C. (760 mm.), respectively.) The corresponding specific gravities were 0.6613 and 0.6767 (15.5°/15.5° C.). These boiling points and specific gravities serve to identify the compounds as isohexane (2-methylpentane) and normal hexane. The following boiling points of isohexane are given in the literature: 60.55° to 60.75° C., from petroleum;[10] 60.5° to 61.0° C., prepared synthetically;[11] and 60.15° to 60.20° C., prepared synthetically.[12] The corresponding specific gravities obtained by these authors are 0.6728 (0°/4° C.); 0.6583 (17°/4° C.); and 0.6580 (15°/15° C.), 0.6712 (0°/4° C.). These are equivalent to 0.6593, 0.6603, and 0.6582, 0.6576; average 0.6589 (15.5°/15.5° C.). The exact boiling point of hexane as determined by Young[10] is 68.95° C. (760 mm.) and its specific gravity is 0.6770 (0°/4° C.),[13] or 0.6635 (15.5°/15.5° C.).

[8] In these recalculations the specific gravities at $t/4°$ C. were converted to those at $t/15.5°$ C., and then to specific gravities at 15.5°/15.5° C. by the equation in Bur. Standards, Tech. Paper 77, 18.
[9] Bull. Roy. Soc. Belg., 24, 244 (1910); C. A., 4, 2896 (1910).
[10] Young, J. Chem. Soc. (London), 73, 905 (1898).
[11] Zelinsky, Ber., 40, 4743 (1907).
[12] Risseghem, Bull. soc. chim. Belg., 30, 8 (1921).
[13] J. Chem. Soc. (London), 73, 930 (1898); 83, 56 (1893).

In Fractionation I a pronounced maximum in the $\Delta w/\Delta t$ value was obtained at 64° to 65° C. (corrected) and the two fractions from 64° to 66° C. had the odor of benzene, C_6H_6. The maximum disappeared, however, in the second and third fractionations. According to Young's work on the composition of crude petroleum, benzene, if present, should distil over with the hexanes in a constant boiling mixture at 65° to 68° C. This would seem to indicate that a small amount of benzene was present in the original gasoline sample. (See also paragraph on Specific Gravity–Boiling Point Relations.)

HEPTANE FRACTIONATIONS—The data obtained in two typical heptane fractionations are summarized in Tables IV and V. The total weight of the preliminary fractions taken for the heptane work (299 grams) was used as the basis for calculating the percentage weights.

TABLE IV—HEPTANE FRACTIONATION X

Fraction No.	Final Temperature (760 Mm.) °C.	Volumes of Fractions Cc.	Specific Gravity 15.5°/15.5° C.	Weight Δw Grams	$\frac{\Delta w}{\Delta t}$	Percentage Weight	Total Percentage Weight
1	88.0	4.5	...	3.2	0.6	1.1	1.1
2	90.0	9	...	6.3	3.2	2.1	3.2
3	91.0	26	0.7018	18.0	18.0	6.0	9.2
4	92.0	27.5	0.7018	19.1	19.1	6.4	15.6
5	94.0	21.5	...	15.0	7.5	5.0	20.6
6	96.0	11.5	...	8.0	4.0	2.7	23.3
7	98.0	24.5	0.7081	17.1	8.6	5.7	29.0
8	99.0	34	0.7154	24.0	24.0	8.0	37.0
9	100.0	40	0.7273	28.7	28.7	9.6	46.6
10	101.0	5	...	3.6	3.6	1.2	47.8
Residue	Above 101.0	7	...	5.1	..	1.7	49.5

Δw = volume × observed specific gravity. Percentage weight = $\Delta w/299 \times 100$.

TABLE V—HEPTANE FRACTIONATION XII

Fraction No.	Final Temperature (760 Mm.) °C.	Specific Gravity 15.5°/15.5° C.	Weight Δwa Grams	$\frac{\Delta w}{\Delta t}$	Percentage Weight	Total Percentage Weight
1	88.0	...	8.12	1.62	2.7	2.7
2	90.0	...	3.25	1.63	1.1	3.8
3	91.0	0.6997	20.11	20.11	6.7	10.5
4	92.0	...	6.91	6.91	2.3	12.8
5	94.0	...	5.92	2.96	2.0	14.8
6	96.0	...	7.32	3.66	2.5	17.3
7	98.0	...	6.92	3.46	2.3	19.6
8	99.0	0.7117	26.54	26.54	8.9	28.5
9	100.0	0.7280	16.46	16.46	5.5	34.0
10	101.0	...	5.62	5.62	1.9	35.9
Residue	Above 101.0	...	8.96	..	3.0	38.9

[a] Determined by weighing. Percentage weight = $\Delta w/299 = 100$.
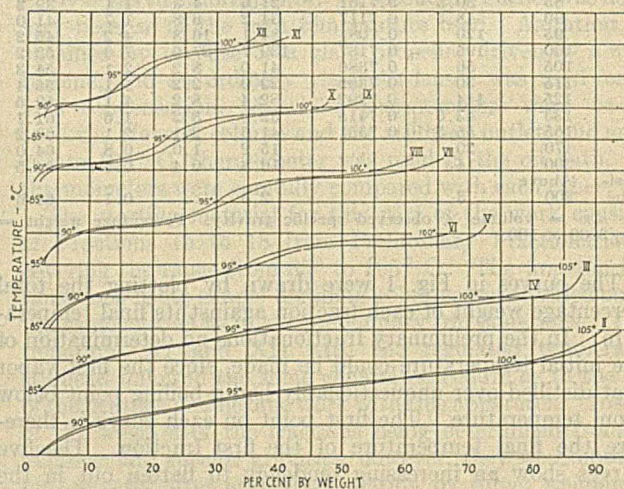

FIG. 4—HEPTANE FRACTIONATIONS

As shown by the curves in Fig. 4, the fractions at 90.0° to 91.0° C. and 98.0° to 99.0° C. (760 mm.) indicate the presence of two hydrocarbons with boiling points in these ranges. (Redetermination of the boiling point ranges by distillation in a small flask gave 90.4° to 91.8° C. and 98.2° to 99.3° C. (760 mm.), respectively.) The specific gravities obtained, 0.6997 and 0.7117 (15.5°/15.5° C.), respectively, and the boil-

ing points indicate that the compounds are isoheptane (2-methylhexane) and normal heptane. The most accurate values of the constants of these compounds as isolated from petroleum by Young[14] were isoheptane, b. p. 89.9° to 90.4° C., specific gravity 0.7067 (0°/4° C.) or 0.6936 (15.5°/15.5° C.), (this value of the specific gravity was considered slightly high by Young); normal heptane, b. p. 98.25° to 98.45° C., specific gravity 0.70186 (0°/4° C.) or 0.6888 (15.5°/15.5° C.). Thorpe's[15] pure isoheptane, synthetically prepared, had b. p. 90.3° C., specific gravity 0.69692 (0°/4° C.) or 0.6838 (15.5°/15.5° C.); and his pure normal heptane from *Pinus sabiniana* had b. p. 98.43° C., specific gravity 0.70048 (0°/4° C.) or 0.6867 (15.5°/15.5° C.).
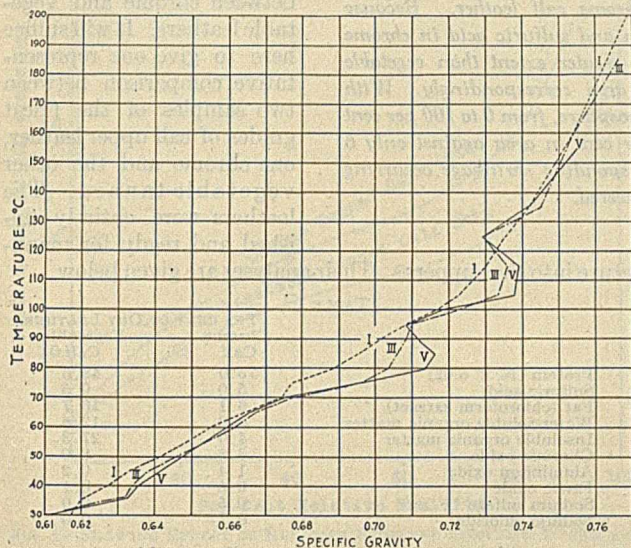
FIG. 5—PRELIMINARY FRACTIONATIONS

Young was unable to separate the two heptanes in a very pure state by fractional distillation alone and found it necessary to resort to fractional distillation of the bromo derivatives under reduced pressure, followed by reduction. He concluded, however, that there was little evidence of the presence of other isomeric heptanes in petroleum, and it seems reasonable to suppose that this would also hold for natural gas gasoline.

Since the volumes of the fractions became too small for successful handling, the heptane fractionations were not continued further. In view of the difficulty of separating the heptanes it was considered that the separation and purities obtained were as satisfactory as could be expected under the conditions.

QUANTITATIVE COMPOSITION—An estimate of the quantitative composition of this sample of gasoline may be made from the fractionation data. The measurement of the volumes of the fractions immediately after collection and again before the next fractionation gave figures on the volume losses which could be classified into two kinds—evaporation losses during handling and while standing in the bottles between fractionations, and distillation losses due to the presence of liquid boiling at or near ice temperature. This careful record of losses showed that an excessive distillation loss occurred in the preliminary and pentane fractionations, amounting in the former to 1.8 and in the latter to 3.1 times the handling and shrinkage loss, and this could be ascribed only to the escape of propane and butanes. Calculations from these losses showed that the total propane and butane content constituted approximately 20 per cent by volume of the original sample. Assuming gasoline to be an "ideal solution," theoretical calculations based on the law of mixtures for such

[14] J. Chem. Soc. (London), **73**, 905, 920 (1898).
[15] Ibid., **37**, 73, 76 (1880).

a solution showed also that the maximum butane content at 20° C. of a gasoline with an assumed composition with respect to the hydrocarbons pentane to octane (45, 35, 15, and 5 per cent by weight, respectively) could be as high as 26.6 per cent by volume.

The amount of the two pentanes was estimated from the pentane curves and the fact that the propane, butanes, and pentanes together constituted approximately 50 per cent by volume of the mixture. The octane and absorption oil (residues) were estimated from the preliminary curves and the fractionation data, respectively. The figures for the hexanes and heptanes were determined by difference, the relative amounts of the two being obtained from the curve for Preliminary Fractionation V. The relative proportions of the isomers in the cases of pentane, hexane, and heptane were determined from the corresponding curves. These estimates gave the following results as to the probable composition of this sample of gasoline in terms of percentage by volume: propane and butanes 20 per cent, isopentane 13 per cent, n-pentane 17 per cent, isohexane 9 per cent, n-hexane 15 per cent, isoheptane 8 per cent, n-heptane 12 per cent, octane 4 per cent, and absorption oil 2 per cent.

SPECIFIC GRAVITY–BOILING POINT RELATIONS—When plotted against the corresponding boiling points in the preliminary fractionations, as shown in Fig. 5, the specific gravities give an indication of the probable presence in small amounts of the hydrocarbons, benzene and toluene. The sudden increase in the specific gravities of the fractions in the ranges 75° to 95° C. and 100° to 120° C. points to the presence of these aromatic hydrocarbons, which have higher specific gravities than the paraffins of corresponding boiling points. It is quite possible that traces of these aromatic derivatives remained in the final fractions of the hexanes and heptanes, which would account for the high specific gravities obtained for these hydrocarbons. Further investigation on this point is being carried out.

Cyanogen Chloride–Hydrocyanic Acid Gas Fumigation

The Public Health Service has for some years been seeking a substitute for hydrocyanic acid gas for fumigating purposes, and about a year ago called upon the Chemical Warfare Service for assistance. Chloracetophenone was first tried, and was found to give ample warning, but was so persistent as to cause annoyance, and, when used on ships, delay in returning them to duty. The use of cyanogen chloride, also a tear gas, with the hydrocyanic acid gas was then suggested. Cyanogen chloride, although it is a poisonous gas, produces lachrymation when the amount of gas is one-eighth of that which is dangerous to human beings. It is nonpersistent, but the lachrymatory effect continues sufficiently long after the concentration has ceased to be dangerous, so that fumigation with a mixture of these two gases can be accomplished with little danger to the personnel. A process for producing the mixture of hydrocyanic acid gas and cyanogen chloride on shipboard has been perfected, and this method of fumigation has been adopted by the Public Health Service.

There have been many casualties in the past where hydrocyanic acid gas was used alone for fumigation. In one case in San Francisco where the trained men of the Public Health Service were fumigating a ship, a large number of them were overcome by the hydrocyanic acid gas and five died. Such accidents are practically impossible by the new method, which is also applicable to buildings such as barracks, storehouses, kitchens, etc., where rats, mice, cockroaches, flies, or any other kind of vermin, rodents, or insects are a nuisance or a menace.

Amendment No. 6 to the U. S. Quarantine Regulations, Public Health Service, gives a description of the method for generating the gas and for its use in fumigation. A copy of this amendment may be obtained upon application to the Public Health Service, Washington, D. C.

Chemistry and Comfort[1]

Relation between the Chemical Composition of Leather and the Comfort of Shoes Made Therefrom

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Shoes made from vegetable-tanned calf leather hold their shape better and are very much more comfortable to wear than shoes of the same size and shape made from chrome calf leather. Because of the much higher contents of protein and sulfuric acid in chrome leather, it absorbs water to a much greater extent than vegetable leather, increasing in volume and area correspondingly. With increasing relative humidity of the atmosphere, from 0 to 100 per cent chrome leather increases about 18 per cent in area against only 6 per cent for vegetable leather, a corresponding shrinkage occurring when the relative humidity is again lowered.

THIS is the first of a series of investigations being made to determine how the comfort of shoes is affected by differences in chemical composition of the leather used in making them. The work described herein is limited to a comparison of vegetable-tanned leather with chrome leather. It seemed logical to start with such a comparison, not only because nearly all leather is made either by chrome or vegetable tanning, but also because there is a much greater difference between vegetable and chrome leathers generally than is found between different samples of either kind to be found on the market.

The comfort of a shoe depends very largely upon how well it fits the foot. In comparing the comfort of vegetable and chrome leathers it is therefore necessary that the shoes be made exactly the same size and shape. It has been the writers' experience, when this is done, that the shoes made from vegetable-tanned leather are invariably much more comfortable to wear and also hold their shape much better. The difference in comfort is very marked when taking long walks or when remaining long in a warm, dry atmosphere.

In all similar tests by others of which the writers are aware, the results have invariably favored vegetable leather as against chrome. Greeves[2] quotes an officer of long experience in the late war, and one who knew a great deal about leather, to the effect that chrome shoes were most uncomfortable to sleep in, many soldiers risking trench feet and frostbite rather than lying down in chrome shoes. Sportsmen who have made the test say that at the end of a day's tramping for shooting the feet ache less in vegetable than in chrome-tanned leathers. It is also reported that there was always a rush on the part of soldiers who knew the difference in comfort to get vegetable-tanned shoes.

The preliminary work of this investigation indicated pretty clearly that the discomfort experienced in wearing chrome shoes was due mainly to their marked tendency to change in size with changing relative humidity of the atmosphere, which, in turn, is a function of the tendency of the leather to take on or give up water to the atmosphere, a property possessed by most materials to a greater or less degree. Therefore, experiments were made to determine the extent to which each kind of leather takes up water and increases in area with changing relative humidity of the atmosphere.

Leather Samples Examined

Several samples of each kind of leather were used in making the tests. In one experiment a fresh calfskin was cut into halves along the line of backbone and one-half was chrome-tanned and the other vegetable-tanned. In all experiments,

however, essentially the same difference was found between chrome and vegetable leathers. It will suffice here to give one representative comparison between two samples of the finest grades of calf upper leather, one chrome and the other vegetable-tanned. The leathers were entirely finished and ready for manufacture into shoe uppers. Their analyses are given below.

Table I

	Per cent of Dry Leather	
	Chrome Calf	Vegetable Calf
Protein (N × 5.62)	75.0	48.6
Sulfuric acid	5.0	0.5
Fat (chloroform extract)	6.1	10.7
Water-soluble organic matter	0.0	12.6
Insoluble organic matter	4.0	27.3
Chromic oxide	6.8	0.0
Aluminium oxide	1.4	0.2
Ferric oxide	0.5	0.1
Sodium sulfate	0.5	0.0
Sodium chloride	0.7	0.0

The insoluble organic matter is usually considered as combined tannin, but really includes dyestuffs and other organic matters. The sulfuric acid is not free, but is combined with the protein matter; when the leather is brought into contact with water, the protein-acid compound hydrolyzes, giving up a small amount of acid to the water.

Procedure

The advantages of sulfuric acid solutions for humidity control have been described by R. E. Wilson,[3] whose compilations were used in making up solutions to give definite relative humidities. Airtight desiccators proved to be very convenient receptacles for the work. Atmospheres of 100 per cent relative humidity were created by covering the bottoms of the desiccators with water, 0 per cent by using pure sulfuric acid, and intermediate degrees of relative humidity by using sulfuric acid of various concentrations taken according to Wilson's tables.

Strips of leather were cut 50.8 cm. (20 inches) long and 15 mm. (0.6 inch) in width, the length running parallel to the line of the backbone but several centimeters away from it. The cutting was done so as to make all strips from one skin practically identical in composition. The strips were carefully weighed and their areas determined accurately by means of instruments. Each strip was then coiled loosely and suspended above the acid solution in the desiccator upon a cross of copper wire. Each day the strips were removed from the desiccators for a fraction of a minute to permit making measurements of area and weight. After 32 days the strips were put into the oven at 100° C. and left until their weights were constant, thus giving the dry weight of each strip. This and the weight of the strip from the desiccator made it possible to calculate the water content of the leather at any time during the experiment.

[2] *Leather World*, **15**, 1077 (1923).

[3] This Journal, **13**, 326 (1921).

RESULTS

The water contents of the leathers after 32 days' contact with atmospheres of constant relative humidity are shown in Fig. 1. At zero relative humidity both leathers still contained
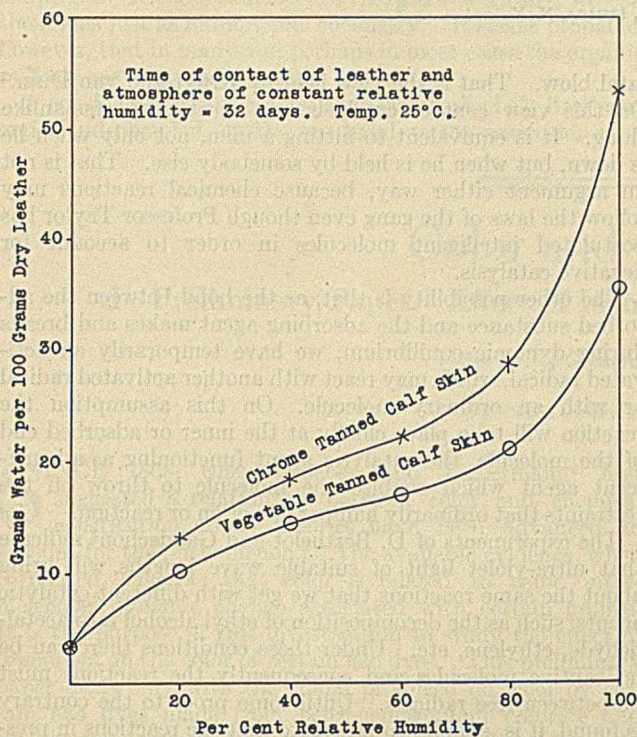
in volume by absorption of water, a property which can be greatly increased by combining strong mineral acid with the protein. It is probably because of its much greater contents of protein and sulfuric acid that chrome leather shows so much greater power of water absorption than vegetable leather.
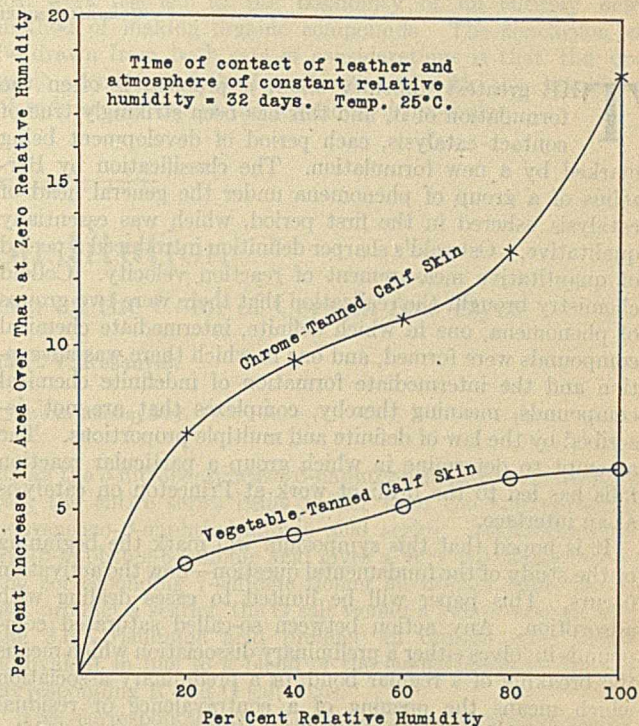

FIG. 1—SHOWING EFFECT OF RELATIVE HUMIDITY UPON THE WATER CONTENT OF CHROME AND VEGETABLE-TANNED LEATHERS

FIG. 2—SHOWING HOW THE AREA OF CHROME AND VEGETABLE-TANNED LEATHERS CHANGES WITH RELATIVE HUMIDITY OF THE ATMOSPHERE

3.5 parts of water per 100 of dry leather; in the case of the chrome leather this increased with relative humidity up to 53.2, against only 35.4 for the vegetable leather. Apparently, the systems had not reached absolute equilibrium, but the daily changes had become almost immeasurably small.

Fig. 2 shows the effect of water absorption upon the areas of the strips. The area at zero relative humidity was taken as unity and the percentage increase due to water absorption calculated from this. The curve for chrome leather is of the same general shape as that for water absorption, with a point of inflection at about 50 per cent relative humidity, but that for the vegetable leather has two points of inflection. This might have been attributed to experimental error were it not for the fact that it occurred also with the other vegetable leathers examined. The magnitude of the changes in area is really startling. The increase of 6.2 per cent in the case of the vegetable leather is large, but the increase of 18.2 per cent for the chrome leather is sensational.

The processes were found to be entirely reversible and the rate of approach towards equilibrium similar for the two kinds of leather. When the dry leather is put into a desiccator at 100 per cent relative humidity, in the first day it takes up 50 per cent and in 2 days 60 per cent as much water as it will take up in a total time of 1 month, the same being true for either chrome or vegetable leather. Leathers kept over water for a month and then placed over pure sulfuric acid gave up 70 per cent of their water the first day and 85 per cent by the end of the second day. The changes in area corresponded to the changes in water content.

DISCUSSION

Collagen, the leather-forming protein of skin and the parent substance of gelatin, is noted for its power to increase

It is estimated that a total change in area of shoe leather of about 4 per cent, or rather plus or minus 2 per cent from the normal value, is about all the average foot can stand without some discomfort. Both leathers show changes exceeding this, but the wonder regarding chrome leather is that the discomfort is not even greater than that actually found. Probably the pinching effect of chrome leather upon shrinking, in actual wear, is lessened by the ease with which the leather stretches and becomes distorted, which explains the greater tendency of chrome shoes to lose their shape.

The problem of making chrome leather more comfortable is not simply one of neutralizing the sulfuric acid. This acid appears to be necessary to give the leather certain desirable properties, and when its amount is reduced below a certain value the leather becomes brittle. Lowering the protein content without altering the desirable properties of chrome leather presents an even greater problem. Vegetable-tanned leathers have low protein contents naturally and do not require mineral acid to give them the properties desirable in shoe leather.

The writers believe that this series of experiments relating shoe comfort to the chemical composition of the leather will result in compelling tanners to add shoe comfort to the many properties they are now required to furnish in shoe leather.

Contact Catalysis and Photochemistry[1]

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THE greatest difficulty about a problem is often the formulation of it, and this has been strikingly true of contact catalysis, each period of development being marked by a new formulation. The classification by Berzelius of a group of phenomena under the general head of catalysis ushered in the first period, which was essentially qualitative. Ostwald's sharper definition introduced a period of quantitative measurement of reaction velocity. Colloid chemistry brought the realization that there were two groups of phenomena, one in which definite, intermediate chemical compounds were formed, and one in which there was adsorption and the intermediate formation of indefinite chemical compounds, meaning thereby, complexes that are not described by the law of definite and multiple proportions. The attempt to determine in which group a particular reaction falls has led to the brilliant work at Princeton on catalysis at an interface.

It is hoped that this symposium will mark the beginning of the study of the fundamental question—how the activation occurs. This paper will be limited to cases dealing with adsorption. Any action between so-called saturated compounds involves either a preliminary dissociation which means the breaking of a regular bond, or a preliminary association which means the opening of a contravalence or residual valence. Nef believed that all reactions were preceded by dissociation, while Michael defends the view that all reactions are preceded by the formation of addition compounds. The real truth probably lies somewhere between these two extreme views, and it is very much to be hoped that the organic chemists will go over their field and point out definitely in which cases we are justified in saying that we have preliminary dissociation, in which cases we know we have preliminary association, and what is lacking in the other cases to enable us to decide where these cases belong. A committee to do this has been appointed by the National Research Council.

The next problem in contact catalysis is therefore to determine in each case which bonds have been broken or opened. To simplify matters this problem will be discussed solely on the assumption that adsorption involves dissociation. It will be a simple matter for anybody to translate this into terms of opening contravalences. We owe to Langmuir the important conception of oriented adsorption, meaning that acetic acid, for instance, when adsorbed by charcoal may attach itself by the methyl carbon, by the carboxyl carbon, or by either of the oxygens. If we are dealing with association, it may also attach by any of the hydrogens. Langmuir has been very definite as to what he means by oriented adsorption in the case of oil films on water, but he has been very indefinite with regard to what he means in the case of contact catalysis, even though he has given one picture.

After postulating oriented adsorption and the opening of particular bonds, there are still two ways in which reaction may take place. The adsorbed or captive molecule may be bombarded effectively by a free molecule, in which case the outer end of the molecule is the reacting one and the catalytic agent merely holds the victim in place until it receives the fatal blow. That is the view held by Kruyt and van Duin.[2] On this view contact catalysis is a most unsportsmanlike thing. It is equivalent to hitting a man, not only when he is down, but when he is held by somebody else. That is not an argument either way, because chemical reactions may follow the laws of the gang even though Professor Taylor has postulated intelligent molecules in order to account for negative catalysis.

The other possibility is that, as the bond between the adsorbed substance and the adsorbing agent makes and breaks during dynamic equilibrium, we have temporarily an activated radical, which may react with another activated radical or with an ordinary molecule. On this assumption the reaction will take place chiefly at the inner or adsorbed end of the molecule, the catalytic agent functioning as a beneficent agent which enables the molecule to throw off the restraints that ordinarily hamper its action or reaction.

The experiments of D. Berthelot and Gaudechon[3] indicate that ultra-violet light of suitable wave lengths will bring about the same reactions that we get with different catalytic agents, such as the decomposition of ethyl alcohol into acetaldehyde, ethylene, etc. Under these conditions there can be no captive molecules and consequently the reactions must be between free radicals. Until some proof to the contrary is found, it is simpler to postulate that the reactions in presence of solid catalytic agents are reactions of free radicals and not of captive molecules. Since there can be no formation of definite or indefinite intermediate compounds between alcohol, for instance, and light, it must be concluded, until further notice, that the formation of definite or indefinite chemical compounds with the solid catalyst is not in itself the essential thing, but is merely the step in the formation of the free radical which is the real reacting substance.

The problem on the photochemical side is to determine what radicals are formed and what ultra-violet rays produce them. The step after that is the really fascinating one. If, as seems probable, each chemical bond corresponds to one or more absorption lines, which will lie in the ultra-violet or infra-red in the case of colorless compounds, it should be possible, theoretically, to break or open any desired bond in any given substance by the use of suitable monochromatic light of sufficient intensity under favorable conditions. In other words, we see the possibility of developing an absolutely new technic for organic chemistry.

One of the things that worries the thoughtful physical chemist, if this is not a tautological phrase, is the apparent difference between inorganic and organic reactions. Several years ago the attempt was made to bridge the gap by postulating that all reactions in organic chemistry were ionic reactions, but that postulate was so obviously wrong that it did not get anywhere. The reasoning put forward with regard to reactions between saturated compounds applies just as much to inorganic as to organic reactions. We must postulate a preliminary dissociation or association. On this basis the ordinary reactions in dilute aqueous solutions at once become a part of the general plan. We are dealing with activated molecules which have become activated by dissociation into electrically charged radicals, to which we

[2] *Rec. trav. chim.*, [4] **2**, 249 (1921).

[3] *Compt. rend.*, **150**, 1169, 1327, 1517, 1690; **151**, 395, 473, 1349 (1910); **152**, 262, 376, 522; **153**, 383 (1911).

give the name of ions. In organic chemistry we get activation and reaction as a result of the formation of radicals, using the word in its broadest sense to mean the products obtained when a regular bond is broken or a contravalence is opened. If these radicals are charged electrically, we call them ions just as in inorganic chemistry. It seems probable, however, that in many and perhaps in most cases the organic radicals are electrically neutral.

A consideration of the photochemical work of D. Berthelot and Gaudechon led, on the one hand, to the conclusion that the function of the solid catalyst is to bring about the formation of free radicals, the reaction probably not taking place in general with the captive molecule at its outer end. On the other hand, a consideration of this same photochemical work has led to the possibility of an entirely new method of making organic compounds. The conclusion to be drawn from both sets of considerations is that the organic chemistry of the future will deal with the reactions of radicals instead of the reactions of molecules.

Color and Constitution[1]

I—Preliminary Paper. Effect of Isomerism on the Color of Certain Azo Dyes

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SINCE 1868, when Graeber and Liebermann[2] first suggested a relationship between color and chemical constitution, many theories have been advanced to account for the phenomenon.[3] The available evidence, when correlated, suggests that color is related to some intramolecular dynamic change associated with certain groups. It is the purpose of this investigation to study the effect of isomerism on the color of certain azo dyes. This preliminary paper deals only with the colors produced on wool by certain azo dyes made from benzenediazonium chloride and substituted products by coupling with the salts of β-naphtholsulfonic acids. The results of the absorption spectra work will be reported at some future time.

Benzeneazo-β-naphtholsulfonic Acids

The sodium salt of benzeneazo-β-naphthol-6-sulfonic acid, made by coupling Schaeffer salt with diazobenzene chloride, dyes wool from an acid bath a red-orange color. The isomeric product having the sulfonic acid group in position 7 gives a much yellower color, and the corresponding isomer having the sulfonic acid group in position 8 gives the yellowest color of the three. The introduction of a second sulfonic acid group in position 3 on the ring already containing one sulfonic acid group in position 6 shifts the color back towards red. R salt, the salt of 2-naphthol-3,6-disulfonic acid, coupled with diazobenzene chloride gives a color much redder than that of benzeneazo-β-naphthol-6-sulfonic acid. If the two sulfonic acid groups are in positions 6 and 8, as in the case of G salt, the salt of 2-naphthol-6,8-disulfonic acid, then the resulting dye, benzeneazo-β-naphthol-6,8-disulfonic acid, gives a color which is the yellowest of the series, the color being shifted in the yellow beyond that of the benzeneazo-β-naphthol-6-sulfonic acid. This striking difference in the color produced by R and G salt dyes holds true for all the products so far studied and runs parallel with the difference in the reactivity of the two isomers.

The dye obtained by coupling β-naphthol-3,6,8-trisulfonic acid with diazobenzene chloride gives a color about midway between the colors produced by the R and the G salt dyes.

Nitrobenzeneazo-β-naphtholsulfonic Acids

The introduction of a nitro group on the benzene ring in an ortho position to the diazo group shifts the color produced by all the o-nitrobenzeneazo-β-naphtholsulfonic acids towards red, the entire series being redder than the corresponding benzeneazo-β-naphtholsulfonic acid series. o-Nitrobenzene-azo-β-naphthol-6-sulfonic acid gives a very red-orange color, the corresponding 7-sulfonic isomer an orange color, the R salt product a scarlet, the G salt isomer a yellow-orange, and the 3,6,8-trisulfonic acid product an orange color about equivalent in hue to a blend of the colors produced by the corresponding R and G salt dyes.

The corresponding m-nitrobenzeneazo-β-naphtholsulfonic acids give colors much yellower than the ortho products, and, in fact, much yellower than the colors of the benzeneazo-β-naphtholsulfonic acid series.

This influence of the meta position is true for all the substituents studied. The same relative differences in hue of the members of the series are maintained. The R salt product gives the deepest and the G salt the lightest hue.

The p-nitrobenzeneazo-β-naphtholsulfonic acid series is slightly redder than the corresponding o-nitro series, but the difference is not very marked. This close similarity between the colors produced by the ortho and para isomers is true in all the cases studied.

Methylbenzeneazo-β-naphtholsulfonic Acids

The methyl group affects the color of the dyes of the benzeneazo-β-naphtholsulfonic acid series to a less extent than the nitro group. The influence of the position of the methyl group is consistent with the results obtained with the nitro group. Of the substituents studied the methyl group is exceptional in its influence on the reactivity of the diazo group. o-Methyldiazobenzene chloride does not react with G salt and the salt of β-naphthol-3,6,8-trisulfonic acid under the usual conditions of coupling. It reacts slowly with G salt at temperatures above 25° C., with accompanying decomposition of the diazo compound. The writers have not yet succeeded in coupling the trisulfonic acid with any diazo compound containing a methyl group in an ortho position to the diazo group. The o-methylbenzeneazo-β-naphthol-sulfonic acid series gives redder hues than the corresponding benzeneazo-β-naphtholsulfonic acid series. The dye from R salt again gives the reddest hue of the series; that from the 2,7-sulfonic acid a yellower hue than that from the 2,6-sulfonic acid. The last two are red-orange and the former is a scarlet. The introduction of the methyl group in a meta position to the diazo group shifts the color of the entire series towards yellow, but the change is not so pronounced as that caused by a nitro group. The methyl group in para

[2] *Ber.*, 1, 106 (1868).
[3] Watson, "Colour in Relation to Chemical Constitution," 1918.

position shifts the color of the entire series towards the red. The para series is slightly redder than the corresponding ortho series. Both G salt and β-naphthol-3,6,8-trisulfonic acids couple with m- and p-methylbenzenediazochlorides.

Chlorazo-β-naphtholsulfonic Acids

The introduction of one chlorine atom on the benzene ring in benzeneazo-β-naphtholsulfonic acids has very little effect on the color produced by the dyes. The entire series is slightly yellower than the corresponding benzeneazo-β-naphtholsulfonic acid series. The m-chlorazobenzene-β-naphtholsulfonic acid dyes are slightly yellower than the corresponding ortho and para series. In addition to causing a slight change in hue, chlorine enhances the brilliancy of all the colors, and appears to increase the affinity of the dyes for wool, since their aqueous solutions exhaust in the dye bath more readily and more completely than the solutions of the corresponding benzeneazo-β-naphtholsulfonic acids.

Sulfobenzeneazo-β-naphtholsulfonic Acids

The sulfonic group on the benzene ring in sulfobenzeneazo-β-naphtholsulfonic acids shifts the color towards yellow in all cases, having the greatest effect in the meta position. Benzeneazo-β-naphthol is insoluble. m-Sulfobenzeneazo-β-naphthol is quite soluble and gives an orange color in hue slightly yellower than that produced by the p-sulfo compound. The corresponding product from β-naphthol-7-sulfonic acid gives a much yellower color. The R salt dye produces an orange color while the corresponding G salt dye gives a yellow color. All the p-sulfobenzeneazo products are redder than the corresponding meta products.

Chemical Constitution and Reactivity of β-Naphtholsulfonic Acids

The marked difference in the reactivity of the two isomeric β-naphtholdisulfonic acids, R, 2-3-6, and G, 2-6-8, has been observed by several investigators. The 2-3-6 isomer reacts with nitrous acid to give 1-nitroso-2-naphthol-3,6-disulfonic acid, while the 2-6-8 isomer does not react with nitrous acid. The former isomer reacts readily with diazo compounds, giving the corresponding dyes, while the latter does not react under the usual conditions of coupling with certain diazo compounds—e. g., o-methyldiazobenzene chloride and diazotized m-4-xylene chloride in which one methyl group is ortho to the diazo group. Certain diazo compounds react with both the R and G isomers, but at widely different rates. Smith[4] measured the comparative rates of reaction of R and G salts with p-diazotoluenechloride and found that under the same conditions over 85 per cent of the G remained unchanged when all the R had combined.

The monosulfonic acids, Schaeffer (2-naphthol-6-sulfonic acid) and crocein (2-naphthol-8-sulfonic acid), show similar differences in chemical reactivity. The influence of the sulfonic group in position 8 on the reactivity is also shown by the 2-naphthol-3,6,8-trisulfonic acid, which behaves like the 2-6-8 isomer. The influence of the sulfonic group in the peri, or 8, position on the reactivity of the hydrogen in position 1 has been ascribed to "steric hindrance,"[5] but this hypothesis does not satisfactorily explain the facts.

Of the several hydrogen atoms in the β-naphtholsulfonic acid molecule, only that adjacent to the hydroxy group is usually replaced by the diazo group with its attached radical and also by the nitroso group. It is also the first to be replaced by other substituents, such as nitrous oxide, chlorine, bromine, and iodine. It has been shown that when the peri position is unoccupied by a sulfonic group, the substituent in position 1 is replaced by a diazo group and the resulting compound has the same constitution as that obtained from the unsubstituted sulfonic acid.[6] The effect of the sulfonic group in position 8 on position 1 is shown by the marked difference in behavior of 1-brom-2-naphthol-6-sulfonic acid and 1-brom-2-naphthol-8-sulfonic acid with diazo compounds.[7] The bromine is readily replaced by the diazo group in the former case and is not reacted on in the latter. Similarly, Witt[8] showed that β-naphthylamine-8-sulfonic acid reacts with diazotized sulfanilic acid to give the corresponding diazoamido compound and not the amidoazo product.

This evidence suggests that a peculiar relationship between the hydrogen adjacent to the hydroxyl group and the rest of the molecule is in some way induced by the hydroxyl group. The reactivity of the molecule is dependent upon this relationship. The degree of this activity is also dependent upon the influence of other substituents and upon the position which they occupy with respect to the hydroxyl group. The influence of hydroxyl on the reactivity of certain groups adjacent to it in the benzene series has been pointed out by Gibbs and Pratt.[9]

R salt reacts with diazo-m-4-xylene chloride, but G salt does not. When a mixture of R and G salts is used to couple with a diazo compound that will react with both R and G salts, the R salt couples first and apparently no G salt reacts with the diazo compound, at least not so as to give a permanent stable dye molecule, until all the R salt has been removed by coupling from the solution. If there is only a sufficient amount of diazo compound to couple with the R salt present, then no G salt couples, and it can be recovered quantitatively. When all the R salt has been coupled out of the mixture, the remaining G salt will couple with the same diazo compound, but at a much slower rate than the R salt coupled. That addition is the initial step in all chemical reactions is shared in common by many of the modern theories of chemical reactivity. The "force field" theory of Baly[10] is particularly important, in view of increasing evidence in its favor. The reaction between diazo compounds and naphthols has been assumed to take place by direct addition of the diazo to carbon through the medium of conjugated double bonds,[11] the reaction capacity of which is intensified by the hydroxyl group and also through the primary formation of unstable oxonium compounds.[12] Much evidence has been secured in support of the part the hydroxyl group plays in such reactions.[13]

When R salt reacts with a diazo compound, the diazo compound adds to the naphtholsulfonic acid molecule through the weak position in the neighborhood of the hydrogen atom as soon as interlacing of the respective molecules takes place. The resulting molecule then undergoes cleavage into the more stable molecular systems—the salt of benzeneazo-β-naphtholsulfonic acid and sodium chloride. R salt may then be said to have an "open reactive field." In the case of G salt the hydrogen atom adjacent to the hydroxyl group is stabilized by the sulfonic acid group in position 8 and the molecular system is not so readily penetrated by the diazo molecule. The G salt may then be said to represent a "closed reactive field."

If the diazo group is also stabilized or its reactivity neutralized by its interrelation with an adjacent group, no addition is possible between it and a molecule having a closed field of reactivity until the field of reactivity is opened in one or the other of the two molecules. If the diazo group is

[4] J. Chem. Soc. (London), 89, 1505 (1906).
[5] Ibid., 89, 1505 (1906).

[6] J. Chem. Soc. (London), 89, 1167 (1906).
[7] Ibid., 89, 1505, 1167 (1906).
[8] Ber., 21, 3483 (1888).
[9] Philippine J. Sci., 8, 33 (1913).
[10] J. Am. Chem. Soc., 37, 979 (1915).
[11] Ann., 398, 66 (1913); J. Chem. Soc. (London), 109, 1031 (1916); 111, 958 (1917); 121, 427 (1922).
[12] Ber., 47, 1286 (1914).
[13] Ibid., 40, 2, 4, 40, 404, 460 (1907); 41, 4012 (1908); 50, 1534 (1917).

free to add to the G salt molecule, a reaction will take place, but the reaction will be slower than the corresponding one with R salt. There are then three cases:

1—That of an open reactive field in both the diazo- and the naphtholsulfonic acid molecules—for example, diazobenzene chloride and R salt.

2—An open reactive field in but one—for example, (a) diazo-*m*-4-xylene chloride and R salt, and (b) diazobenzene chloride and G salt.

3—A closed reactive field in both—for example, diazo-*m*-4-xylene chloride and G salt.

In the selective coupling of R salt'out of a mixture of R and G salt by diazobenzene chloride, the diazo compound itself, having an open reactive field, reacts preferentially with the naphtholsulfonic acid having an open reactive field—that is, the R salt. The G salt, having a closed reactive field, cannot form an addition product with the diazo compound until the R salt, which has an open reactive field, is wholly converted into dye through the formation of a preliminary addition product.

The sulfonic group in the β-naphtholsulfonic acid molecule appears to affect the energy relationship of the OH group and the adjacent hydrogen atom with respect to the rest of the molecule, and this is manifested in both the reactivity of the sulfonic acid and the color of the dye it produces. The maximum bathychromic effect is manifested by a sulfonic group in position 3, adjacent to the hydroxyl group. The hue lightens with the shifting of the sulfonic to position 6. The maximum hypsochromic effect is manifested by the sulfonic group in position 8, where it also has the maximum stabilizing effect on the diazo group in position 1, and where it has less stability than in the other positions on the ring, with the exception of position 1. These seem to be significant, and relate facts which, when supported by additional evidence, should lead to a better understanding of the mechanism of such reactions and their relation to color.

Naphthalenesulfonic Acids[1,2]

V—The Quantitative Estimation of 2,6- and 2,7-Naphthalenedisulfonic Acids

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Pure lead salts of 2,6- and 2,7-naphthalenedisulfonic acids are prepared through the sulfonic chlorides and free acids, and the solubility at 25° C. of known mixtures of the two lead salts is determined. The results so obtained are plotted in a curve. With the aid of this curve the proportion in which the two isomers are present in an unknown mixture can be ascertained by determining the solubility of a weighed quantity of the mixture of the two lead disulfonates.

A LTHOUGH the naphthalenesulfonic acids have been known for over a hundred years and have been extensively investigated, only one method has been proposed for estimating quantitatively the monosulfonic acids,[3] and so far as can be ascertained no method has been suggested for determining quantitatively the disulfonic acids.[4]

It is well known that when naphthalene is sulfonated isomers are always produced. For example, when naphthalene is disulfonated at 160° C., the 2,7-naphthalenedisulfonic acid that is first formed, under the influence of heat and excess acid, is slowly converted into the isomeric 2,6-disulfonic acid. Thus it will be seen that any method proposed for estimating quantitatively naphthalenesulfonic acids, in order to be serviceable, should determine not only the total sulfonic acids, but also the proportion in which the isomers are present.

The usual method[5] of isolating the sulfonic acids of naphthalene is to boil an aqueous solution of the sulfonation product with calcium carbonate and filter off the precipitated calcium sulfate. The filtrate, which contains the calcium salts of the sulfonic acids with some calcium sulfate, since the calcium salts of naphthalenesulfonic acids are excellent solvents for calcium sulfate, is treated with sulfuric acid drop by drop as long as a precipitate is produced. The precipitate is filtered off and the aqueous solution of the sulfonic acid is evaporated to dryness. The dissolved calcium sulfate may be removed by adding a little alcohol to the aqueous solution, filtering, and again evaporating. The procedure obviously does not lend itself to quantitative work; besides, it does not distinguish between isomers.

In an exhaustive study on the formation of the naphthalene-monosulfonic acid, Ewes[3] devised a rather ingenious method for the determination of α- and β-monosulfonic acids in the presence of one another. He prepared the lead salts of both acids and then determined the mutual influence of these salts on their solubility in water at 25° C. An excess of the lead beta salt was always added to 100 cc. of water and to this definite weighed quantities of the alpha salt were added. The total solubility of the mixture was then determined. From the data obtained a curve was plotted, from which, after determining the solubility of a weighed quantity of an unknown mixture of lead salts of α- and β-naphthalenesulfonic acids, the composition of the mixture could be ascertained.

The method proposed in this paper is similar to the one mentioned above. Lead salts of 2,7-naphthalenedisulfonic acid and 2,6-naphthalenedisulfonic acid were prepared and the solubility of known mixtures of the two salts was determined. Since the two isomers contain different amounts of water of hydration, all calculations were made on the basis of the anhydrous salts.

PREPARATION OF THE LEAD SALTS OF THE TWO ACIDS

Since the two lead salts accompany one another in the ordinary method of preparation, and since it is very difficult to separate them by the usual methods of crystallization, they were prepared through the sulfonic chlorides. These can be easily separated and prepared pure. After purification they were converted into the free acid and these in turn converted into the lead salts.

[3] Ewes, *Rec. trav. chim.*, **28**, 298 (1909).

[4] Only those sulfonic acids that are produced by direct sulfonation are here considered.

[5] Ebert and Merz, *Ber.*, **9**, 592 (1876).

SULFONATION OF NAPHTHALENE—Naphthalene was sulfonated with five times its weight of concentrated sulfuric acid at 160° C. for 4 hours. The sulfonation mass was poured into water and neutralized with calcium carbonate. The precipitated calcium sulfate was filtered off and washed with water. The filtrate and washings were evaporated to dryness. After grinding and dehydrating at 200° C., the crude salts, which consisted of a mixture of calcium 2,7- and 2,6-naphthalenedisulfonates with some calcium sulfate, were added to boiling water (3 parts of crude salts to 5 parts of water), in which the calcium 2,7-naphthalenedisulfonate is much more readily soluble after having been dehydrated than the calcium 2,6-naphthalenedisulfonate. The mixture was rapidly filtered and both the undissolved portion and the filtrate were saved. The filtrate, which contained the calcium 2,7 salt, was treated with sodium carbonate. The precipitated calcium carbonate was filtered off and the solution evaporated to dryness. The undissolved portion of the calcium salts was largely the 2,6 sulfonate. This was stirred with water and treated with sodium carbonate, and after filtering off the calcium carbonate the solution was evaporated to dryness.

CONVERSION TO THE SULFONIC CHLORIDE—One hundred grams of sodium salt which had been thoroughly dried were intimately mixed with 130 grams of phosphorus pentachloride and the mixture was heated in an oil bath to 150°–160° C. After most of the phosphorus oxychloride had been distilled off the reaction mixture was cooled and treated with water. The reaction product formed lumps, which were crushed, then washed thoroughly with hot water, and finally dried. The procedure up to this point was the same for both the isomeric acids.

The crude 2,6-naphthalenesulfonic chloride was extracted twice with small amounts of acetone, which removed considerable tarry material, and then recrystallized several times from xylol, from which it deposits as short beautiful colorless needles, having a melting point 228° to 229° C. (corrected).

In preparing the 2,7-naphthalenesulfonic chloride, it was found that however thoroughly the reaction product was washed with water, when it was treated directly with glacial acetic acid after drying, hydrochloric acid was always evolved. This reaction did not take place, however, after preliminary washing with a small amount of acetone. The chloride was then recrystallized several times from glacial acetic acid. (This effectively removed the chloride of any 1,6 sulfonic acid that may have been present. Armstrong[6] reports that the 1,6 acid is produced in small amounts when naphthalene is disulfonated to produce the 2,7 and 2,6 isomers.) Its melting point was 158.5° to 159.5° C. (corrected).

PREPARATION OF THE ACIDS—The free acids were obtained by heating the naphthalenesulfonic chlorides with water in sealed glass tubes at 140° to 150° C. for 3 to 4 hours. After cooling, the solution was filtered and evaporated to dryness. Water was added several times and the evaporation repeated until a solution of the acid in water gave no test for chlorides. The acid was finally placed in a vacuum desiccator over soda lime for 24 hours. The lead 2,7 salt was formed by neutralizing a solution of the free acid with precipitated lead carbonate (Kahlbaum), filtering, and evaporating the solution to dryness.

The lead 2,6 salt can be prepared in a similar manner. Since, however, the lead 2,6-naphthalenedisulfonate is only slightly soluble, an excess of lead carbonate should be avoided. The following procedure gave more satisfactory results and was adopted: Ten grams of 2,6-naphthalenedisulfonic chloride, 22 grams of potassium hydroxide, and 250 cc. of water were heated to boiling until all the disulfonic chloride was in

6 *Ber.*, **15**, 204 (1882).

solution. After cooling the solution the precipitated potassium salt was filtered off and washed with 95 per cent alcohol. It was finally recrystallized from 45 to 50 per cent alcohol. To an aqueous solution of this salt a solution of lead nitrate was added, and the lead 2,6 salt formed was filtered off and washed with cold water.
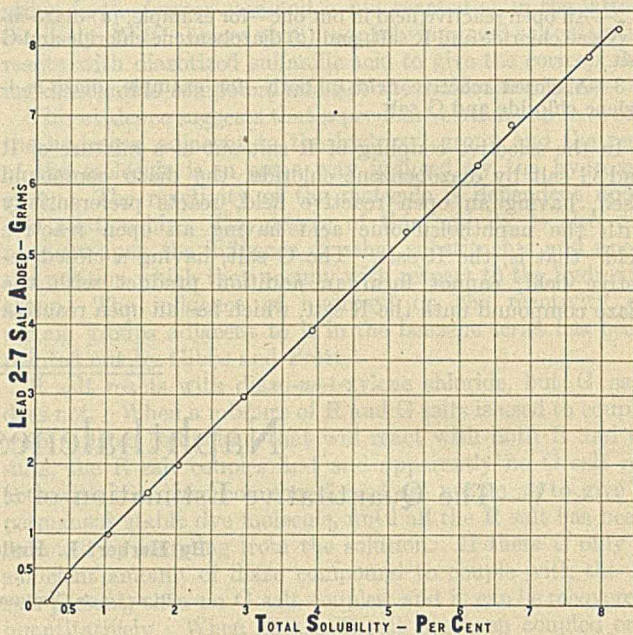

FIG. 1

TABLE I—ADDITION OF EXCESS OF LEAD 2,6-NAPHTHALENEDISULFONATE AND A VARIABLE QUANTITY OF LEAD 2,7-NAPHTHALENEDISULFONATE TO 100 CC. OF WATER AT 25° C.

(All results are on the basis of the anhydrous salts)

Lead 2,7 Salt (Anhydrous) Added Grams	Total Solubility, Per cent	Lead 2,7 Salt (Anhydrous) Added Grams	Total Solubility, Per cent
0	0.187	3.92	3.92
0	0.188	3.92	3.92
0	0.188	5.33	5.26
0.395	0.484	5.33	5.22
0.395	0.481	6.28	6.27
0.98	1.046	6.29	6.23
0.98	1.043	6.86	6.72
1.58	1.59	6.86	6.72
1.58	1.60	7.85	7.83
1.966	2.008	7.82	7.81
1.966	2.043	8.23	8.18
2.96	2.93	8.23	8.20
2.97	2.98	..	..

DETERMINATION OF SOLUBILITY

The solubilities of the pure salts were first determined. An excess of the pure salt was placed in a glass-stoppered flask and about 100 cc. of water were added. The flask was then placed in a tumbling apparatus contained in a water bath which was kept at a constant temperature of 25° C., and was tumbled for 24 hours. It was then removed from the bath and a portion of the solution was filtered off, the first runnings being discarded. After weighing the sample the lead was determined as chromate. The solubility of lead 2,7-naphthalenedisulfonate is 8.2 grams in 100 grams of water at 25° C., and that of lead 2,6-naphthalenedisulfonate is 0.19 gram in 100 grams of water at 25° C.

In order to analyze mixtures of varying proportions of the two salts, it was first necessary to determine the influence that a certain quantity of lead 2,7 salt exercises on the solubility of the lead 2,6 salt. In order to accomplish this an excess of the lead 2,6 salt (about 0.3 gram) was always added to the flask and quantities of the lead 2,7 salt varying from 0.4 gram to 8.2 grams were added. One hundred cubic centimeters of water were always employed as solvent. After the solution had been agitated for 24 hours at 25° C., the amount of salts dissolved was determined as described in

the preceding paragraph. In this manner the results given in Table I were obtained.

The table indicates that the solubility of the 2,6 salt rapidly diminishes as the quantity of the 2,7 salt increases. All results are given on the basis of the anhydrous salts. The total solubility increases regularly, as shown in Fig. 1.

PROCEDURE—In order to determine the proportion in which the isomers are present in any mixture of the two acids, the following procedure is suggested:

Dilute the mixed acids with water and heat to boiling. Add slowly lead carbonate until the acid solution is neutralized and a slight excess of lead carbonate is present. (In neutralizing the acid mixture it is necessary to use a grade of lead carbonate equal in purity to Kahlbaum's precipitated lead carbonate. The commercial C. P. lead carbonate, owing to its preparation by precipitation with sodium bicarbonate from lead acetate or lead nitrate solution, contains alkalies. The presence of even small amounts of alkalies vitiates the results, because of the formation of disulfonates of the alkali present.) Allow the precipitate to settle. Decant off the hot solution and wash the precipitate several times with boiling water. Evaporate the filtrate and washings to dryness and dry the residue at 100° C. for one hour. Determine the water of hydration in one portion of the dried residue (2 to 3 grams) by heating it at 190° to 200° C. over night. This is necessary since the two salts contain different quantities of water of hydration.

Weigh out another portion of the dried residue which is exactly equivalent to 8.2 grams of anhydrous lead salts. (The anhydrous salts are not used here because they absorb moisture so rapidly that it is almost impossible to make accurate weighings.) Place this portion in a flask fitted with a ground stopper. Add 100 cc. of water and place the flask in a tumbling apparatus contained in water bath maintained at 25° C. and tumble for 24 hours. Remove the flask and filter off a portion of the solution, discarding the first runnings, and determine the lead as chromate in a weighed quantity of the solution. With the solubility thus obtained, the curve (Fig. 1), and the quantity of the anhydrous mixture taken, the composition of the mixture can be readily ascertained.

To show that the foregoing proposed method is accurate, the following experiments were performed: Two mixtures of lead 2,7 and 2,6 salts were prepared, one containing 47.3 per cent lead 2,7 salt, the other 18.4 per cent lead 2,7 salt. (These percentages are for the anhydrous salts.) The mixtures were separately subjected to the same operations that have been described. The per cents of lead 2,7 salt found were 46.3 and 17.5, respectively. Thus it will be seen that the error of the method is about 1 per cent, which, for the majority of practical purposes is not objectionable. The method cannot be employed if 1,6-naphthalenedisulfonic acid is present, owing to the high solubility of its lead salt.

Melting and Freezing Points of Pure Substances and of Eutectic Mixtures[1,2]

Apparatus for Their Determination

By Edward W. Washburn

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THE apparatus is shown in the figure. If constructed of Pyrex glass it can be used for any temperature up to 500° C., and a multiple thermocouple or a resistance thermometer can be substituted for the mercury thermometer. Inasmuch as the walls of the Dewar tube are at substantially the same temperature as the thermometer bulb, no stem correction is necessary, except possibly a very small one in the case of substances melting at very high or very low temperatures. For work at such temperatures a thread thermometer may be fastened to the Anschütz.

DIRECTIONS FOR USE

(1) *For substances melting below room temperature.* Place the Dewar tube, *B*, and its loose-fitting asbestos stopper, *A*, in a compartment surrounded by a cooling bath somewhat below the melting point of the substance under investigation. Place the calibrated Anschütz thermometer, *T*, in the same cooling bath. With the aid of a small casserole or other convenient vessel, cool a sample of the substance under investigation until it crystallizes, stirring it so as to obtain the frozen material in the form of loose crystals. When the Dewar tube has attained the temperature of the bath, remove it from the bath and with a glass rod or small spatula quickly transfer to the Dewar tube a small amount of the crystals. Dry the thermometer quickly and place it in position. Then fill in a sufficient amount of the powder so as to insure the complete covering of the bulb of the thermometer after the powder is melted. Insert the stopper, *A*, and tap and read the thermometer at regular intervals until all the powder is melted, using the thermometer as a stirrer during the process. Plot the time-temperature curve. The horizontal portion of the curve (after applying the necessary thermometer corrections) corresponds to the melting point of the substance. If no horizontal portion is obtained, the substance is impure and further purification should be carried out.

(2) *For substances melting above room temperature.* With the aid of a suitable heating chamber bring the Dewar tube and the thermometer to some temperature above the melting point of the substance. Melt a sample of the substance in a small casserole, remove the Dewar tube and thermometer from the heating chamber, pour into the Dewar tube a sufficient amount of the liquid substance, insert the thermometer and the stopper, *A*, and take readings as under (1). In case of substances that tend to super-cool without crystallization, the stopper may be momentarily removed as soon as the liquid is cooled below its freezing point and a few crystals added in order to seed it.

Procedure 2 may also be used for substances melting below room temperature, provided the Dewar tube is kept surrounded by a transparent bath at a temperature below the melting point of the substance during the readings. For melting points lying in the neighborhood of room temperatures the vacuum jacketing is unnecessary and a small test tube may be substituted for the Dewar tube.

Constancy of melting or freezing point is not in itself a complete criterion of purity, except when checked with different samples of the substance which have been subjected to repeated purifications, preferably by different procedures.

The following are some results obtained with this apparatus:

SUBSTANCE, MANNITE	° C.
Commercial product	165.10
First crystallization	165.84
Second crystallization	165.05
Third crystallization	165.05
Fourth crystallization	165.05
Constant to 0.01° C. during the crystallization, 10 to 15 minutes	

The procedure for determining a eutectic temperature or other invariant point is obvious. Evidently the apparatus may be also used for determining a phase equilibrium diagram by the method of thermal analysis.

The Natural Water Corrosion of Steel in Contact with Copper[1]

By W. G. Whitman and R. P. Russell

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PRESENT opinion on the mechanism of the corrosion of iron and steel by natural waters can be broadly divided into two camps. The first is agreed that corrosion is initiated by a reaction of metallic iron and hydrogen ion, producing ferrous ion and nascent hydrogen. The other group centralizes on a colloidal explanation of the process and considers that hydrogen is not involved in natural water corrosion.

The first position is presented by Wilson[4] in a paper which embodies several important advances over the views of earlier writers. Wilson divides the subject of submerged aqueous corrosion of steel into three fields—alkaline, natural water, and acid—and enumerates the controlling factors in each. The primary reaction in all cases is that between metallic iron and hydrogen ion.

$$Fe + 2H^+ = Fe^{++} + 2H \qquad (1)$$
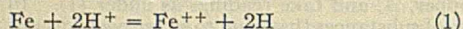
In alkaline water the rate of corrosion is limited by the low concentration of H^+. Since the nascent hydrogen is formed only slowly, it can readily be removed by oxidation by the dissolved oxygen in the solution to form water

$$2H + \tfrac{1}{2}O_2 = H_2O \qquad (2)$$

Reaction 1 speeds up as the H^+ is increased towards the neutral point, until it becomes faster than the depolarizing reaction (2). Under these conditions the rate of corrosion is limited by the rate at which the polarizing film of hydrogen can be removed by oxidation, and Reaction 2 becomes controlling. Wilson further states that the speed of the depolarizing reaction is determined almost solely by the rate at which dissolved oxygen can diffuse into the metal surface, and it is practically independent of hydrogen-ion concentration and composition of steel within the limits of natural waters.

Further increase in H^+ concentration finally results in the evolution of hydrogen gas, and the reaction

$$2H = H_2 \qquad (3)$$

proceeds in parallel with oxygen depolarization to remove the polarizing film of hydrogen. In this acid range overvoltage is an important factor because of its relation to gas evolution.

Experiments are described wherein the natural water corrosion of steel in contact with a metal lower in the electromotive series has been quantitatively determined. The results show that the total corrosion is the same with bare steel plates as with steel specimens of the same size having 75 per cent of their surface copper-plated—i.e., in the latter case the corrosion per unit area of steel is four times as great as in the former. The total corrosion observed is determined by the total effective surface available for the depolarization of hydrogen by dissolved oxygen, the actual corrosion occurring on the steel alone.

These results are not readily explainable by the colloidal theories of corrosion advanced by Friend[2] or Bengough and Stuart,[3] both of which agree that hydrogen is not an essential in natural water corrosion. The data are, however, in entire accord with an electrolytic mechanism of corrosion. The electrolytic theory explains these results by picturing the increased corrosion per unit area of steel as caused by the depolarization of a film of nascent hydrogen. This film is deposited on the steel and on the adjacent copper surface, and its removal is effected by diffusion of dissolved oxygen in to the metal. The rate of corrosion is limited by the rate at which oxygen can diffuse in to react with the surface film of nascent hydrogen.

The importance of these quantitative data in deciding as to the mechanism of the corrosion of steel is emphasized from both theoretical and practical points of view.

The various colloidal theories which have been proposed agree that the function of oxygen in natural water corrosion is either to oxidize ferrous iron to ferric, which then corrodes the metal and is reduced to ferrous, or to oxidize the metal directly.[2,3,4] Although the exact concepts of the different writers vary, they are in general agreement that hydrogen is not an essential part of the corrosion under these circumstances.

EFFECT OF DISSIMILAR METALS IN CONTACT

Walker,[5] discussing the mechanism of corrosion when two metals are in contact, shows that a circuit is built up whereby the metal that is the anode goes into solution while hydrogen is deposited on the cathode. Thus iron in contact with zinc is protected and the zinc corrodes, while iron in contact with copper corrodes at a higher rate than if the copper were absent. Aluminium and other metals that rapidly form a protective oxide film do not exert the action exhibited by zinc.

For corrosion of steel in natural water, the increased rate due to contact with copper or other metals lower in the electromotive series should be due to the greater surface available for hydrogen depolarization by dissolved oxygen. Wilson points out that the overvoltage or specific catalytic properties of the second metal are not concerned unless conditions are such that hydrogen can be removed by gas evolution or by depolarization by oxidation from agents other than dissolved oxygen. Where dissolved oxygen alone is concerned, as with most natural waters, the rate of oxygen diffusion to the polarized surface is the main factor that determines the rate of depolarization and hence of corrosion.

The effective area of the cathodic metal in accelerating corrosion is determined by the relative rates of hydrogen deposition and of oxygen diffusion. At any point where hydrogen is deposited more rapidly than oxygen can depolarize it, the area may be considered equivalent to an equal area of steel. This means that the total area for depolarization (area of steel plus effective area of other metal) determines the *rate of corrosion*, although the *actual corrosion* is localized on the steel alone.

Since the hydrogen deposition depends on an electrochemical reaction, the factors that must be considered are (a) difference in potential between the metals, (b) conductivity of the liquid-metal circuit, and (c) rate of oxygen depolarization. It is clear that the distance over which

[2] *Iron Steel Inst.* (London), *Carnegie Schol., Mem.*, **11**, 125 (1922).

[3] Sixth Report to the Corrosion Research Committee of the Institute of Metals, **1922**.

[4] THIS JOURNAL, **15**, 127 (1923).

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

acceleration can occur will be determined largely by the conductivity of the solution. It should be understood that a copper surface on which the rate of hydrogen deposition is lower than the potential rate of oxygen diffusion (because of insufficient electrolytic action) is not so effective as an equal area of steel.

According to the foregoing viewpoint the effect of bringing a unit area of copper into "effective" contact with a unit area of steel would be to double the area for oxygen depolarization and hence to double the actual amount of corrosion occurring on the unit area of steel. Similarly, the result of copper-plating small areas of a piece of steel would be to localize the same total amount of corrosion on the uncoated areas, with a certain degree of pitting.

PLAN VIEW

CONSTANT HEAD BOX

EXIT SAMPLE

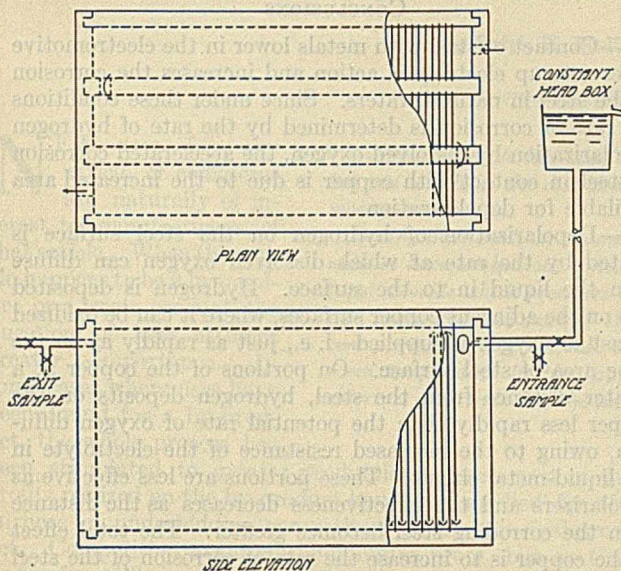ENTRANCE SAMPLE

SIDE ELEVATION

FIG. 1

It was realized that an experimental study of the foregoing conditions would be of considerable value in deciding the relative merits of the present theories for corrosion in natural water. The following experiments were initiated with this object in view.

METHOD OF ATTACK

The experiments were designed to compare the corrosion of bare steel plates with similar steel specimens of the same size which had been copper-plated over 75 per cent of their area. The rate of corrosion was determined by the decrease in oxygen content of the water passing over the plates. This method was developed by Speller, and is described in an article by Speller and Kendall on the corrosion of steel pipe.[6]

APPARATUS

The corrosion cell (Fig. 1) was constructed of 2.5 cm. cypress, the joints being tongued to prevent leaks. The plates used (5.1 × 15.2 cm. active surface of 20-gage mild steel plate) were forced into grooves cut 0.5 cm. deep in the wooden sides. Grooves were cut 0.5 cm. deep in the bottom of this cell for those alternate plates that did not extend to the top. One hundred and twelve plates were used (area, 17,400 sq. cm.) and the mean hydraulic radius of the water passage (area divided by wetted perimeter) was 0.31 cm. These two factors made the cell equivalent to 150 feet of commercial 3/8-inch pipe.

By-passing between any of the three passes or from plate to plate was prevented by means of rubber gaskets and a

series of heavy yokes (not shown in Fig. 1) which exerted a high pressure on all sides of the cell.

EXPERIMENTAL METHOD

The plates were first washed in gasoline to remove any oil or grease and the surface was taken down slightly with emery paper. The copper-plated specimens (75 per cent of the surface copper-plated 0.0075 cm. per side) were slightly polished with No. 0000 emery paper. After placing the plates in the cell, the yokes were tightened to prevent by-passing and the flow was adjusted to about 1000 cc. per minute. During the operation of the cell the rate of flow was determined before and after each set of samples for analysis, by noting with a stop watch the time required for 1000 cc. to flow into a calibrated graduate. The water was Cambridge tap water analyzing 76 p. p. m. total solids and 29 p. p. m. hardness. The amount of dissolved oxygen was determined by the Winkler method[7] and the temperature read from a thermometer in the effluent water.

RESULTS

TABLE I

Note.—Each of the oxygen analyses and specific corrosion rates is the average of at least two determinations.

Days Running	Temperature °C.	Rate of Flow Cc. per Min.	Entrance Oxygen Cc. per Liter	Exit Oxygen Cc. per Liter	Ratio Ent. O₂ / Exit O₂	Specific Corrosion Rate —Ka per Liter
			Bare steel plates			
1	19.0	838	5.13	2.47	2.08	63.3
3	21.8	1500	4.62	3.00	1.54	67.2
4	21.2	970	4.68	2.80	1.67	51.7
4	Cell opened and plates pickled in HCl					
5	22.0	1095	5.79	3.35	1.73	62.0
6	22.0	1000	4.88	2.80	1.74	57.6
6.5	22.0	1025	5.70	3.47	1.64	52.7
	At end of long run					
25	21.1	1075	5.84	3.62	1.61	53.6
26	20.8	1075	6.05	3.80	1.59	51.7
		Same plates, 75 per cent surface copper-plated				
1	22.0	1230	4.90	2.60	1.88	80.5
3	22.0	1580	4.88	3.00	1.63	80.0
5	21.5	1330	4.92	3.12	1.57	62.8
6	20.9	855	5.26	2.99	1.76	50.0
7	21.3	1100	5.13	3.18	1.61	52.5
8	21.3	1130	4.99	3.19	1.56	52.5

a Milligrams iron corroded per square centimeter per year per cubic centimeter oxygen per liter.

Table I gives the values for specific rates of corrosion obtained with bare steel plates and with plates that had been partly copper-plated. The rates were calculated in the following manner:

1 cc. oxygen is equivalent to 3.32 mg. Fe as Fe_2O_3

$$K = \frac{\text{Cc. O}_2 \text{ consumed per year} \times 3.32}{\text{Area of iron surface in sq. cm.} \times \text{average concentration O}_2}$$

$$= \frac{4,020,000 \times \text{liters water per minute} \times \log(\text{initial O}_2/\text{final O}_2)}{\text{Area of iron surface in sq. cm.}}$$

It is significant to note that after a short initial period of high corrosion the rate becomes constant, irrespective of whether the surface is all steel or three-quarters copper and one-quarter steel. At the end of the run with copper-plated specimens the copper surface was bright and untarnished (with the exception of pinholes in the plate), showing that all the corrosion occurred on the steel.

ACCURACY OF DATA

In determining corrosion rates by means of drop in oxygen concentration, the chief sources of error lie in (1) the assumption that 1 cc. of oxygen is equivalent to 3.32 mg. of iron corroded, (2) the Winkler method for determining dissolved oxygen, and (3) the measurement of water velocity. In the experiments described above the corrosion rate had become constant, and therefore any error in the relation

between oxygen and iron would be the same for all cases and would not vitiate the comparison. Since both the Winkler method for determining oxygen and the method used for measuring velocity are good to within 1 per cent in the ranges, the combined accuracy of the data for comparative purposes is probably within 5 per cent for the results italicized in Table I. Other work on this apparatus (to be published shortly) has shown that the initial high rate of corrosion drops to a constant value after about 4 days of steady operation.

Other Experimental Work

In beaker tests previously carried out in this laboratory with pieces of sheet copper in mechanical contact with steel, it was found that in Cambridge water the distance through which the copper was effective as additional depolarizing surface was about 0.75 cm., while in 0.001 N sodium chloride the limit was not reached in the maximum length studied (6.35 cm.). These distances were determined both by loss of weight of steel and by observation of the distance through which the copper remained untarnished. For example, in the case of Cambridge water the copper remained bright for 0.75 cm. from the point of contact with the steel over the whole period of the tests (1 month). In the salt solution no cases of tarnished copper appeared. In another series of experiments with both plain and platinized platinum foil in mechanical contact with steel in water, substantially the same results were obtained. In neither of these series of experiments was the total corrosion found to be more than proportional to the increased surface afforded for hydrogen depolarization.

Discussion of Results

The results of Table I show the same total rate of corrosion for bare steel as for the same area of steel when copper-plated over 75 per cent of its area. In the latter case this corrosion is localized on the steel alone, as is proved by the absence of any tarnishing on the copper surface and by the deeper corrosion of the exposed area of steel. The corrosion per unit area of exposed steel is therefore four times as great with the copper-plated specimens, since the same total corrosion is concentrated on one-fourth the area. It will be noted that protection of the copper apparently extends over greater distances than the 0.75 cm. observed in beaker tests; this is probably due to presence of pinholes in the plated copper.

These observations confirm the theory that the rate of corrosion is determined by the rate of oxygen diffusion to the metal surface where hydrogen is deposited. Hydrogen deposition in the first experiments occurred over the total surface of steel, and the oxygen diffusing in performed the dual function of depolarizing hydrogen and oxidizing the outer layer of rust from ferrous iron to ferric. In the experiments with copper-plated surfaces oxygen diffusing to the copper served only to depolarize hydrogen, while that diffusing to the steel oxidized both hydrogen and ferrous iron. In any event, the equal corrosion obtained from bare and plated samples demonstrates that under normal conditions the function of the copper surface is very simple and that oxygen diffusion to remove the hydrogen film is the controlling factor. These results cannot be reconciled with the colloidal theory proposed by Friend. Friend states his theory as to the mechanism of natural water corrosion as follows:

In neutral solution, therefore, process No. 2 predominates (corrosion proceeds by catalysis, the catalyst consisting of a colloidal iron hydroxide) and the *rate of corrosion depends almost entirely upon sol formation*. (Italics are the authors'.)

It is obvious that the "colloidal iron catalyst" does not exist on the surface of the copper, and therefore that Friend's theory cannot explain the fact that total corrosion is the same when steel surface is replaced by copper. (The authors do not believe that positive evidence of the catalytic effect of colloidal iron hydroxide on the corrosion of steel has yet been presented.)

The results of the beaker tests on the corrosion of steel in contact with copper and platinum agree with the concept of hydrogen depolarization. Wilson has pointed out the fallacy of applying the ferroxyl indicator test as a measure of natural water corrosion, since an additional depolarizer (ferricyanide) is introduced. The absence of any specific catalytic corrosion effects from platinized platinum in the beaker tests demonstrates that the process is controlled by oxygen diffusion rather than by a rate of chemical reaction.

Conclusions

1—Contact of steel with metals lower in the electromotive series sets up electrolytic action and increases the corrosion of the steel in natural waters. Since under these conditions the rate of corrosion is determined by the rate of hydrogen depolarization by dissolved oxygen, the accelerated corrosion of steel in contact with copper is due to the increased area available for depolarization.

2—Depolarization of hydrogen on the steel surface is limited by the rate at which dissolved oxygen can diffuse from the liquid in to the surface. Hydrogen is deposited also on the adjacent copper surfaces, where it can be oxidized as fast as oxygen is supplied—i. e., just as rapidly as on the same area of steel surface. On portions of the copper at a greater distance from the steel, hydrogen deposits on the copper less rapidly than the potential rate of oxygen diffusion, owing to the increased resistance of the electrolyte in the liquid-metal circuit. These portions are less effective as depolarizers and the effectiveness decreases as the distance from the corroding steel becomes greater. The total effect of the copper is to increase the rate of corrosion of the steel proportionately to the increase in the "effective" area for depolarization. Increased conductivity of the solution permits the copper to act as a depolarizing surface at greater distances from the steel.

3—The older theories of the specific catalytic properties of metals as depolarizers, or of their effects in lowering overvoltage, have no bearing on the normal corrosion of steel in natural water at room temperature.

4—The results offer experimental confirmation of the electrolytic mechanism of corrosion and of Wilson's predictions as to the magnitude of the accelerated corrosion of steel in contact with lower metals.

5—The results cannot be explained on the basis of those theories of Friend[2] or Bengough and Stuart,[3] which involve direct oxidation of the metal or metal ion and which neglect electrolytic action.

Practical Applications

The conclusions from this work are of considerable practical importance in the field of corrosion. It has long been recognized that contact with metals of lower potential, including mill scale and areas of lower potential on the steel itself, accelerates corrosion locally on the steel and often results in severe pitting. This work indicates that the local corrosion is due solely to the fact that the inert surfaces afford extra areas for hydrogen depolarization. Quantitatively, the increased local corrosion is equal to the increased "effective" surface available for oxygen diffusion. It should be understood that these considerations apply to the corrosion of ordinary commercial steels and irons by natural waters. Special cases of resistant ferrous alloys or of special corroding solutions (acids, protective salts, alkalies, etc.) do not fall in this category.

This concept explains why *pitting* is more marked in steels of nonuniform surface structure (areas of differing potential) than when the surface is uniform, *although the actual corrosion*, which is determined by oxygen diffusion over the total area, *is the same.* Similarly, the corrosion of steel in salt solutions results in pitting, since the increased conductivity creates a larger area of hydrogen deposition and depolarization from a central point of attack.

In the case of imperfect coatings of lower metal on steel, such as exist in copper, lead, or tin plate, the amount of corrosion at the point of imperfection is determined by the amount of depolarization afforded by the adjacent plated area. It should, therefore, be possible to calculate the depth of pitting which results from the concentration of this corrosion on a very small area of steel.

Sulfuryl Chloride[1]

I—Principles of Manufacture from Liquid Sulfur Dioxide

By Ralph H. McKee and Carroll M. Salls[2]

Columbia University, New York, N. Y.

Sulfuryl chloride has been one of the medium priced chemicals, but one which, if the cost were cheap enough, would have a much more extensive use.

Basing their work on the modern theories of contact catalysis, the authors have worked out a new method for the manufacture of sulfuryl chloride which promises to place this chemical industrially in the "heavy chemical market" class. Over 99 per cent yield of 98 per cent purity sulfuryl chloride is obtained by direct combination at room temperature in iron apparatus of pure sulfur dioxide and chlorine, and removal of the catalyst by filtration.

N EW uses for any article of commerce are naturally of interest to manufacturers of that article. When the article happens to be a by-product or a waste product, the question of uses assumes greater importance. In some cases where uses have been found for a by-product, the whole process has been stimulated to greater production because part of the profits realized on the by-product have been applied for the purpose of underbidding competitors on the principal product. Competition eventually eliminates profit, but as that state of equilibrium is approached the cost of the principal product is decreased to such a degree that entirely new fields of technology may be opened up in which the principal product can be applied.

Sulfur dioxide and chlorine are both by-products of large-scale operations and, in addition, their toxic action makes it difficult to throw either material away even when that is economically possible. Consequently, a simple method of combining these two materials to make a useful product should be of interest to producers of both materials.

Brallier[3] has recently expressed the urgent need of finding new tonnage uses for chlorine. Over one-half of the installed capacity of the country is lying idle and there is no prospect of utilizing more than a small fraction of this idle equipment. After a review of the production statistics for chlorine products and analysis of possible outlets for chlorine, this author expresses the opinion that manufacturers of chlorine should make a coöperative effort to develop products that will provide some return on the millions of dollars of capital now invested in chlorine plants. Such constructive and united action has certain undeniable advantages in the direction of education of consumers, and it might lead to the building up of consuming capacity to the present producing capacity, or even further.

As for sulfur dioxide, the Chandler Lecturer for 1923[4] at Columbia University brought out very forcibly the reasons for the endless litigation directed against smelter operators by the pooled agrarian interests of the community. One large smelter discharged daily through a single tall stack several thousand tons of sulfur dioxide gas among other waste products. Sulfur dioxide from smelting operations of this kind has injured vegetation for miles around and polluted the air of nearby towns. Consequently, it has been profitable to wash a part of the stack gases and sell the sulfur dioxide in the form of liquid for the cost of recovery. One smelter (Tacoma, Wash.) has sold liquid sulfur dioxide to paper manufacturers at $12.00 a ton.

It is true that combination with chlorine could at best utilize only a small part of this sulfur dioxide, but it might at least mitigate the nuisance of one of the smaller smelters to such a degree as to satisfy the demands of the community.

The writers' investigation has developed a method for the manufacture of sulfuryl chloride which they believe to be much cheaper than methods hitherto used, possibly cheap enough to permit the manufacture of sulfuric acid and hydrochloric acid from it by the addition of water.

When produced at this cost, a long list of applications of this remarkably active chemical would be opened up. Sulfuryl chloride is a vigorous chlorination agent, producing in general—not always—the same products as elementary chlorine. It will be shown in a subsequent article that it is especially applicable in gaseous reactions such as the chlorination of methane, because the reacting mixture cannot explode and undesirable reactions are much more easily controlled. The use of sulfuryl chloride in the manufacture of acetic anhydride has the advantages of forming less chloracetic acid, of supplying exactly the molecular proportions required by the reaction, of eliminating the necessity of removing free sulfur from the product, and of a price differential due to the fact that one of the present processes uses liquid sulfur dioxide and liquid chlorine whereas sulfuryl chloride can be produced, if desired, by the combination of sulfur burner gas with the chlorine as it leaves the electrolytic alkali cells. Chlorosulfonic acid—a material for which there is some demand—can be readily made directly from sulfuryl chloride. Like sulfur chloride, S_2Cl_2, sulfuryl chloride, SO_2Cl_2, vulcanizes rubber; but as yet no method of controlling the action to avoid the production of a brittle product has been found. The literature describes many other po-

[1] Received August 25, 1923.

[2] Goldschmidt Fellow. Paper submitted in partial fulfilment of the requirements for the degree of doctor of philosophy, Department of Chemical Engineering, Columbia University.

[3] *Chem. Met. Eng.*, **28**, 846 (1923).

[4] Swain, This Journal, **15**, 296 (1923).

tentially valuable reactions of sulfuryl chloride, but the few applications mentioned here show sufficiently well that a cheap method for the manufacture of sulfuryl chloride will be instrumental in finding a use for some of the idle chlorine equipment of the country.

Old Processes

Sulfuryl chloride has been prepared by bringing sulfur dioxide and chlorine together in the presence of ethylene,[5] camphor,[6] acetic anhydride,[7] and many other organic compounds such as esters, terpenes,[8] formic acid, glacial acetic acid, charcoal,[9] etc. It is formed slowly when a mixture of chlorine and sulfur dioxide is exposed to sunlight, and more easily by heating chlorosulfonic acid in the presence of a catalyst.[10] It is commonly prepared technically by adding liquid chlorine gradually to liquid sulfur dioxide in which camphor has been dissolved.[11] Pope[12] makes the charcoal method continuous by passing equimolecular proportions of chlorine and sulfur dioxide into a reaction chamber packed with chunks of charcoal, but the method is not one that lends itself to production on a manufacturing scale. The sulfuryl chloride is drained off the bottom or removed as a vapor. Pope says, "due to the low thermal conductivity, it is difficult to maintain a uniform temperature throughout the catalyst in the mass of which the reaction is taking place." This matter is important because the yield of sulfuryl chloride decreases rapidly with rise of temperature. Moreover, in the operation of the Pope patent it is necessary to use equimolecular proportions of the reacting gases.

New Process

Sulfur dioxide and chlorine are continuously dissolved in a body of liquid sulfuryl chloride which carries activated carbon in suspension. When the reacting substances are nearly pure, the combination takes place rapidly and completely at room temperature. The carbon catalyst effects the combination of the dissolved substances, thus producing fresh solvent. Sulfuryl chloride is removed from the carbon by filtration, and the liquid is run directly into iron drums for shipment. Measurement of gases is avoided by the use of a volume of sulfuryl chloride sufficiently large to dissolve the total supply of either gas for several hours if necessary. When dilute gases are used, it is preferable to reduce the vapor pressure of the sulfuryl chloride in the catalyzing chamber by cooling to 0° C. or by adding a solvent. Sulfuryl chloride vapors are removed from the exit gases by absorption in a solvent such as chlorosulfonic acid or pentachlorethane.

Since the carbon effects the reaction by virtue of selective surface action, it is obvious that the process is subject to the ills that attend contact catalysis. It is therefore important to point out as clearly as possible the action of the catalyst under the conditions of this process. The writers have succeeded in defining the peculiar conditions that govern the selection and use of a catalyst having a high activity and a long life.

Catalysis by Active Carbon

Within the past few years several types of highly activated carbon have been put on the market at a reasonable price. It has been known since 1873 that charcoal will catalyze the reaction between sulfur dioxide and chlorine, but in view of Trautz'[13] statements that coconut charcoal has almost no action and that two hundred and seventy out of three hundred experiments with animal charcoal had to be rejected, it was not at all certain that these highly activated carbons would be suitable for a commercial process. Behrend[14] reported a very poor yield when charcoal is used as the catalyst, and decidedly preferred the chlorosulfonic acid method. Apparently, there is some fundamental difference in the several types of carbon other than extension of surface which affects their catalytic activity. It seems to be the opinion of those who have had experience with this reaction that the camphor or the chlorosulfonic acid methods are the best. The first method, however, requires two distillations to produce a pure product, and there is a large loss of camphor due to reaction with sulfuryl chloride and sulfuric acid at the temperature required for distillation. The second method does not use elementary chlorine. A thorough study of the fundamental characteristics of the reaction in the presence of carbon has led the writers to disagree with this prior opinion.

Chlorine and sulfur dioxide are quite soluble in liquid sulfuryl chloride.[15] If carbon is added to a saturated solution of chlorine in sulfuryl chloride, the saturation disappears and the temperature of the liquid increases slightly. The liquid is now capable of dissolving more gas. The dissolved chlorine has been adsorbed by the carbon in a manner similar to the adsorption of acetic acid from aqueous solution. The same thing happens in a saturated solution of sulfur dioxide in sulfuryl chloride. If the carbon contains other gases, such as oxygen, nitrogen, carbon dioxide, or hydrogen chloride, they are almost completely displaced when brought in contact with either chlorine or sulfur dioxide. Hence this is an example of selective adsorption. The greater part of the foreign gas is displaced immediately, but the last part is displaced more slowly. The concentration of foreign gas above the carbon must be decreased to a very small value before the last trace is removed.

If sulfuryl chloride is saturated with chlorine and sulfur dioxide in equimolecular proportions and carbon is added, the saturation disappears as before; but in this case it is not possible to saturate the liquid again by slowly passing in chlorine and sulfur dioxide in equimolecular proportions. The solute reacts to produce the solvent. This process goes on indefinitely and the number of grams of carbon per cubic centimeter of solvent continuously decreases, but the velocity of reaction remains constant provided that the concentration of dissolved gases stays constant and that the carbon surfaces remain intact. Consequently, the carbon has appeared in the role of a catalyst.

It may be possible to learn a little more about contact catalysis from this rather novel system. Such information would be of first importance to the writers, not in order to aid in the development of a general theory of catalysis by comparing their results with those of others, but to find out which theory of catalysis best explains the characteristics of this particular reaction. Then the facts that have been gathered around this theory will be more likely to aid in establishing the conditions necessary for the most economical operation of the process.

Faraday's conclusion[16] concerning the combination of gases in the presence of platinum, stated in modern language, is: Two reacting gases are absorbed by the platinum and, being thus brought into intimate contact with each other,

[5] Regnault, *Ann. chim. phys.*, **69**, 170 (1838).
[6] Schultze, *J. prakt. Chem.*, **24**, 168 (1881).
[7] Aktien-Gesellschaft f. Anilin Fabrik, German Patent 226,218 (1909).
[8] Durrans, British Patent 124,542 (1918).
[9] Melsens, *Compt. rend.*, **76**, 9204 (1873).
[10] Wohl and Ruff, *Ber.*, **34**, 3509 (1901); German Patent 129,862 (1902).
[11] Badische, German Patent 138,531 (1901).
[12] Pope, British Patent 122,516 (1918).

[13] *Z. Elektrochem.*, **14**, 534 (1908).
[14] *J. prakt. Chem.*, [2] **15**, 23 (1877).
[15] Schultze, *Ibid.*, [2] **24**, 176 (1881).
[16] Experimental Researches, Sixth Series, Vol. I, p. 165; also paragraph 361.

proceed to react. Thomson[17] has shown that the surface tension of the absorbed film changes as the chemical reaction proceeds. The physical state of the catalyst itself changes during the reaction. Crystalline manganese dioxide used as a catalyst for the potassium chlorate decomposition becomes amorphous.[18] Clean platinum gauze used as a catalyst in the oxidation of ammonia becomes covered with a spongy deposit. Finely divided metals for hydrogenation change[19] their surface structure. These examples show that there is an interchange of energy between the catalyst and the reacting substances. Consequently, in the case of carbon it is probable that the energy which appears at the surface due to fine subdivision leaves the surface, is added to the driving force of the reaction, and returns to the catalyst when its work is done. This energy would appear as the excess of heat of absorption over heat of compression when there is no substance present with which the absorbed film can react. When a reaction takes place the energy would be returned to the catalyst by release of the product from the high pressure existing in the absorbed film.

Without committal concerning the mechanism of catalysis, we may, for the present, consider a positive catalyst as a substance that is capable of delivering a certain amount of energy per unit of time, and apply it in the same place and in the same direction as the energy that tends to drive the chemical reaction, thus causing an increase in the velocity of the chemical reaction. The mechanism may consist in the formation of intermediate chemical or other compounds, but that is not essential to such a conception of catalytic activity.

A chemical reaction results in a change of spatial relations through the application of forces associated with the constituent particles, the work balance usually appearing as the heat of reaction. The introduction of a time factor gives power. Hence catalytic activity has the dimensions of power.

In general, a small quantity of catalyst is sufficient to act upon a very large quantity of the reacting substances, but the *rate* at which the reacting substances will be converted does depend on the quantity of catalyst present. A definite quantity of catalyst can supply a certain maximum impulse and no more. The increase in the rate of hydrolysis of methyl acetate by increasing quantities of acetic acid is the best known example of this fact. A change in the extent and character of contact surfaces is known to affect the efficiency of the catalyst in heterogeneous systems.

The impulse supplied to a mixture of chlorine and sulfur dioxide by a unit weight of carbon is much smaller than is ordinarily the case with metallic catalysts—i. e., a comparatively large weight of carbon must be used to produce the same number of pounds of product per hour. One gram of the best carbon working at full capacity will produce 0.5 pound of sulfuryl chloride per hour, whereas 1 gram of platinum will produce several hundred pounds of sulfur trioxide per hour. The necessity for using this comparatively large quantity of catalyst makes it possible to subject the catalyst to ordinary quantitative manipulations such as purification and weighing with a percentage accuracy of the same magnitude as the rest of the experiment, and still keep within the limits of laboratory apparatus in measurements on the product and on the gases which go to make the product. The measurement of the maximum impulse imparted by several types of adsorbent carbon is described below. The fact that the reaction proceeds at a very slow rate in the absence of carbon makes it possible to stop the reaction at any time by a simple filtration through paper. The data

on relative carbon activity supply a standard upon which to base calculations concerning the probable cost for catalyst, capacity per unit volume of reaction chamber space, and the yield of sulfuryl chloride.

RELATIVE CARBON ACTIVITY

A saturated solution of chlorine and sulfur dioxide in sulfuryl chloride at 25° C. contains 5 per cent of dissolved gases. At equilibrium at 25° C. sulfuryl chloride contains 1 per cent of dissolved sulfur dioxide and chlorine. Unsaturated sulfuryl chloride dissolves chlorine and sulfur dioxide at a rate far above the capacity of the meters used by the writers.[20] Carbon adsorbs chlorine and sulfur dioxide from a saturated solution very rapidly, but by working with a small sample of carbon it is possible to supply the gases at such a rate that the vapor pressure of the liquid remains at 760 mm.—i. e., the liquid remains saturated. Then the meter readings give directly the rate at which a known weight of carbon is producing a combination of chlorine and sulfur dioxide at any instant.

Although the chlorine and sulfur dioxide gases taken from cylinders were further dried by sulfuric acid and by passing through a tube containing phosphorus pentoxide on glass beads, it was found that the catalytic activity of the carbon gradually decreases, probably due to amounts of impurities too small for detection by the ordinary methods of gas analysis. It may be due to a change in the physical constitution of the catalyst itself, but this is improbable as the carbon can be reactivated by a simple washing and drying.

In order to determine the relative activity of several types of activated carbon, a series of experiments with each carbon was carried out in which the rate of supply of the gases was constant and the weight of carbon changed until the smallest weight was found that would cause the vapor pressure of the solution to remain below 760 mm. for 1 hour. Comparison of the minimum weights of carbon required thus expresses the relative activity of these carbons with sufficient accuracy, considering the large differences that were found.

The chlorine and sulfur dioxide gases from the meters were mixed in equimolecular proportions and passed into a 500-cc. flask immersed in a thermostat at 20° C. The flask contained the same quantity of redistilled sulfuryl chloride in each experiment. The sample of dry carbon was suspended in the sulfuryl chloride. The gas mixture was admitted to the flask through a 3-mm. ($^1/_8$ inch) i. d. glass tube at a constant rate of 147 liters per hour equivalent to 453 grams (1 pound) of sulfuryl chloride per hour. This made the linear velocity through the inlet tube 51.5 meters per second. The gases were completely absorbed—i. e., the yield of sulfuryl chloride was approximately 100 per cent of theory. In fact, a slight suction persisted in the outlet tube during the greater part of the experiment. In the absence of a catalyst the amount of liquid taken for each experiment would be, at this rate, saturated with the gas mixture in 2 minutes. Then the gas mixture would come through the liquid unchanged. The gases rising part way through the liquid produced a vigorous agitation. Since the number of grams sulfuryl chloride formed per minute was constant, thermometers inside and outside of the flask showed nearly a constant temperature difference of 10° C.

The minimum weight of catalyst required to bring 453 grams (1 pound) per hour of an equimolecular mixture of chlorine and sulfur dioxide to equilibrium is given in Table I.

Silica gel does not catalyze the reaction between dry chlorine and sulfur dioxide. It adsorbs a gas by virtue of

[17] "Application of Dynamics to Physics and Chemistry," **1888**, pp. 206 and 236.

[18] Sodeau, *J. Chem. Soc.* (London), **77**, 137, 717 (1900); **79**, 247, 939 (1901); **81**, 1066 (1902).

[19] Sabatier, "La catalyse en chimie organique," **1913**, p. 55.

[20] Benton, THIS JOURNAL, **11**, 623 (1919); Arndt, "Handbuch der physikalisch, chemischen Technik," **1915**, p. 230; Oberfell and Mase, THIS JOURNAL, **11**, 294 (1919).

capillary attraction only, and therefore the adsorbed film does not make effective contact with the surface. The energy cannot leave the surface.

TABLE I

		Grams
Norit		1.8
Darco		2
McKee carbon		8
Filtchar		15
Blood charcoal		25
Camphor		30
Animal charcoal		70
Coconut charcoal		75
Whetlerite		90
Batchite		110
Oak charcoal		140
Birch charcoal		160
Nitrobenzene		600
Silica gel	Over	20,000

Inspection of the table shows that those carbons that are capable of delivering a relatively large impulse are all decolorizing carbons, and that acid-treated carbons are more active than alkaline carbons. When the energy exists on the surface of the carbon in the form of a positive charge, there is apparently a greater acceleration of the reaction between negative radicals.

The highly activated carbons that were developed during the war for the purpose of absorbing gases were found to possess comparatively small catalytic activity for this reaction. Decolorizing carbons such as Norit and Darco have about forty times as great activity as a good coconut charcoal obtained from the Edgewood Arsenal. This coconut charcoal had a 40-minute chloropicrin activity, accelerated test. Whetlerite, a copper-impregnated charcoal, had a 30-minute activity, accelerated test.

The great difference between the catalytic activity of gas carbons and decolorizing carbons can be explained on the basis of diameter and length of capillaries. The uncombined chlorine and sulfur dioxide must diffuse through the sulfuryl chloride that fills the capillaries in order to reach the catalyzing surface, where combination takes place rapidly and a corresponding amount of sulfuryl chloride is pushed out of the capillary. When the capillary is long and narrow, as in gas carbons, the solute diffuses to the walls before it can penetrate very far. Hence the bottom of the capillary must be filled with pure sulfuryl chloride and the concentration of solute continuously increases as the entrance is approached. The result is that only the carbon near the entrance of the capillary is exerting its catalytic action. A fish-scale structure, on the other hand, as claimed for Darco carbon, offers much less opportunity for long capillaries, and consequently a much larger proportion of the carbon is active.

The carbon is very easily separated from the sulfuryl chloride by filtration through paper. The sulfuryl chloride runs through faster than clear water. The filtrate is a light yellow, transparent liquid containing over 98 per cent SO_2Cl_2. The remainder is free chlorine and sulfur dioxide. This is pure enough for most purposes, but if a still purer product is desired the liquid may be distilled and the first 20 per cent of the distillate reworked. The remaining 80 per cent distils between 60° and 70° C. as a water-white distillate. There is no distillate above 70° C. The pure product may be distilled with less than 1 per cent loss, showing that sulfuryl chloride is a stable compound. No evidence of decomposition could be detected in several 8-pound bottles that had been standing for 2 years in diffused sunlight.

CATALYST POISONS

Moisture, sulfuric acid, chlorosulfonic acid, and nitrobenzene poison the catalyst. Carbon tetrachloride, pentachlorethane, tetrachlorethane, benzene, kerosene, etc., do not poison the catalyst. Moisture hydrolyzes some of the

sulfuryl chloride, producing sulfuric acid, which forms a protective film over the surface of the carbon. A catalyst that has been poisoned by the addition of water can be completely regenerated by washing thoroughly with water and then drying in any suitable manner. Suitable methods of drying are: heating at 150° C. preferably *in vacuo;* heating to 500° C.; heating in a current of a dry gas such as hydrogen chloride, air, chlorine, sulfur dioxide, or carbon dioxide; washing with alcohol and ether. Absorption of moisture from the air can be prevented by saturation of the dried catalyst with chlorine. This also prevents scattering of the catalyst when sulfuryl chloride is added. Since a good grade of decolorizing carbon can be obtained for 7 cents a pound, it is probably advisable to throw the catalyst away when it becomes inactive. Table I shows the cost for catalyst should be less than 40 cents per ton of sulfuryl chloride.

MATERIALS OF CONSTRUCTION

Sulfuryl chloride has almost no action on iron at room temperature. The same applies as well to dry sulfur dioxide and dry chlorine. In the experimental work iron vessels in continuous service for months have shown almost no corrosion. Sulfuryl chloride is commonly shipped in ordinary sheet steel drums.

COST OF OPERATION

Simplicity, small capital investment, and flexibility of operation are the outstanding features of the equipment required for the manufacture of sulfuryl chloride from liquid sulfur dioxide. The total cost of operation, which includes the cost of the carbon at 7 cents a pound, water, steam, and air, labor at $5.00 a day, repairs, overhead, interest on investment at 6 per cent, and amortization over a period of 3 years, is estimated at about $10.00 per ton of sulfuryl chloride on a production of 10 tons of sulfuryl chloride per day. Taking 5 cents per pound as the cost of liquid sulfur dioxide in ton lots and 2.5 cents for chlorine as it comes from the cells, the cost of sulfuryl chloride by this new process should be less than 5 cents per pound.

If sulfuryl chloride is to be used to make hydrochloric acid, liquid sulfur dioxide is too expensive at the present time. In another paper the use of the cheap sulfur burner gas in the manufacture of sulfuryl chloride will be described.

Wood Blocks to Measure Soil Moisture

The study of soil moistures has heretofore largely been left to laboratory investigators and omitted from forest field work because of the absence of any sucessful methods of measuring the moisture applicable to the field. Recent experiments, however, have introduced a method of field measurements which appears to be both simple and effective. W. G. Wahlenberg, forest examiner at the Priest River Forest Experiment Station in Montana, has for some time been employing cypress blocks for this purpose. These may be left in the soil for a short time and may then be easily remeasured. The blocks are very carefully air-dried before being used, and therefore absorb water very readily. The resultant changes in volume are read with the help of a micrometer. A definite relation exists between the swelling of the blocks and the amount of water absorbed, and it is believed that a corresponding relation can be worked out with the soil moisture content. Mr. Wahlenberg has obtained similar results with an ordinary lead pencil, left in the soil for a time and afterwards weighed.

Course in Dye Testing

Persons desiring to take the laboratory course in textile chemistry and dyeing which is being given two evenings per week at the Brooklyn Technical Evening School, should register at once. The course will comprise the methods of dye testing, application of all classes of dyes to all fibers, fastness test, color matching, properties of textiles, etc. The instructor is one of the dye experts of the U. S. Government, passing on the competitiveness of imported dyestuffs.

A Chemical Study of Canned Salmon[1,2]

I—Variations in Composition of the Pacific Coast Salmons and Steelhead Trout as Influenced by Species and Locality where Caught

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The characteristics of the five species of Pacific Coast salmon, the Atlantic salmon, and the steelhead trout, both before and after canning, are described briefly.

The composition of the individual salmon varies greatly in different parts of its body. For this reason special packs of salmon in which each can contained approximately the same section of an individual fish were prepared. Of these, 659 cans were analyzed either separately to determine individual composition, or in composite samples of six cans to determine average composition.

Since special packs could not be obtained from all districts, a number of samples from the regular commercial packs were obtained and 127 cans analyzed. The results for special and commercial packs do not vary greatly, the commercial packs averaging slightly higher in calorific value.

A striking variation (from 6.7 to 27.2 per cent) was found in the fat content of different salmon of the same species caught in the same locality. A yearly variation in the average fat content of the chinook and chum salmon running into the Yukon River is brought out by the analyses, which covered the runs of three years. This variation in the case of the chum ranged from 6.45 to 15.19 per cent.

The variation in composition of the different species in all the principal American packing centers has been brought out in a series of tables. An inspection of these tables will also show the variation between the different species in each of the districts.

Since the protein represents to a large extent the living tissue or protoplasm, the percentage of protein did not vary greatly between individual fish, different species, or fish from different localities, the extreme variation being from 17.18 to 22.81 per cent.

The salt-free ash was uniform in percentage when the bones were carefully removed.

The fat content varied greatly between individual fish, between species, between localities, and between years, the extreme variation being from 2.65 per cent to 27.26 per cent.

The moisture content also varied greatly, but inversely with the fat—that is, as the fat increased the moisture decreased.

The food value is given in Calories, and on account of the high calorific value of fat this constituent largely determines the food value which, in the case of the individual fish analyzed, varied from 490 to 1511 Calories.

T HE canning of salmon forms one of the most important industries of the Pacific Coast of North America from the Sacramento River northward to the Yukon River in Alaska. The following table gives the total number of cases packed in this region since the inception of the industry in 1864.

TABLE I—PACK OF CANNED SALMON SINCE THE INCEPTION OF THE INDUSTRY (NORTH AMERICAN COAST)

Period	Cases (48 Pounds per Case)
1864 to 1871	504,000
1872 to 1881	5,013,861
1882 to 1891	11,709,915
1892 to 1901	26,864,515
1902 to 1911	43,244,258
1912 to 1921	73,377,223
1922	6,443,349
TOTAL 1864 to 1922	167,157,121
ESTIMATED 1923 pack	7,750,000

Recent years have witnessed the introduction and gradual growth of the industry on the coasts of Siberia and northern Japan, and the annual pack from these sources now amounts to approximately 750,000 cases. The total annual pack of canned salmon averages between 7,000,000 and 8,000,000 cases, and represents a value to the canner of about $55,000,000 to $65,000,000.

The salmon filled an important position in the economic life of the lands bordering the North Pacific Ocean long before the white man entered the region. The white men soon learned to value the salmon and preserved them by salting and drying. The first salmon cannery was established on the Sacramento River, California, in 1864, and the first packer peddled his cans from door to door in San Francisco

to introduce them. From this point the industry spread to the Columbia River in 1866, to Puget Sound in 1877, to Alaska in 1878, and to British Columbia in 1881. Rather recently, canneries have been built along the Siberian and Japanese coasts. Altogether, over two hundred canneries were operated during the season of 1923.

At present the per capita consumption of canned salmon in the United States is about 1.7 pounds, which accounts for 3,900,000 cases of the total American pack of 1922. The remaining 1,330,000[†] cases were exported to various other countries, notably to the United Kingdom, which is our best customer for canned salmon, and to Australia and also the Orient. The amount of salmon exported annually amounts to approximately 25 per cent of the pack of the American-owned canneries. British Columbia, with a pack of 1,300,000 cases in 1922, and Siberia, with 720,000 cases, are our keen competitors in the United Kingdom and Continental markets.

The Canning of Salmon

As the salmon are brought into the cannery they are fed either by conveyor or by hand to a table near the fish dressing and cleaning machine known as the "iron chink," so named because it does the work of several Chinamen. This is a complicated machine which, by a series of knives and brushes, rapidly removes the heads, fins, tails, and entrails of the fish under running water. Any blood, slime, loose membranes, etc., left by the iron chink are washed off either by hand or in a "sliming machine." The cleaned fish are then fed into a cutting machine, where rapidly revolving circular knives cut them into slices of the proper length to fill the cans. The empty cans are fed into an automatic filling machine, which fills each can with the proper amount of fish and salt ($1/4$ ounce in 1-pound cans). A recent type of filling machine cuts the fish into slices, salts the cans, and fills them at the rate of 115 to 125 per minute. Many of the flat cans are

filled by hand; this is particularly true of the chinook and sockeye salmon. The filled cans are inspected for fill and appearance as they pass on a belt to the "clincher machine," where the tops are loosely crimped on the cans to prevent particles of fish from getting out of the cans and condensation water from getting into the cans during their passage, lasting several minutes, through live steam in the "exhaust box." The function of the exhaust is primarily to heat the filled cans sufficiently to drive out some of the air and gases, thus insuring the presence of sufficient vacuum in the can after cooking to keep the ends concave under all conditions of temperature and altitude.[1],* The cans pass from the exhaust box to the "closing machine," which rolls the tops on very firmly, hermetically sealing the can. The sealed cans, in iron trays on small cars, are rolled into horizontal retorts where 1-pound cans are cooked with live steam at a pressure of 10 to 13 pounds (240° to 245° F.) for about 90 minutes. Half-pound cans are cooked from 70 to 75 minutes at the same temperature. After cooking, the cans are cleaned, cooled, defective ones removed, and the rest labeled. Salmon is commonly packed in 1-pound tall, and 1-pound and 1/2-pound flat cans. A few 1-pound and 1/2-pound oval cans are also packed.‡

SPECIES

Five species of salmon are found in the Pacific Ocean, all belonging to the genus *Oncorhynchus* (meaning "hooked snout"). The Atlantic salmon is quite distinct and belongs to the genus *Salmo*. It was formerly found in great numbers along the North Atlantic coast and in the rivers of that region, but through a number of causes not many remain. However, a few are being canned in Newfoundland and Labrador. The steelhead trout found on the Pacific Coast also belongs to the genus *Salmo*, but is sometimes incorrectly classed as a salmon. Each of the seven species of fish mentioned above is known by its scientific name and some of them by several common names, as shown in Table II. The use of several names for the same species is confusing to the laymen and even at times to people familiar with the industry. Fishermen have been known to argue at great length upon the relative merits of the silver and coho, for instance, not knowing that both were referring to the same fish. In Table II the most commonly accepted name in the different regions is given, but all the other names may occasionally be heard.

* Numbers in text refer to bibliography at end of article.
‡ The reader who is interested in the inspection of canned salmon, either from the commercial or pure food standpoint, is referred to the following technical publications: Clark, Clough, Fellers, and Shostrom, "Examination of Canned Salmon," *Pacific Fisherman*, 21, Nos. 9 and 10 (1923) (reprinted in pamphlet form); Clough, "A Biochemical Study of Pacific Coast Salmon with Particular Reference to the Formation of Indol and Skatol during Decomposition," publication Puget Sound Biological Station, 3, No. 67, 195 (1922), University of Washington, Seattle.

TABLE II—SCIENTIFIC AND LOCAL NAMES OF THE DIFFERENT SPECIES OF SALMON AND STEELHEAD TROUT

SCIENTIFIC NAME	PUGET SOUND	COLUMBIA RIVER	ALASKA	OTHER NAMES
Oncorhynchus nerka	Sockeye	Blueback	Alaska red (sockeye)	Quinault, redfish, red salmon
Oncorhynchus tschawytscha	Spring	Chinook	King (chinook)	Tyee, quinnat
Oncorhynchus kisutch	Coho, silver	Silver	Medium red, coho	Silversides
Oncorhynchus gorbuscha	Pink	Pink	Pink	Humpback
Oncorhynchus keta	Chum	Chum	Chum	Keta, dog, calico
Salmo gairdneri		Steelhead trout		
Salmo salar		Atlantic salmon		

These species of fish differ greatly in size, shape, color of flesh, and distinguishing marks. The largest and most widely distributed is the chinook, or king salmon, which is found all along the northern Pacific coastline from central California to northern China. The average weight of this fish is about 22 pounds, but specimens have been taken weighing well over 100 pounds. The flesh is usually red, but a portion of the fish, ranging from 2 or 3 per cent in some localities to as high as 20 per cent in southeastern Alaska, or 90 per cent on Puget Sound near the end of the season, have no color in their flesh. The flesh of other individuals is colored in many peculiar ways, sometimes varying from a deep red near the gills to white at the tail, or having one side red and the other white or pink, etc. No explanation has been found for these variations. Since color is one of the most important qualities influencing the sale of salmon, the chinook salmon is graded by color, the reddest fish bringing the highest price. Those individuals having little or no color in the flesh are either salted and smoked, or, if canned, are sold as chum salmon at a much lower price than canned red chinook salmon commands.

The sockeye or red salmon covers about the same geographical range as the chinook, except that it is not found so far south. It is a much smaller fish than the chinook, averaging about 6 pounds. On account of its deep red color it is in great demand for canning purposes, and the canned product commands a good price, varying considerably according to the district of packing. Puget Sound sockeye usually brings the highest market price for this species.

The coho is also called the medium red salmon, because the color of its flesh is between that of the red and the pink species. Its range is practically the same as that of the chinook, but it is not found in very large numbers in any place. It is an excellent food fish, but on account of its lighter color has a much lower market value than the red, although its food value averages practically the same.

The flesh of the pink salmon is lighter in color than that of the medium red, but it has very nearly the same market value. It is the smallest of the salmons, averaging about 5 pounds. It matures early, returning to fresh water to

TABLE III—DESCRIPTION OF DIFFERENT SPECIES OF SALMON AND STEELHEAD TROUT BEFORE CANNING

SCIENTIFIC NAME	WEIGHT Maximum Pounds	WEIGHT Average Pounds	LENGTH INCHES	SHAPE OF BODY	SIZE OF SCALES	COLOR OF RAW FLESH	DISTINGUISHING MARKS
Oncorhynchus nerka (red salmon)	11	6	15 to 32	Symmetrical	Medium	Deep red	No spots
Oncorhynchus tschawytscha (chinook salmon)	100	22	24 to 60	Robust	Large	Red to white	Back, dorsal fin, and tail covered with round, black spots
Oncorhynchus kisutch (coho salmon)	25	9	20 to 33	Elongated and flattened	Medium	Light red	Faint spots on back, dorsal fin and upper part of caudal fin
Oncorhynchus gorbuscha (pink salmon)	14	5	17 to 27	Slender	Small	Pink	Large, oblong, black spots all over tail and on back
Oncorhynchus keta (chum salmon)	16	10	25 to 35	Robust	Large	Light pink to grayish white	No spots
Salmo gairdneri (steelhead)	45	12	....	Slender	Large	Very pale pink	Small black spots on dorsal, adipose and caudal fins
Salmo salar (Atlantic salmon)	40	15	....	Symmetrical	Rather large	Light pink	Numerous black spots on head-body, and fins

TABLE IV—DESCRIPTION OF DIFFERENT SPECIES OF SALMON AND STEELHEAD TROUT AFTER CANNING

SCIENTIFIC NAME	COLOR OF OIL	COLOR OF FLESH	TEXTURE OF FLESH	SIZE OF FLAKES	SIZE OF VERTEBRAE	SIZE OF SCALES	MARKET VALUE[a]
Oncorhynchus nerka (red salmon)	Deep red	Brick-red	Very firm	Small, thin	Small	Medium	$2.25 to 4.50
Oncorhynchus tschawytscha (chinook salmon)	Light red through yellow to almost white	Bright-red to white	Soft	Large, thick	Large	Large	1.75 to 3.50
Oncorhynchus kisutch (coho salmon)	Light red to yellowish pink	Light red with orange shade	Rather firm	Large to medium, thick	Large	Large	1.35 to 1.50
Oncorhynchus gorbuscha (pink salmon)	Pink to light yellow	Pink	Inclined to be soft	Small, thin	Small	Small	1.15 to 1.25
Oncorhynchus keta (chum salmon)	Light pink with orange shade to yellow	Light pink to grayish white	Firm	Medium	Medium	Medium	1.15 to 1.20
Salmo gairdneri (steelhead)	Light orange to yellow	Light orange	Rather soft	Large, thick	Large	Large	1.25 to 1.50
Salmo salar (Atlantic salmon)	Light orange to yellow	Light orange	Rather soft	Large, thick	Very large	Large	....

a Packers' opening price for 1923 based on 1 dozen 1-pound cans.

spawn when two years old, whereas the other varieties usually return in their third or fourth year, with the exception of a small percentage which return in their fifth or sixth year. The males, before spawning, develop hooked jaws and become humped or distorted in shape, thus accounting for the name "humpback" salmon.

The chum salmon is the lowest in market value of the five species, owing largely to its very pale color and, to a lesser extent, to the small amount of fat that it usually contains. Specimens have been analyzed, however, having a color equal to the average pink salmon and as much fat as the average chinook. Although inferior for canning, for many other uses, particularly for drying, it is esteemed as highly as the other species. On account of its low fat content it is more easily dried and frequently used as dog food in the far north, and has therefore acquired the name of "dog" salmon.

The steelhead trout differ from the Pacific salmon in one very important particular—death does not follow the act of spawning, but the same fish may spawn several times. In this respect they resemble the Atlantic salmon. The flesh is very pale in color, and for this reason few are canned. Most of those caught are sold in the fresh fish market or frozen. They are exceptionally rich in fat and consequently high in food value.

Other distinguishing characteristics are given in Table III. The distinguishing characteristics of the different species after canning are given in Table IV.

THE SPAWNING MIGRATION

The five species of Pacific salmon vary somewhat in habit and life history, but all are alike in one essential—they are anadromous; that is, when they reach maturity each species comes surging in from the sea to some fresh water stream or lake to spawn, after which nearly all of them die and thus complete their life history. The fertilized eggs hatch after an interval of several weeks and the young fish spend some time in fresh water before going to their ocean home. The steelhead and Atlantic salmon also spawn in fresh water, but death does not follow the act of spawning. The same fish may spawn several times. It is believed that the Pacific salmon do not commonly feed after entering fresh water. Therefore, it is the stored fat and protein that are transformed into the necessary energy or transferred to the reproductive organs. There is consequently a gradual deterioration in the quality of the fish during the migration. These changes have been investigated by C. W. Greene[2,3] and Carl H. Green.[4] Their researches show that the flesh of salmon caught in the upper waters of the Columbia River is lower in both fat and protein than the flesh of those caught near the mouth. Inversely, the percentage of moisture is higher. The salmon industry depends to a large extent upon this spawning migration, for it is only at this time that the salmon

may be caught in quantity. Coming in from the open sea in immense schools, they fall an easy prey to various types of nets and traps.

DESCRIPTION OF SAMPLES USED

While canned salmon forms a very important item among the food resources of the nation, very little work has been done to determine its food value, and few analyses appear in the literature. Atwater[5] in 1888 gave a summary of the analyses which had been made up to that time. Most of these were of the Atlantic salmon. Cobb[6] gives a review of the literature, including analyses from Langworthy,[7] Wiley,[8] Knisely,[9] Loomis,[10] and Elliott and Clemens.[11] Most of these analyses represent cans of salmon taken from the retailers' stocks and about whose history little or nothing was known. On account of the inadequate information available on the composition and food value of canned salmon, an extensive investigation was undertaken. The results are reported in this paper.

There is a wide variation in the composition of different parts of the same salmon. This variation is brought out very clearly in Table V.

TABLE V—VARIATION IN COMPOSITION OF DIFFERENT PARTS OF SAME FISH

DESCRIPTION OF SAMPLE	Moisture Per cent	Ether Extract or Fat Per cent	Salt-free Ash Per cent	Protein (N × 6.25) Per cent	Calories per Pound
Spring salmon having deep red flesh:					
(1) Section cut through neck, included belly and back	60.53	20.15	1.19	17.62	1178
(2) Section cut through tail	68.13	11.11	1.12	17.93	802
Spring salmon having white flesh:					
(1) Section cut through neck, included belly and back	64.29	15.10	1.40	19.00	990
(2) Section cut through tail	70.20	8.10	1.31	19.93	712

This variation in composition of commercial cans of salmon purchased in the market renders them unsuitable for a series of analyses designed to bring out a comparison between different species and localities. For this reason special packs of canned salmon were prepared in various canneries for analysis. In these packs the same section of flesh was used from each individual fish and the factor of varying composition in different parts of a fish was eliminated. The part of the salmon used was the second cut from the head and included the entire cross section of the fish. Through the coöperation of some of the salmon canners[§] these special

§ Credit is due to the following canning companies for their cordial and indispensable aid in obtaining these special packs or in furnishing authentic commercial cans from the various districts: Alaska Packers Association, Libby, McNeill & Libby, Columbia River Packers Association, Warren Packing Co., Carlisle Packing Co., Pioneer Packing Co., Seufert Brothers Co., P. J. McGowan & Sons, Macleay Estate Co., and Klamath River Packers Association.

samples of the five species of Pacific salmon were secured from every important canning district in the United States and Alaska. Special samples of steelhead trout were obtained from the Columbia River. In addition to the special samples many commercial cans of salmon selected without regard to the part of the fish represented were also analyzed. These commercial samples included all species of Pacific salmon, the steelhead trout, and the Atlantic salmon.

FIG. 1—SKETCH MAP SHOWING LOCALITIES FROM WHICH SAMPLES WERE OBTAINED

ALASKA	Southeastern Alaska
Western Alaska	Copper River
Yukon River	(14) Abercrombie[a]
(1) Andreafski[a]	(15) Taku[a]
Bristol Bay	(16) Chatham[a]
(2) Nushagak River	(17) Wrangell
(3) Kvichak River	(18) Loring
(4) Naknek River	(19) Metlakatla[a]
(5) Egegik River	(20) Tokeen[a]
(6) Ugashik River	UNITED STATES
Central Alaska	Puget Sound
Alaska Peninsula	(21) Blaine, Wash.
(7) Herendeen Bay[a]	(22) Bellingham, Wash.[a]
(8) Isanotski Straits[a]	Washington Coast
(9) Chignik River	(23) Quinault River[a]
Kodiak Island	Columbia River
(10) Karluk River	(24) Near mouth
(11) Alitak Bay	(25) 200 miles from mouth
Cook Inlet	Oregon Coast
(12) Kenai River[a]	(26) Nehalem River[a]
(13) Kasilof River	(27) Coquille River
	(28) Rogue River
	California Coast
	(29) Klamath River

[a] Commercial samples, no attention being paid to the section of the fish included in the can.

Fig. 1 is a sketch map showing the places from which the samples were obtained. These places are numbered consecutively from north to south beginning with the Yukon River, Alaska, and ending with the Klamath River, California. In all the tables the districts bear the same numbers. The only samples whose source is not shown are the Atlantic salmon from Newfoundland and Labrador.

METHODS

HISTORY OF SAMPLES—As already stated, most of the special packs of salmon were prepared by the canners in the different districts. A few were prepared by inspectors of the National Canners Association. Some districts were represented by these special packs either inadequately or not at all. In such cases commercial cans of salmon were obtained from the canners in those districts. All the samples were received soon after the close of the canning season and were analyzed within a few months after being canned. Each of the samples as received consisted of from 12 to 48 cans.

PREPARATION OF SAMPLE FOR ANALYSIS—From three to five cans of each sample were analyzed separately to show the variation between individual fish, and then six additional cans were composited and analyzed. Finally, the results of the separate and composite analyses were averaged, and these are the figures that appear in the tables.

The gross weight of the can and contents was determined and the liquid drained from the can into a graduated cylinder, where it was allowed to stand for a few minutes until the oil rose to the top. The liquid and oil were measured in cubic centimeters and recorded. The can and solid contents were then weighed, and finally the can alone. Practically all the bones were removed from each can of salmon and weighed separately. The flesh was then passed through a meat grinder and the liquid and oil added. Some of the ground flesh was used to remove any oil adhering to the graduated cylinder, and the entire contents of the can, with the exception of the bones, was mixed and passed through the grinder two or three times more. A sub-sample of about 100 grams was placed in a tightly stoppered bottle and the analytical samples were weighed out as soon as possible.

In the case of the composite samples the same procedure was followed as with the individual can samples, and the contents of the six cans thoroughly mixed by grinding and stirring.

ANALYSIS—The methods used for the determination of moisture, total nitrogen, fat, ash, and sodium chloride were those adopted by the Association of Agricultural Chemists and published in the "Methods of Analysis," revised edition, 1919. Total nitrogen was determined by the method of Kjeldahl and Gunning, and protein was calculated by the use of the factor 6.25.

Calories were calculated by the factors of Rubner—on the basis of 1 pound, each per cent of protein is equivalent to 18.6 Calories, and each per cent of fat to 42.2 Calories.

RESULTS

The results of the several hundred analyses have been arranged in a number of tables designed to bring out the variation in composition within each species and the variation between the different species. Each of the results given is the average of several analyses. Individual fish within the same species and at the same locality differ greatly in composition. This is brought out in Table VI, which gives the composition of chinooks caught near Ilwaco, Washington, at the mouth of the Columbia River. Chinooks on the Columbia River are usually packed in three or four grades, according to color and fatness of the flesh, No. 1 grade being
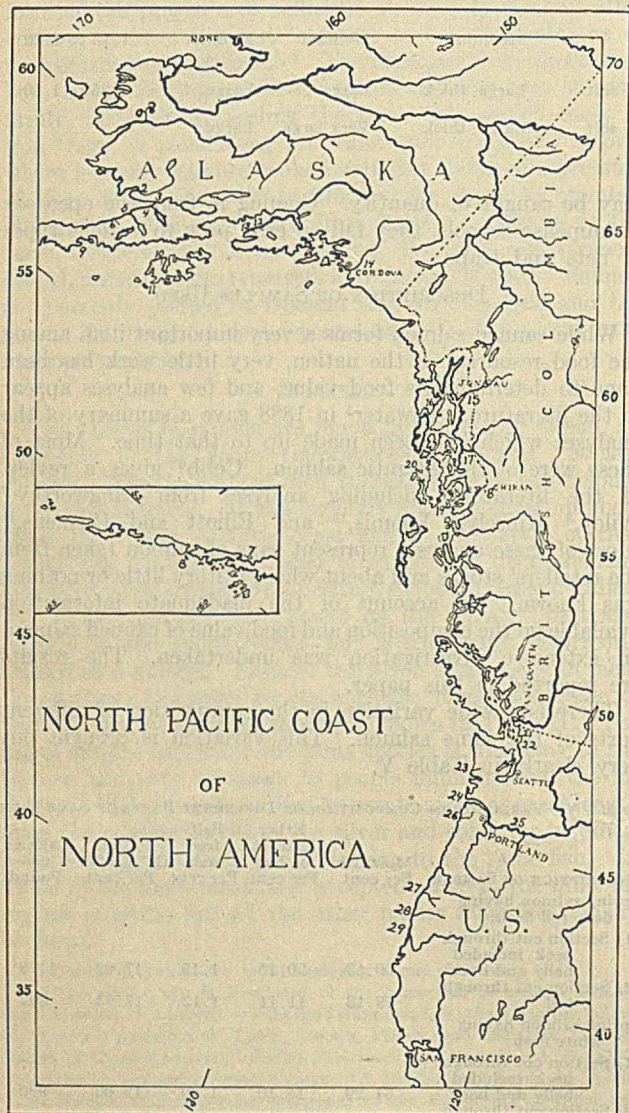
TABLE VI—COMPOSITION OF INDIVIDUAL CHINOOK SALMON[a]

DESCRIPTION OF SAMPLE	Number of Sample	Bone Per cent	Moisture Per cent	Fat Per cent	Salt-free Ash Per cent	Protein (N × 6.25) Per cent	Calories Per pound
No. 1 grade chinooks. Packed July 17, 1921. Caught in gill nets in brackish water. Average weight, 23 pounds. No vertebrae in cans	85	0.03	64.48	12.93	1.30	20.18	921
	85 A	0.01	58.25	19.96	1.53	17.75	1172
	85 B	0.05	51.97	27.13	1.21	17.31	1466
	85 C	0.04	51.81	25.67	0.94	18.75	1432
	85 D	0.06	51.45	27.26	1.02	19.43	1511
Composite of 6 cans	85 E	2.11[b]	62.99	14.49	1.16	19.75	978
Average of 11 cans		1.17[b]	59.63	18.17	1.18	19.26	1124
No. 2 grade chinooks. Packed August 16, 1921. Caught by trolling in salt water, possibly immature. Fish cleaned as caught and well iced. Average weight 19 pounds	88	4.36[b]	67.89	9.35	1.20	20.37	773
	88 A	0.03	57.39	20.32	1.22	19.31	1216
	88 B	0.61	65.00	12.36	1.19	19.57	885
	88 C	0.03	69.46	7.82	1.20	20.81	716
	88 D	0.04	70.10	7.92	1.16	20.00	706
Composite of 6 cans	88 E	3.17[b]	67.07	9.99	1.22	18.35	764
Average of 11 cans		2.19[b]	66.57	10.70	1.20	19.10	807
No. 2 grade chinooks. Packed August 16, 1921. Caught in traps in brackish water. Average weight 26 pounds. No vertebrae in cans	89	0.02	67.40	9.77	1.08	20.18	777
	89 A	0.03	64.72	12.59	1.05	20.00	913
	89 B	0.03	63.50	16.18	1.16	17.81	1014
	89 C	0.02	69.23	8.68	1.13	20.00	738
	89 D	0.02	68.34	9.43	0.98	20.31	775
Composite of 6 cans	89 E	0.61	67.64	8.29	1.09	20.18	725
Average of 11 cans		0.36	67.19	9.67	1.09	19.94	778
No. 3 grade chinooks. Packed August 16, 1921. Caught in traps in brackish water. Average weight 22 pounds. No vertebrae in cans	90	0.03	67.78	9.77	1.18	19.37	772
	90 A	0.08	69.18	7.90	1.15	20.68	718
	90 B	0.08	67.56	9.33	1.17	20.80	780
	90 C	0.04	70.87	6.70	1.28	20.87	670
	90 D	0.02	69.20	7.97	1.15	20.00	708
Composite of 6 cans	90 E	1.34[b]	68.78	7.38	1.13	19.93	682
Average of 11 cans		0.75	68.84	7.81	1.16	20.11	703
AVERAGE OF 44 CANS		1.12	65.56	11.59	1.16	19.60	853

[a] Special packs, each can containing the same section of an individual fish—viz., the second cut back of the gills.
[b] Some vertebrae in these cans.

the richest in fat and brightest in color. To make the table more complete, the analyses of several composite samples made at the same time are given.

Most of these fish are so large that a section as long as the height of the can will easily fill two cans. It was necessary, therefore, to cut the sections into two parts, in one of which was the backbone. This accounts for the wide variation in the amount of bone present in the cans above.

Not only does the composition of a species of fish vary with different individuals, but it also varies with different seasons of the year. This is brought out by Clark and Almy[12] in their work on twenty species of Atlantic food fishes, and by Dill[13] in a study of a number of Pacific food fishes. The average composition may also change from year to year with fish caught in approximately the same locality and in the same part of the fishing season. Table VII gives the average composition of both the chinook and chum salmon caught near the mouth of the Yukon River in 1919, 1920, and 1921. This change in composition may be due to a variation in

amount of available food in the period immediately prior to the spawning migration when the fish were caught.

TABLE VII—YEARLY VARIATION IN COMPOSITION OF CHINOOK AND CHUM SALMON ON THE YUKON RIVER

YEAR	Bone Per cent	Moisture Per cent	Fat Per cent	Salt-free Ash Per cent	Protein (N × 6.25) Per cent	Calories per Pound
Chinook salmon. Six commercial cans taken from pack at random						
1919	1.40	58.17	20.59	1.11	17.62	1196
1920	2.10	61.68	18.09	0.94	18.35	1104
1921	1.28	63.00	16.07	1.38	18.12	1015
Average for 3 years	1.59	60.95	18.25	1.14	18.03	1105
Chum salmon. Six commercial cans taken from pack at random						
1919	2.11	63.71	15.19	1.19	18.81	991
1920	2.18	70.35	7.76	1.08	19.29	686
1921	2.23	71.41	6.45	1.25	19.80	623
Average for 3 years	2.14	68.49	9.80	1.17	19.30	767

The composition of the various species of salmon and the steelhead trout is given in Tables VIII to XIV.

TABLE VIII—COMPOSITION OF THE SOCKEYE SALMON, *Oncorhynchus nerka*[a]

GEOGRAPHICAL LOCALITY	No. of Fish Analyzed	Bone Per cent	Moisture Per cent	Fat Per cent	Salt-free Ash Per cent	Protein (N × 6.25) Per cent	Calories per Pound
ALASKA							
Western Alaska							
Bristol Bay							
(2) Nushagak River	9	1.70	69.83	7.27	1.37	20.60	690
(3) Kvichak River	9	2.09	67.54	8.08	1.23	20.50	722
(4) Naknek River	9	2.12	67.75	7.66	1.28	20.50	705
(5) Egegik River	9	2.33	70.18	5.41	1.44	21.10	621
(6) Ugashik River	9	1.70	69.10	6.09	1.46	21.81	662
Central Alaska							
Alaska Peninsula							
(9) Chignik River	9	1.89	69.00	6.60	1.30	20.92	667
Kodiak Island							
(10) Karluk River	9	2.21	69.53	5.64	1.31	21.59	639
(11) Alitak Bay	9	2.11	67.59	7.85	1.30	21.92	739
Cook Inlet							
(13) Kasilof River	9	2.26	69.00	6.49	1.31	21.52	674
Southeastern Alaska							
(17) Wrangell	9	1.61	67.67	7.82	1.35	21.87	736
(18) Loring	9	1.73	65.58	10.03	1.31	21.25	818
Average for Alaska	99	1.97	68.43	7.17	1.33	21.23	697
UNITED STATES							
Puget Sound							
(21) Blaine, Wash.	9	2.32	63.44	10.29	1.23	20.53	815
Average for Puget Sound	9	2.32	63.44	10.29	1.23	20.53	815
Columbia River							
(24) Near the mouth	9	1.76	60.61	16.35	1.42	20.18	1065
(25) 200 miles from the mouth	9	2.62	61.95	14.56	1.19	20.34	992
Average for Columbia River	18	2.19	61.28	15.45	1.31	20.26	1028
Average of all sockeye salmon from special packs	126	1.96	67.19	8.58	1.32	21.04	753

[a] Special packs.

TABLE IX—COMPOSITION OF THE CHINOOK SALMON, Oncorhynchus tschawytscha[a]

GEOGRAPHICAL LOCALITY	No. of Fish Analyzed	Bone Per cent	Moisture Per cent	Fat Per cent	Salt-free Ash Per cent	Protein (N × 6.25) Per cent	Calories per Pound
			BONE-FREE FISH				
ALASKA							
Western Alaska							
Bristol Bay							
(2) Nushagak River	9	2.88	68.53	9.33	1.19	19.60	758
(3) Kvichak River	9	0.82	67.62	10.30	1.31	19.77	802
(4) Naknek River	9	0.37	67.12	11.12	1.24	19.01	822
Central Alaska							
Alaska Peninsula							
(9) Chignik River	9	0.40	64.06	14.24	1.19	18.29	940
Kodiak Island							
(10) Karluk River	9	1.80	67.77	8.59	1.32	20.92	751
Average for Alaska fish	45	1.25	67.02	10.71	1.25	19.51	814
UNITED STATES							
Puget Sound							
(21) Blaine, Wash.							
A—Red fleshed fish	9	3.90	62.06	12.19	1.15	20.75	900
B—White fleshed fish	9	3.93	61.98	13.24	1.17	19.15	915
Average for Puget Sound	18	3.91	62.02	12.71	1.16	19.95	908
Columbia River							
(24) Near mouth							
A—Grade No. 1	29	1.98	60.69	17.27	1.20	19.26	1086
B—Grade No. 2	40	1.45	64.14	13.59	1.17	19.31	932
C—Grade No. 3	20	1.52	67.94	9.58	1.20	19.98	776
D—White fleshed fish	9	1.81	68.10	10.26	1.21	19.53	796
(25) 200 miles from mouth							
A—Grade No. 1	11	0.51	60.35	16.83	1.18	19.16	1066
B—Grade No. 2	11	2.12	61.39	17.18	1.12	18.80	1074
Average for Columbia River	120	1.58	63.43	14.12	1.18	19.34	955
Oregon Coast							
(27) Coquille River							
A—No. 1 Grade	11	1.70	63.00	12.94	1.26	20.68	931
(28) Rogue River							
A—No. 1 Grade	11	0.88	61.70	15.40	1.23	19.76	1017
Northern California Coast							
(29) Klamath River							
A—No. 1 Grade	11	2.38	61.29	16.36	1.20	19.94	1061
Average for Oregon and Californian coastal rivers	33	1.65	62.00	14.90	1.23	20.13	1003
Average of all chinook salmon from special packs	216	1.78	63.98	13.41	1.21	19.51	928

[a] Special packs.

TABLE X—COMPOSITION OF THE COHO SALMON, Oncorhynchus kisutch[a]

GEOGRAPHICAL LOCALITY	No. of Fish Analyzed	Bone Per cent	Moisture Per cent	Fat Per cent	Salt-free Ash Per cent	Protein (N × 6.25) Per cent	Calories per Pound
			BONE-FREE FISH				
ALASKA							
Western Alaska							
Bristol Bay							
(2) Nushagak River	9	1.44	65.83	11.54	1.17	20.70	871
(3) Kvichak River	9	1.70	66.70	9.95	1.26	20.77	805
(6) Ugashik River	9	1.87	67.17	9.44	1.23	21.02	789
Central Alaska							
Alaska Peninsula							
(9) Chignik River	9	1.60	67.84	8.75	1.16	20.97	759
Kodiak Island							
(10) Karluk River	9	1.77	71.11	4.70	1.33	21.49	598
(11) Alitak Bay	9	0.66	69.52	5.58	1.37	21.91	642
Cook Inlet							
(13) Kasilof River	9	2.76	67.31	7.91	1.15	22.08	744
Southeastern Alaska							
(17) Wrangell	9	2.31	68.08	8.07	1.28	21.19	734
(18) Loring	9	2.07	68.00	7.21	1.30	21.93	712
Average for Alaska	81	1.79	67.95	8.12	1.25	21.39	739
UNITED STATES							
Puget Sound							
(21) Blaine, Wash.	9	2.19	65.43	8.95	1.20	20.46	758
Columbia River							
(25) 200 miles from mouth	9	2.39	65.41	11.33	1.22	19.35	838
Average of all coho salmon	99	1.88	67.49	8.49	1.24	21.08	750

[a] Special packs.

TABLE XI—COMPOSITION OF THE PINK SALMON, Oncorhynchus gorbuscha[a]

GEOGRAPHICAL LOCALITY	No. of Fish Analyzed	Bone Per cent	Moisture Per cent	Fat Per cent	Salt-free Ash Per cent	Protein (N × 6.25) Per cent	Calories per Pound
			BONE-FREE FISH				
ALASKA							
Western Alaska							
Bristol Bay							
(2) Nushagak River	9	2.33	68.64	7.94	1.38	20.51	716
(3) Kvichak River	9	2.17	69.60	7.37	1.17	19.98	683
(4) Naknek River	9	2.43	71.18	6.61	1.20	19.69	6.45
Central Alaska							
Alaska Peninsula							
(9) Chignik River	9	2.28	72.15	4.58	1.45	20.69	578
Kodiak Island							
(10) Karluk River	9	2.04	70.25	4.98	1.23	21.44	609
(11) Alitak Bay	9	2.07	71.87	4.16	1.32	20.54	558
Cook Inlet							
(13) Kasilof River	9	2.94	70.02	6.74	1.35	20.91	673
Southeastern Alaska							
(17) Wrangell	9	2.37	69.06	7.31	1.33	20.74	694
(18) Loring	9	2.32	69.51	6.22	1.36	20.42	642
Average for Alaska	81	2.32	70.25	6.21	1.31	20.56	644
UNITED STATES							
Puget Sound							
(21) Blaine, Wash.	9	2.20	68.23	6.11	1.33	20.57	640
Average of all pink salmon from special packs	90	2.32	70.05	6.20	1.31	20.56	644

[a] Special packs.

TABLE XII—COMPOSITION OF THE CHUM SALMON, *Oncorhynchus keta*[a]

			BONE-FREE FISH				
GEOGRAPHICAL LOCALITY	No. of Fish Analyzed	Bone Per cent	Moisture Per cent	Fat Per cent	Salt-free Ash Per cent	Protein (N × 6.25) Per cent	Calories per Pound
ALASKA							
Western Alaska							
Bristol Bay							
(2) Nushagak River	9	2.27	70.51	5.42	1.26	21.56	628
(3) Kvichak River	9	2.52	69.97	6.04	1.27	21.07	646
(4) Naknek River	9	2.59	70.49	5.96	1.25	21.03	642
(5) Egegik River	9	2.51	70.84	5.37	1.28	21.45	625
(6) Ugashik River	9	2.22	71.77	4.19	1.48	21.69	579
Central Alaska							
Alaska Peninsula							
(9) Chignik River	9	1.72	71.28	5.23	1.24	21.16	614
Kodiak Island							
(10) Karluk River	9	1.71	72.63	3.46	1.32	21.42	544
(11) Alitak Bay	9	1.34	70.36	5.84	1.26	21.94	654
Cook Inlet							
(13) Kasilof River	9	2.90	70.73	4.86	1.26	21.79	603
Southeastern Alaska							
(17) Wrangell	9	0.36	72.24	4.54	1.28	21.02	581
(18) Loring	9	1.44	70.60	5.22	1.17	21.60	622
Average for Alaska fish	99	1.96	71.00	5.10	1.28	21.43	613
UNITED STATES							
Puget Sound							
(21) Blaine, Wash.	9	0.90	68.83	5.70	1.30	22.01	649
Average of all chum salmon from special packs	108	1.87	70.85	5.15	1.28	21.48	615

[a] Special packs.

TABLE XIII—COMPOSITION OF STEELHEAD TROUT, *Salmo gairdneri*, AND ATLANTIC SALMON, *Salmo salar*

			BONE-FREE FISH				
GEOGRAPHICAL LOCALITY	No. of Fish Analyzed	Bone Per cent	Moisture Per cent	Fat Per cent	Salt-free Ash Per cent	Protein (N × 6.25) Per cent	Calories per Pound
ALASKA							
Central Alaska							
Cook Inlet			*Steelhead Trout*				
(12) Kenai River[a]	6	1.52	66.56	8.07	1.27	21.83	801
Southeastern Alaska							
(15) Takua	6	2.33	65.27	11.10	1.12	20.93	857
UNITED STATES							
Oregon Coast							
(26) Nehalem River[a]	2	3.35	68.68	7.68	1.25	21.19	718
Average of all steelhead trout from commercial packs (14 cans)		2.13	66.31	9.31	1.20	21.35	813
Columbia River							
(24) Near mouth	11	1.07	57.34	20.18	1.13	19.81	1220
(25) 200 miles from mouth	9	2.27	58.07	20.01	1.29	19.29	1202
Average of all steelhead trout from special packs	20	1.67	57.70	20.09	1.21	19.55	1211
Total number cans of steelhead trout analyzed	34						
			Atlantic Salmon				
Labrador[a]	3	1.31	63.77	12.28	1.26	21.43	916
Newfoundland[a]	3	0.98	64.84	12.71	1.18	20.85	924
Average for Atlantic salmon	6	1.14	64.30	12.49	1.22	21.14	920

[a] Commercial packs. Those not so marked were special packs.

TABLE XIV—SUMMARY. COMPOSITION OF THE PACIFIC SALMONS, STEELHEAD TROUT, AND ATLANTIC SALMON

			BONE-FREE FISH				
SPECIES OF FISH	No. of Cans Analyzed	Bone Per cent	Moisture Per cent	Fat Per cent	Salt-free Ash Per cent	Protein (N × 6.25) Per cent	Calories per Pound
Special packs							
Sockeye salmon	126	1.96	67.19	8.58	1.32	21.04	753
Chinook salmon	216	1.78	63.98	13.41	1.21	19.51	928
Coho salmon	99	1.88	67.49	8.49	1.24	21.08	750
Pink salmon	90	2.32	70.05	6.20	1.31	20.56	644
Chum salmon	108	1.87	70.85	5.15	1.28	21.48	615
Average for all species	639	1.96	67.91	8.37	1.27	20.73	738
Steelhead trout	20	1.67	57.70	20.09	1.21	19.55	1211
Commercial packs							
Sockeye salmon	41	2.37	64.78	11.22	1.23	20.80	860
Chinook salmon	24	2.21	63.17	15.72	1.21	17.67	991
Coho salmon	0	...	...	...	...	...	...
Pink salmon	9	2.53	69.80	6.99	0.76	21.40	696
Chum salmon	33	2.23	70.04	6.69	1.02	20.67	524
Average for all species	107	2.33	66.95	10.52	1.05	20.13	768
Steelhead trout	14	2.40	66.84	8.95	1.21	21.32	792
Atlantic salmon	6	1.14	64.30	12.49	1.22	21.14	920
Total number cans of fish analyzed	786						

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The Nature of Corrosion in Canned Fruits[1]

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PERFORATIONS, hydrogen swells, and hydrogen springers constitute the fruit canner's greatest technical hazard. In a sense these three types of nonmerchantable cans all belong in the same category. They are all the result of corrosion or, in other words, oxidation of the can. This cannot be regarded as a simple reaction of the acid (hydrogen ions) of the fruit with the metal of the container, for no definite parallelism with the hydrogen-ion concentration exists. The extent of corrosion—that is, the amount of metal going into solution—and the amount of hydrogen formed are not always in the same order of magnitude. For example, gooseberries packed in May in No. 2 plain cans were observed by the following August to have among them a considerable proportion of hydrogen swells, but with no appearance of bad corrosion of the cans. On the contrary, rhubarb packed in May in No. 10 plain cans had most of the tin stripped from the plate by the following August, but there was no trace of hydrogen in the cans. It may therefore reasonably be expected to have perforations with a great variation in the amount of hydrogen formed, and hence in the relative proportion of swells and springers.

A consideration of the different action of fruits in plain and enamel-lined cans presents some suggestive features. The great bulk of perforations, as well as of hydrogen swells and springers, occurs in enamel-lined cans. In most instances the same kind of fruit is not packed in both types of cans, but this would hold true even if such were the practice. This behavior has been explained by the theory that in the enameled cans the action is concentrated on the small areas where there is a break in the enamel. To give significance to this idea one must assume that when spread over the entire area of a plain can the active agent is spent before much injury results. If this conception is correct, the very fact that enameled cans are more troublesome is evidence that acidity is not the deciding factor, because the quantity of acid is so great that the concentration of its action on a small area should not be necessary to be effective. In fact, the hydrogen-ion concentration of canned fruits is not materially lowered by the action of the acid on the can.

The possibility that the process of enameling the can affects the metal in such a way as to weaken it against the acid or other corrosive agents should be considered. It may be suggested that the enamel itself may influence the action of the fruit on

The acidity of fruits is not the primary factor involved in causing perforations, hydrogen swells, and springers, inasmuch as there is no relationship between the hydrogen-ion concentration of the different fruits and the extent to which they cause trouble, and perforations, hydrogen swells, and springers occur least in plain cans. The fact that enameled cans give rise to more perforations, hydrogen swells, and springers is taken to indicate that the causative factor is present in limited quantity, which can be taken care of without much injury by the entire area of the plain can, but not by the small unprotected area in the enameled can. A small amount of oxygen in a No. 2 can acts in this manner with canned apples. The removal of oxygen by means of a vacuum does not eliminate perforations with all fruits as it does with apples. This indicates other oxidizing agents in such fruits. It is suggested that these may be intermediary respiratory substances resembling oxyhemoglobin or hydrogen acceptors, possibly the fruit colors, the anthocyans. The most practical method for removal of oxygen is to employ the respiratory process in the fruits.

The fact that oxygen disappears slowly and hydrogen formation follows soon after its disappearance in enameled cans, whereas in plain cans the oxygen disappears rapidly but hydrogen formation is much delayed, is shown to indicate that there is a protection of some sort in the can against acid alone but the combination of acid and oxygen is able to break this protection to enable the acid to continue its action even after the oxygen is used up. There is no evidence to indicate the nature of this protection.

the metal, either catalytically, by depolarization, or in some other manner. It would not be unreasonable to expect different enamels to have different properties in this respect, but no enamel has been developed with which perforations are not more abundant than with plain cans.

In spite of variations in the can, such as the seam, the base plate, the tin coat, the enamel, etc., as well as the time and temperature of storage after canning, it is believed that there are in the fruit some substances other than acids which in actual commercial practice are very important factors in determining the extent to which the fruit corrodes the can. It seems probable that their amount varies greatly, particularly in the fruits after canning, due in part to variations in the manner of handling. In some fruits that perforate enameled cans badly but not plain cans, the quantity of these substances must be relatively small if this difference is explained as being due to their action all being exerted on the small areas not protected by the enamel in the enameled cans. The following data are presented to show that oxygen acts in such a manner in causing perforations, hydrogen swells, and hydrogen springers. It is not to be implied that the idea that oxygen is a factor in this respect is new. It has often been mentioned in this connection. Sellars' patent[2] for removing the oxygen from apples previous to canning by means of a vacuum is based on this idea. But the data here presented analyze the effect of oxygen and the nature of its action in a way that should throw some light on this important problem.

EXPERIMENTAL

In a preliminary experiment York Imperial apples were peeled, quartered, filled into the cans without water, and subjected to a vacuum of 710 to 740 mm. (28 to 29 inches) three successive times, and the vacuum was released each time with oxygen as described in a previous paper.[3] The apples so treated were then divided into two lots, one of which was given no exhaust before canning while the other was given a 2-minute exhaust in boiling water. These two lots are represented, respectively, by Curves I and II in Fig. 1, where a slight effect of the exhaust is shown in delayed perforations. The striking thing in this experiment, however, is that at the same time apples were also filled with nitrogen instead of oxygen and perforations have not occurred up to the present time after a period of 45 weeks, although there are now 16.6 per cent springers and swells among them,

[2] U. S. Patent 1,279,379 (September 17, 1918).
[3] Kohman, THIS JOURNAL, 15, 527 (1923).

most of which formed after the oxygen-filled apples had practically all perforated.

In this experiment, as well as the succeeding one represented by Fig. 2 and described below, No. 2 enameled cans were used and the canned apples were stored in an incubator at approximately 37° C. (99° F.) for the greater part of the time. For three short intervals adding up to a total of 4 weeks the incubator had to be used for another purpose. Because of the higher temperature of storage the action on the can was more severe than would have been the case in commercial practice.
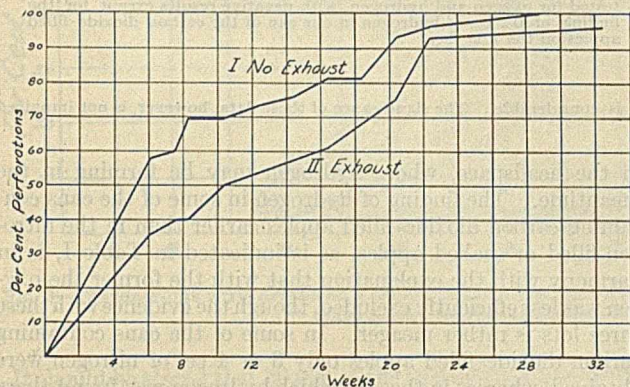
Fig. 1—Perforations with Oxygen-Filled Apples, Held at 37° C. (99° F.). Nitrogen-Filled Apples Canned at the Same Time Formed No Perforations, Swells, or Springers up to 40 Weeks. Between the 40th and 45th Weeks 16.6 Per cent Swells and Springers Developed

Fig. 2 represents an experiment with Yellow Newton apples, with which a greater number of variations in oxygen content was employed and a different lot of cans used. The 80 per cent oxygen curve represents apples peeled, quartered, and subjected to a vacuum of 710 to 740 mm. (28 to 29 inches) three successive times, the vacuum being released each time with oxygen. After this treatment the gas in the apples was found by analysis to be 80 per cent oxygen. The 32 per cent oxygen curve represents apples subjected to a vacuum of 380 mm. (15 inches) but once, the vacuum being released with oxygen. The 13 per cent oxygen curve represents untreated apples. The nitrogen and the carbon dioxide

curves represent apples subjected to a vacuum of 710 to 740 mm. (28 to 29 inches) three successive times, the vacuum being released each time with nitrogen and carbon dioxide. The curve designated as "soaked" represents apples peeled, quartered, and held under a 2 per cent salt solution for 16 to 18 hours at ordinary temperature. This is a practice developed commercially by apple canners to prevent the apples from darkening slightly during the process, such discoloration being due to their oxygen content. The oxygen is consumed by the respiratory processes in the apples during the soaking period. The salt solution prevents additional oxygen from the atmosphere from diffusing into the apples and the salt apparently functions in preventing peroxidase discoloration on the surface of the pared apples. After this preliminary treatment the various lots of apples were all canned in the same manner with a 2-minute exhaust in boiling water and 5-minute process.

In Fig. 2 there is brought out a striking relationship between the quantity of oxygen in the can and the rate of loss due to perforations, swells, and springers. In round numbers, the apples in a can contained 55 cc. of gas, irrespective of its composition, except in the case of the carbon dioxide–filled apples, from which 85 to 90 cc. per can were obtained by the method of analysis used. This was probably due to a considerable amount of carbon dioxide dissolving in the apples as well as filling the intercellular spaces. It may be of interest to state that apples, when repeatedly subjected to a vacuum out of contact with water, will take in, when the vacuum is released, approximately the same volume of gas that was withdrawn. Most fruits, however, will suck in their own juices to a large extent, and it is therefore impossible to replace the gas in them with an equal volume of another gas, as is the case with apples. Moreover, there is evidence that the removal of oxygen by vacuum does not reduce perforations and hydrogen formation with other fruits as it does with apples, indicating that in them there is a substance other than oxygen but whose effect is similar to that of oxygen.

Method of Gas Analysis—The can was punctured by means of a modified Doremus apparatus, consisting of a hollow needle which passed through a rubber stopper acting as an airtight gasket. This needle led to an inverted liter flask filled with water that had been rendered air-free by boiling and cooling out of contact with air. From a second hole in the stopper of the flask
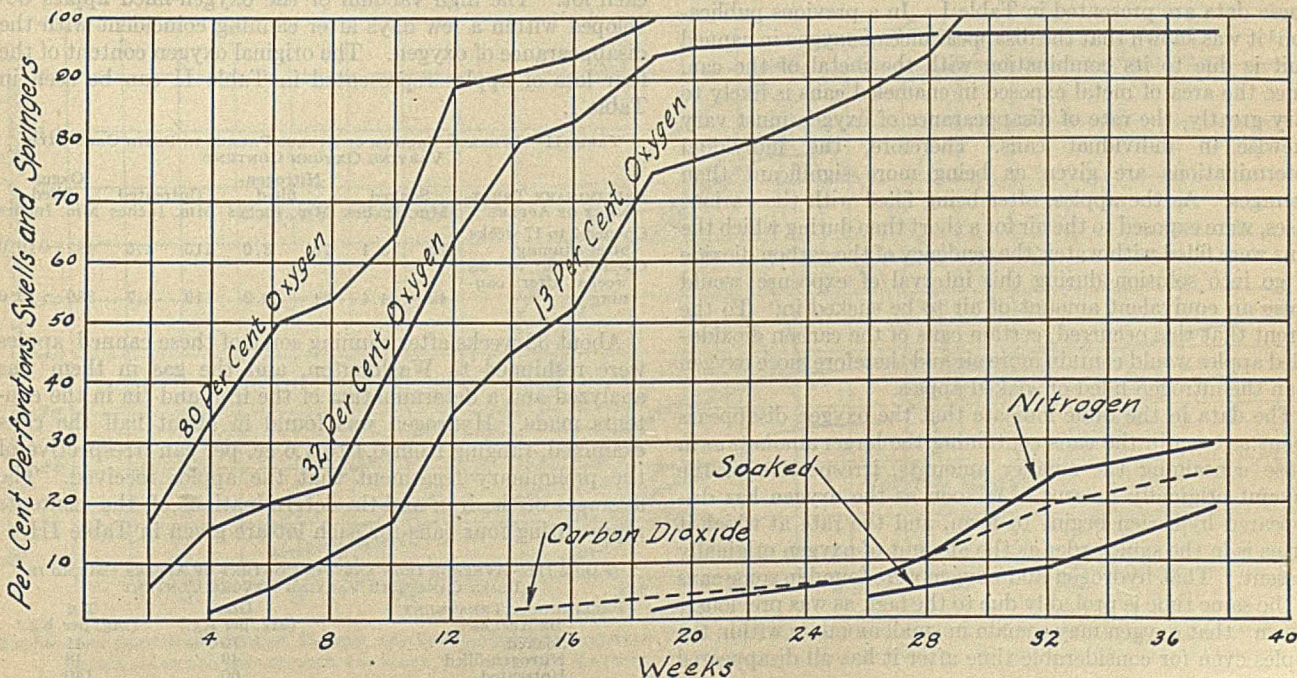

Fig. 2—Per cent Perforations, Swells, and Springers from Apples of Varying Oxygen Content Held at 37° C. (99° F.)

TABLE I—DISAPPEARANCE OF OXYGEN AND APPEARANCE OF HYDROGEN IN CANNED APPLES
[Volume, cc., per No. 2 can (11 ounces of apples)]

Days after Canning	Normal Apples		Half Oxygen-filled Apples		Oxygen-filled Apples		Soaked Apples		Nitrogen-filled Apples		Carbon Dioxide-filled Apples	
	O_2	H_2	O_2	H_2	O_2	H_2	O_2	H_2	O_2	H_2	O_2	H_2
a	6.2	..	18.6	..	45.4	..	0.3	..	0.5	..	0.5	..
	4.7	..	18.6	..	42.7	..						
b	3.9	..	9.9	..	33.0	..	..	..	0.5	..	0.5	..
	3.0	..	10.6	..	27.9	..						
19	1.4	0.0	0.3	0.2	9.1	1.9						
	0.8	0.0	2.0	0.3	8.8	2.3						
20	0.7	0.1	0.4	1.4	0.1	6.3						
	1.3	0.0	0.3	1.1	1.5	5.7						
21	0.4	0.2	..	..	..	..						
	0.3	1.2	..	..	..	..						
	1.4	0.1	5.8	0.4	0.1	5.4						
	0.0	1.6	0.2	1.2	5.3	5.1						
28	0.2	0.2	0.0	7.0	1.0	12.4						
	0.5	3.4	0.1	7.0	0.6	9.8						
42	0.0	3.8	0.0	12.4	0.0	24.3						
	0.0	8.3	0.0	20.1	0.0	23.3						

a Examined immediately after canning, before processing.
b Examined immediately after processing.
Note.—With small amounts the error in gas analyses, when made over water, is considerable. The significance of these data, however, is not impaired by ignoring the smaller figures.

Examination of the first three lots showed no oxygen or hydrogen to be present up to the 56th day after canning. At this time two cans each of the soaked and nitrogen-filled apples and five of the carbon dioxide–filled apples were examined but oxygen and hydrogen were absent in all except two cans of the carbon dioxide–filled apples, in which 2.3 and 2.5 cc. of hydrogen were found. On the 71st, 98th, and 127th days after canning two cans each of these three lots were tested for oxygen and hydrogen, with negative results except for the finding of 0.2 cc. of hydrogen in one can of the carbon dioxide–filled apples on the 71st day

the water was withdrawn by means of a vacuum of 710 to 740 mm. (28 to 29 inches). While this vacuum was being applied, the can, as well as all connections with the flask, was immersed under water to avoid leaks. Moreover, the can was jarred either by tapping it sharply with a metal bar or by tapping it on the bottom of the pail in which it was immersed. As was previously pointed out,[4] this is necessary to facilitate liberating gases in solution. Finally, the gas in the headspace was forced into the flask by compressing the sides of the can. The flask was then disconnected and allowed to fill with air-free water and the gas immediately transferred to a gas apparatus and analyzed. In this work a vacuum pump was used. In more recent work the puncturing needle was connected with a liter aspirator bottle filled with mercury. This bottle was connected by means of a rubber tube to a second aspirator bottle which could be lowered at will to create a vacuum by allowing the mercury to flow into it. By raising the second aspirator bottle so the mercury flowed back into the first, the gas could be transferred directly to the gas apparatus without contact with water, and hence without loss of any of the gases by their solution in water. However, the error due to this, as a consideration of the solubility of the gases will disclose, is not sufficient to affect the conclusions drawn in this paper. This device is portable and suitable for field work, and the vacuum is more directly under control than when a pump is used.

In order to obtain a closer insight into the nature of the action of oxygen in canned fruits, from time to time an analysis was made of the gas in the six lots of canned apples represented in Fig. 2. For this purpose a separate pack was put up from the same apples and using the same methods. These data are presented in Table I. In a previous publication[3] it was shown that the disappearance of oxygen in canned fruit is due to its combination with the metal of the can. Since the area of metal exposed in enameled cans is likely to vary greatly, the rate of disappearance of oxygen must vary likewise in individual cans. Therefore, the individual determinations are given as being more significant than averages. As the apples, after being filled with the various gases, were exposed to the air for a short time during which the cans were filled with water, the tendency of the carbon dioxide to go into solution during this interval of exposure would cause an equivalent amount of air to be sucked in. To the extent that this occurred, certain cans of the carbon dioxide–filled apples would contain more air and therefore more oxygen than the nitrogen-filled or soaked apples.

The data in the table indicate that the oxygen disappears about as soon in the cans containing the larger amounts as in those containing the smaller amounts, irrespective of the amount originally present. As soon as the oxygen has disappeared hydrogen begins to form, and the rate at which it forms is in the same order as the amount of oxygen originally present. That hydrogen and oxygen were found in some cans at the same time is probably due to the fact, as was previously shown,[3] that oxygen may remain in small amounts within the apples even for considerable time after it has all disappeared

[4] Kohman, THIS JOURNAL, 15, 273 (1923).

in the headspace, where hydrogen may be forming in the meantime. The finding of hydrogen in some of the cans containing carbon dioxide–filled apples earlier than in the nitrogen-filled or soaked apples, as is indicated in Table I, is in harmony with the explanation that with the former the oxygen was less efficiently excluded, though the evidence with these three lots is rather meager. In some of the cans containing carbon dioxide–filled apples only 3 or 4 cc. of nitrogen were obtained, whereas in those in which hydrogen was found there were about 10 cc., which no doubt were originally accompanied by a proportionate amount of oxygen.

The following data relating to soaked, nitrogen-filled, normal, and oxygen-filled apples packed in plain cans are presented as a contrast to and a comparison with the same products packed in enameled cans considered under Fig. 2 and Table I. These four lots of apples were canned in the plain cans precisely as in the enameled cans, at approximately the same time but for another purpose, for which they were shipped to New York. There, before they were opened—one can of each lot every other day during two different periods—the vacuum was taken. The averages for from 22 to 30 cans per lot for each period are recorded in Table II. In considering these figures it should be borne in mind that immediately after canning all four lots had approximately the same vacuum ranging from 101 to 127 mm. (4 to 5 inches) within each lot. The high vacuum of the oxygen-filled apples developed within a few days after canning coincident with the disappearance of oxygen. The original oxygen content of the four lots of apples represented in Table II can be seen in Table I.

TABLE II—AVERAGE VACUUM OF APPLES PACKED IN PLAIN CANS WITH VARYING OXYGEN CONTENT

PRELIMINARY TREATMENT OF APPLES	Soaked		Nitrogen-filled		Untreated		Oxygen-filled	
	Mm.	Inches	Mm.	Inches	Mm.	Inches	Mm.	Inches
Opened 7 to 17 weeks after canning	79	3.1	76	3.0	115	4.5	482	19.0
Opened 31 to 38 weeks after canning	42	4.4	81	3.2	119	4.7	380	15.0

About 38 weeks after canning some of these canned apples were reshipped to Washington, and the gas in them was analyzed and a determination of the iron and tin in the contents made. Hydrogen was found in about half the cans examined, ranging from 0.4 to 1.6 cc. per can irrespective of the preliminary treatment that the apples received. The averages of the iron and tin determinations of the contents representing four cans for each lot are given in Table III.

TABLE III—AVERAGE IRON AND TIN CONTENT OF APPLES PACKED IN PLAIN CANS WITH VARYING OXYGEN CONTENT

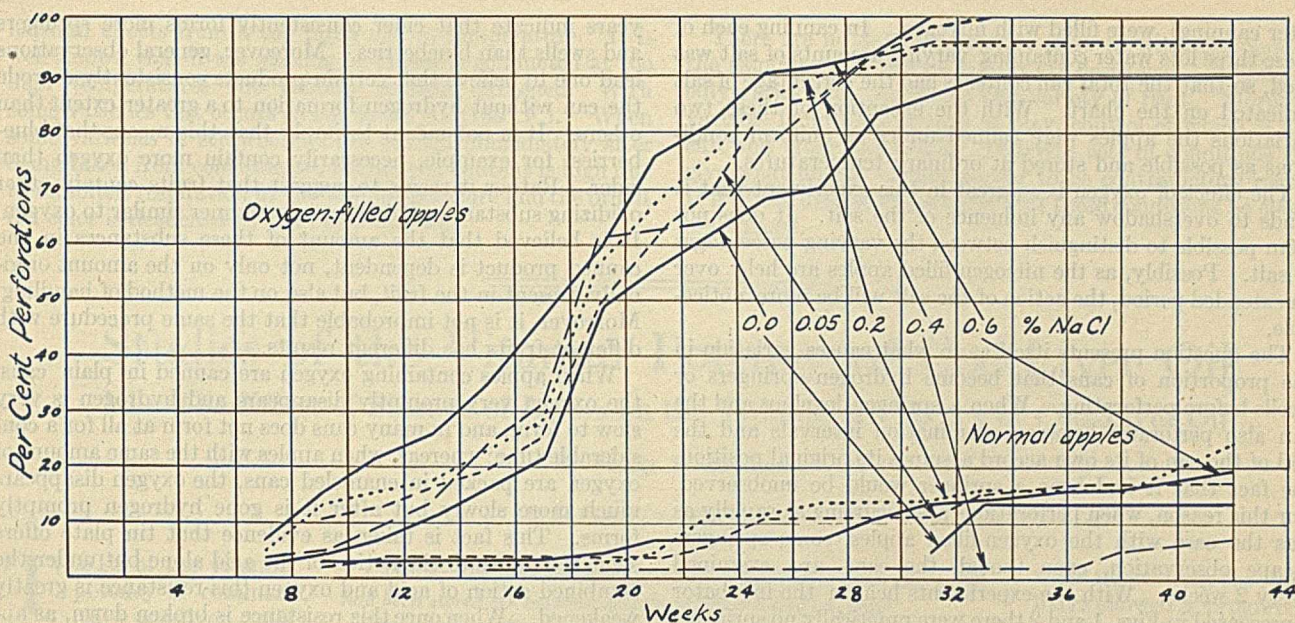| PRELIMINARY TREATMENT OF APPLES	Iron (Mg. per Kg.)	Tin (Mg. per Kg.)
Soaked	70	41
Nitrogen-filled	49	48
Untreated	60	140
Oxygen-filled	121	513

Fig. 3—Perforations with Apples of Varying Oxygen and Varying Salt Content. Nitrogen-filled Apples with the Same Salt Content Have Shown No Perforations, Swells, or Springers to Date (42 Weeks)

It should be stated that 30 mg. of the iron given in the table were originally in the apples, only the remainder coming from the can; also that the iron content in the individual cans of the same lot of apples varied greatly. For example, one can of the oxygen-filled apples contained only 33 mg. iron per kg., which is about the amount contained by the apples before canning. With respect to the tin content, however, the individual cans fall in three well-defined groups, the soaked and nitrogen-filled apples constituting one, the normal and oxygen-filled apples the other two. It is possible that there is significance in the difference between the averages of the soaked and nitrogen-filled apples, but as there is some overlapping in individual cans more data are necessary to establish it.

Clark[5] has reported some results on the effect of salt on perforations in canned apples, in which he points out that if the canned apples were grouped in the order of their salt con-

[5] *The Canner*, **56**, 249 (1923).

tent the number of perforations were in the same order. The variation in salt noted by him was a result of the variation in handling, which may have had some influence on the results obtained. His results are based on apples canned in plain cans.

In order to obtain the effect of salt on perforations in enameled cans, to determine not only the action of salt in particular but of an electrolyte in general, the experiment represented in Figs. 3 and 4 was made, in which there are three lots of apples. In Fig. 3 only perforations are represented, while in Fig. 4 hydrogen swells and springers as well as perforations are included. The apples in one lot, represented by the upper group of curves, were filled with oxygen; the apples of a second lot, represented by the lower group of curves, had their normal gas content; the apples of the third lot, not represented on the charts because no perforations, hydrogen swells, or springers had occurred up to the time of writing (42 weeks
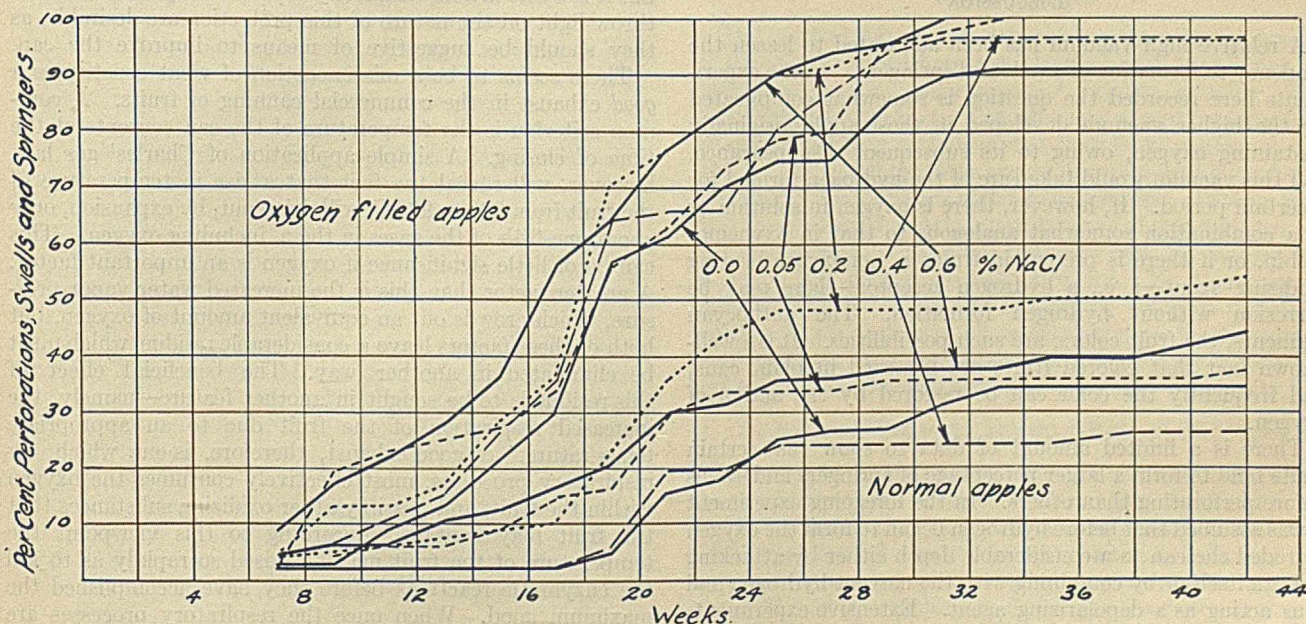
Fig. 4—Per cent Perforations, Swells, and Springers from Apples of Varying Oxygen and Salt Content Held at Ordinary Temperatures. Nitrogen-filled Apples with the Same Salt Content Have Shown No Perforations, Swells, or Springers to Date (42 Weeks)

after canning), were filled with nitrogen. In canning each of these three lots water containing varying amounts of salt was used, so that the total can contents had the percentage of salt indicated on the chart. With the exception of these two variations the apples were canned under as uniform conditions as possible and stored at ordinary temperatures.

The effect of oxygen is so great in this experiment that it tends to overshadow any influence of the salt. It does not seem possible to distinguish between the varying percentages of salt. Possibly, as the nitrogen-filled apples are held over an extended period, the action of the salt will be more noticeable.

The question presents itself as to what causes variation in the proportion of cans that become hydrogen springers or swells before perforating. When a springer develops and the can also perforates between examination intervals and the end of the can of its own accord assumes its original position, the fact that it had been a springer would be unobserved. For this reason, when perforations are occurring as rapidly as was the case with the oxygen-filled apples, some springers escape observation, even though the cans are examined every 2 weeks. With the experiments held in the incubator represented in Figs. 1 and 2 there were practically no springers or swells observed among the oxygen-filled apples and the number observed with the other lots was in the reverse order of the oxygen content. This relationship is more evident in the experiment represented in Figs. 3 and 4. A comparison of these two charts reveals the fact that few swells and springers were observed among the oxygen-filled apples, but with the untreated apples containing less oxygen decidedly more occurred. This is brought out more clearly in Table IV. The data given include only 28 weeks, because at the end of that time most of the oxygen-filled apples had perforated and the percentage of springers and swells could not materially increase. Moreover, at that time their formation in the other lots was temporarily arrested owing to the contraction of the can contents with the advent of fall weather.

TABLE IV—PER CENT HYDROGEN SWELLS AND SPRINGERS FROM APPLES OF VARYING OXYGEN AND SALT CONTENTS

	0.0	0.05	0.2	0.4	0.6
Per cent salt in apples	0.0	0.05	0.2	0.4	0.6
Springers and swells from nitrogen-filled apples	0.0	0.0	0.0	0.0	0.0
Springers and swells from untreated apples	28.0	29.2	41.7	23.9	29.2
Springers and swells from oxygen-filled apples	19.6	20.8	27.7	17.4	21.3

DISCUSSION

A relative high vacuum has been advocated to lessen the tendency to formation of swells and springers. In the experiments here recorded the question is somewhat complicated by the higher vacuum developed in those apples originally containing oxygen, owing to its subsequent disappearance, and this vacuum would take care of the hydrogen formed for a certain period. If, however, there is oxygen in solution or in a combination somewhat analogous to that in oxyhemoglobin, or if there is present in fruits a nonoxygen-bearing oxidizing agent—i. e., a hydrogen acceptor—there may be corrosion without hydrogen formation. The anthocyan pigments, the fruit colors, are such possibilities. It is a well-known fact that colored fruits are bleached in plain cans, and frequently the color can be restored by the action of oxygen.

There is a limited amount of data to show that certain fruits tend to form a larger percentage of springers and swells before perforating than others. In the foregoing experiment it was assumed that before hydrogen began to form the oxygen corroded the can to a considerable depth either by attacking the can itself or by combining with the nascent hydrogen and thus acting as a depolarizing agent. Extensive experiments in this laboratory[6] with cider and blueberries in two different

[6] Nat. Canners Assoc., Bull. 22-L.

years indicate that cider consistently forms more springers and swells than blueberries. Moreover, general observations lead one to believe that certain products consistently corrode the can without hydrogen formation to a greater extent than others. It is not meant to imply that this means that blueberries, for example, necessarily contain more oxygen than cider. Rather it seems to suggest that fruits contain other oxidizing substances which act in a manner similar to oxygen. It is believed that the amount of these substances in the canned product is dependent, not only on the amount originally present in the fruit, but also on the method of handling. Moreover, it is not improbable that the same procedure with different fruits has different results.

When apples containing oxygen are canned in plain cans, the oxygen very promptly disappears and hydrogen is very slow to form, and in many cans does not form at all for a considerable time; whereas, when apples with the same amount of oxygen are packed in enameled cans, the oxygen disappears much more slowly but after it is gone hydrogen promptly forms. This fact is taken as evidence that tin plate offers some resistance to the action of the acid alone but under the combined action of acid and oxygen this resistance is greatly weakened. When once this resistance is broken down, as apparently is the case in the enameled cans where the oxygen evidently corrodes to a greater depth than the same amount of oxygen in plain cans, the acid continues to act upon the metal until perforation results. The more rapid formation of hydrogen with the larger original oxygen content may mean that a larger area has been laid bare to the action of the acid.

At present there are no data to throw much illumination on the nature of this protection. It may be merely foreign matter, such as an oily film, or it may be a physical condition, such as polarization, but we should not exclude the possibility that it may be something more substantial, such as a thin film of an alloy or alloys of tin and iron. The gelatin test indicates that iron is exposed in certain spots on tin plate, but this may be iron in the form of an alloy which is subject to the attack of hydrochloric acid but not of the fruit acids. It is recognized that some do not believe iron and tin alloy in the process of tin plating, but the evidence on this point is not regarded as conclusive. This protection is somewhat injured by the bending of the tin plate in the process of closing the can, since most perforations occur at the countersink, but it is by no means completely broken. Any data that will throw light on the nature of this protection are desirable, as they should be suggestive of means to improve the can.

There seems to be a misconception of what constitutes a *good* exhaust in the commercial canning of fruits. A common criterion is the temperature of the can contents at the time of closing. A simple application of Charles' gas law, however, will reveal the fact that a rise in temperature of the fruit from 20° to 90° C. will drive out, by expansion, only about one-fifth of the gases in them, including oxygen. This can be of little significance if oxygen is an important factor. A greater factor than this is the increased water vapor pressure, which crowds out an equivalent amount of oxygen, but both of these factors leave a considerable residue, which must be eliminated in another way. The beneficial effect of this residue is to be sought in another feature—namely, the increased respiration of the fruit due to an appropriate temperature. A good exhaust, therefore, is one which, by respiratory processes, most effectively consumes the oxygen within the fruit, and possibly other oxidizing substances that the fruit may contain. According to this viewpoint the temperature of the fruit may be raised so rapidly as to kill the enzymatic reactions before they have accomplished the maximum good. When once the respiratory processes are destroyed by heat, one of the most effective means of oxygen elimination is lost. There are some striking evidences of

harmful effects from a too rapid rise in temperature. It is well known that if the soaking of apples is conducted at too high temperatures the centers become darkened. With some varieties this occurs as low as 54° C. (130° F.). When some varieties of strawberries are canned immediately after being taken from cold storage, the oxygen content is high due to inhibited respiration at the low temperature and the bright red color is deadened by too rapid heating.

There are no data available to show at what temperature the respiratory processes in fruit are destroyed. It undoubtedly varies with conditions and variety of fruit. Moreover, variable factors are always at play, control of which is difficult and often impossible. Different sets of conditions may give what on the surface appear to be contradictory results. It is of the utmost importance that these conditions be clearly understood.

Studies of the Vitamin Potency of Cod-Liver Oil[1]

VI—The Effect of Storage of Livers on the Vitamin A Potency of Cod-Liver Oil

By Arthur D. Holmes

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TESTS of the vitamin potency of commercial cod-liver oils show that in order to obtain cod liver of highest potency it is necessary to render the cod livers as soon as possible after they are removed from the fish. Accordingly, in attempting to improve the process of manufacture of cod-liver oil, attention has been centered on the type of equipment and the manufacturing conditions that permit most rapid rendering of cod livers. However, in some plants it has been necessary to ice cod livers and hold them for a day or so in order to secure a sufficient quantity for the economical operation of the rendering equipment. This practice naturally raises the question as to what effect "icing" livers has on the vitamin potency of the oil obtained from them.

To secure definite data in this connection, a supply of fresh cod livers was divided into two equal lots, one of which was rendered at once. The second lot was put in a glass container in an icebox. Six months later the livers were still of a normal, cream-white color, although some bloody water had separated at the bottom of the container. However, when the container was opened, no odor of decomposition could be detected. During the 6 months that the livers had been on ice, some oil had exuded from them.

A quantity of this oil sufficient for vitamin tests was removed after which the container was again sealed and placed in the icebox for another 6 months. For a portion of the extreme cold weather of the second 6 months the livers were frozen. Even after the livers had been stored for a year, they appeared to be in fair condition. The external portions of some of the livers had changed from the normal cream-white to a red color. When the container was opened, the livers had a detectable but not pronounced, unpleasant odor. Probably this preservation of the livers was due in part, at least, to the small amount of air in the container. The oil that was obtained from the livers which had been in storage for a year had about the same viscosity and color as oil produced by the short time "rotting process."

The oils that were obtained from the freshly rendered livers, from the livers that had been in storage for 6 months, and from the livers stored for a year, were of noticeably different colors. The oil from the fresh livers was straw-yellow,

Cod-liver oils were rendered from fresh cod livers, from livers that had been stored six months, and from livers stored one year.

The results of three series of comparable tests in which albino rats suffering from vitamin A starvation were fed graduated amounts of the three oils noted above, showed that oils from livers which had been stored at a low temperature out of contact with air had as high a vitamin potency as oil rendered from fresh livers.

One milligram per day of each of the oils contained sufficient vitamin A to insure good growth in albino rats.

while the oil from the stored livers showed a progressive increase in the red color, in all probability due to an increased absorption by the oil of liver decomposition products.

In order to provide data concerning the effect of storage of cod livers on the nature of the oil obtained from them, analyses were made of the three oils in question. The results of the analyses are given in the table.

CHEMICAL AND PHYSICAL CHARACTERISTICS OF OILS FROM STORED LIVERS

	Oil from Fresh Livers	Oil from Livers Stored 6 Months	Oil from Livers Stored 1 Year
Specific gravity at 25° C.	0.919	0.917	0.918
Refractive index at 20° C.	1.4789	1.4775	1.4789
Saponification value	183.400	182.400	185.100
Iodine value	142.700	154.500	142.700
Acid value	0.5903 per cent	15.560 per cent	18.070 per cent

Owing to a limited supply of oils under consideration, the usual colorimetric analysis was omitted.
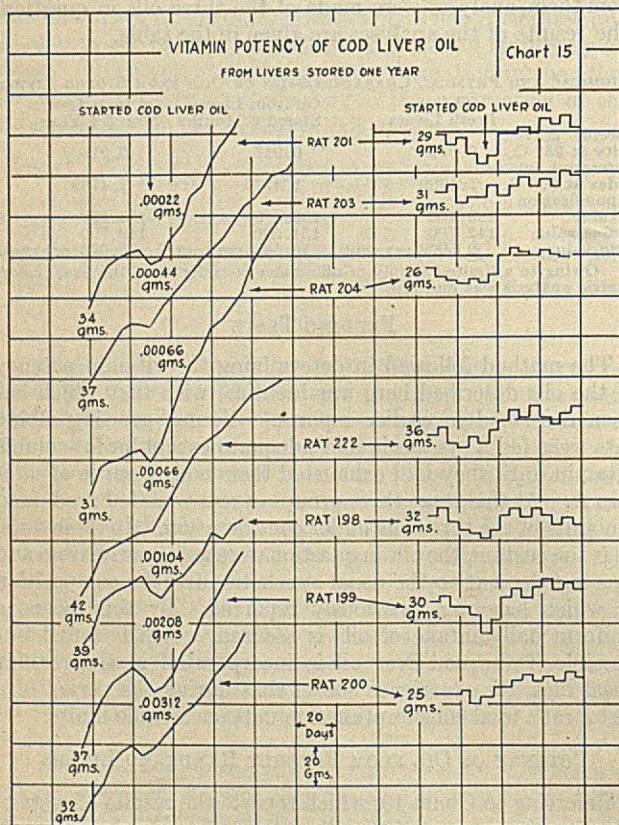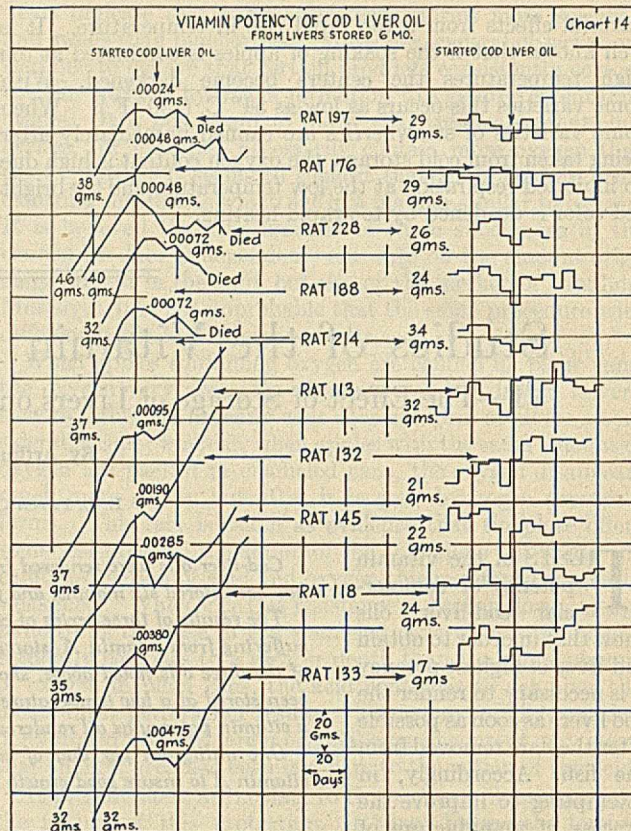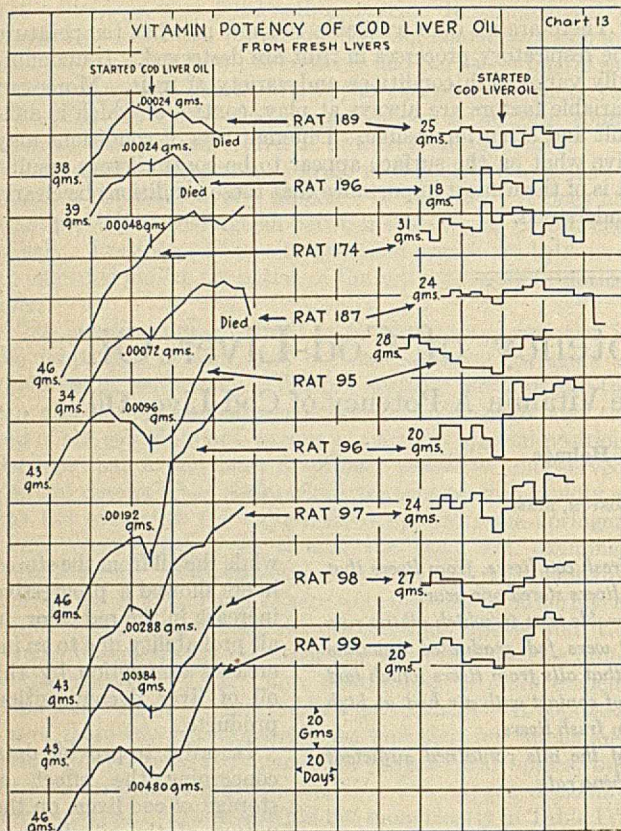
FEEDING TESTS

The method followed in determining the vitamin potency of the oils described here was identical with that which has been described in earlier reports.[2] Young, growing albino rats were fed a synthetic diet adequate except for fat-soluble vitamin until they had exhausted their body reserve of vitamin A. At this stage three groups of rats were fed graduated amounts of the three oils under consideration. In these tests, as is the custom, the oils in question were fed separate from and as a supplement to the usual synthetic diet, the composition of which has been previously reported. By this means a uniform daily intake of oils is secured, which is found impossible if the cod-liver oil is incorporated in the regular basal diet, for experience shows that during the period of a test a rat's food consumption fluctuates over wide limits.

POTENCY OF OIL FROM FRESHLY RENDERED LIVERS

Referring to Chart 13, which reports the results of tests of the vitamin potency of the oil rendered from fresh cod livers, it will be noted that nine animals were used in this test. When the physical condition of these animals indicated that they had exhausted their body reserve of vitamin A, their usual diet was supplemented by cod-liver oil varying in amounts from 0.00024 to 0.0048 gram daily.

[2] *J. Metabolic Research*, **2**, 113 (1922).

VITAMIN POTENCY OF COD LIVER OIL FROM FRESH LIVERS — Chart 13

VITAMIN POTENCY OF COD LIVER OIL FROM LIVERS STORED 6 MO. — Chart 14

VITAMIN POTENCY OF COD LIVER OIL FROM LIVERS STORED ONE YEAR — Chart 15

Rats 189 and 196 received 0.00024 gram of oil per day, but were unable to recover from the effects of vitamin A starvation and subsequently died. When Rat 174 showed the first signs of vitamin A starvation, its diet was supplemented with 0.00048 gram of oil daily. For 20 days this animal continued its previous rate of growth, but during the next 25

days the net gain in weight was only 2 grams. After 45 days the test was discontinued and the animal was transferred to the stock diet, which caused it to make very rapid and continued growth.

When the diet of Rat 187 was supplemented with 0.00072 gram of oil daily, it was able to resume its growth for 25 days. For the next 20 days it maintained its body weight, after which it soon died, showing that for this animal, at least, 0.00072 gram of the oil in question did not contain sufficient vitamin A to meet its needs for growth. Rat 95 showed definite evidence of vitamin A starvation by its consistent loss of weight for 3 weeks; yet on the addition of 0.00096 gram of oil daily to its diet, it soon commenced very rapid and continued growth.

In general, it was found that those animals receiving 0.00096 gram or more of the oil daily were able to recover from their malnutrition and gain weight rapidly. From these observations it is concluded that the daily consumption of 0.00096 gram of this oil provides sufficient vitamin A to meet an albino rat's requirements for growth.

Potency of Oil from Livers Stored 6 Months

The results that were obtained with ten animals in tests of the oil from livers that had been stored 6 months showed it to have a potency equal to oil from fresh livers. Rat 197 was able to maintain its body weight for 10 days on 0.00024 gram oil daily, but after this it failed for 18 days and died. Rat 176, which was fed 0.00048 gram of oil daily from the first evidence of vitamin A starvation, was able to maintain its body weight for 45 days, when the test was discontinued. In a check test, Rat 228, which experienced a greater decrease in body weight before the oil was added to its diet, failed for 25 days and died.

Two rats, 188 and 214, received 0.00072 gram of oil daily, but failed for 35 days and 25 days, respectively, and then died. The remaining five animals, which received daily doses of 0.00095 to 0.00475 gram of oil, all recovered

and grew at a rapid rate. On the basis of these tests, it is evident that the oil from livers stored 6 months is fully as potent as that from fresh livers.

POTENCY OF OIL FROM LIVERS STORED ONE YEAR

The results of tests of the potency of cod-liver oil obtained from livers which had been in storage for slightly over a year are of particular interest. In these tests (Chart 15) seven animals were fed oil in amounts graduated from 0.00022 to 0.00312 gram daily. All these animals promptly responded to the addition of oil to their basal diet. When this series of tests was started, it was questioned whether as little as 0.003 gram of this type of an oil contained enough vitamin to keep a rat alive for the 45-day experimental period, and from past experience it seemed certain that those animals receiving less than 0.001 gram daily could not live long. Consequently, Rat 222 was included in the series as a check on Rat 204. The results of this series show that in one instance, at least, as little as 0.00022 gram daily of the oil obtained from livers

that had been stored for a year contained sufficient vitamin A to meet the requirements of albino rats for growth. It may be noted, however, that the oil rendered from the stored livers was decidedly less palatable than the oil obtained from the fresh livers. As regards appearance and palatability, the oil from the stored livers resembles oil obtained by the "rotting" process and is not in the least comparable to oil rendered from fresh livers.

Comparing these results with those obtained from the study of oil rendered from fresh livers, it appears that cod-liver oil rendered from cod livers which have been stored at a low temperature and out of contact with the air has a higher vitamin A content than that rendered from fresh livers. The investigation of the effects of storage of livers on the vitamin A potency of oil obtained from them is being continued. The results of tests of the vitamin potency of oil rendered from livers which were stored in open containers and exposed to atmospheric changes will be reported in a separate paper in the near future.

Simplification of the Separation of Zinc from Iron and Aluminium[1]

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Zinc can be separated completely from iron, and also from aluminium, by ammonium hydroxide and ammonium chloride in one precipitation. Two-tenths of a gram of each metal, or even more, can be handled with celerity and ease.

Iron and aluminium hydroxides are precipitated in a compact state by evaporating their solutions to a very small volume, adding more than sufficient ammonium chloride to saturate the solution, and then adding concentrated ammonium hydroxide in considerable excess. By using gentle suction the precipitate is easy to wash.

THE determination of zinc in ores always necessitates its separation from iron. This is usually accomplished (1) by repeated precipitation of the iron by ammonia, (2) by ammonium carbonate, (3) as basic acetate, or (4) by precipitation of zinc as zinc sulfide in weakly acidified solution. Not only are all these processes, as usually carried out, time-consuming, but in methods (3) and (4) the conditions must be maintained within quite narrow limits to insure success.

It is the purpose of this article to show that perfect separations can be made quickly and conveniently with ammonia and ammonium salts, even when relatively large quantities of the two metals are present at the same time.

The determination of zinc in ores in North America is invariably carried out volumetrically by the ferrocyanide method. The method was first proposed by Galletti,[2,*] and the modification in use today is very well described in Low's[4] "Technical Methods of Ore Analysis." Schaffner's method[1] never attained any vogue on this continent.

Of all the authorities on the determination of zinc, A. H. Low is the only one who could be found who maintains that this metal can be completely separated from iron (when the latter is present in more than very small amount) by ammonia and ammonium chloride by a single precipitation. All other writers declare a double precipitation to be necessary. Low states that zinc can be completely removed from precipitated ferric hydroxide by washing with a solution containing 100 grams ammonium chloride and 50 cc. concentrated ammonium hydroxide per liter, but he does not give any confirmatory figures, nor state how much iron was present when he carried out the experiments that led to his conclusion.

At one time Kansas, Missouri, Illinois, and Indiana smelters could command a supply of ore averaging 0.5 to 1.5 per cent iron. While, it is true, conditions have changed, ample provision has been made for much higher iron content by employing in the great majority of experiments 0.2 gram iron and 0.2 gram zinc, corresponding to 40 per cent of each metal when 0.5 gram is taken for assay. Ingalls[12] states that low-grade calamines assaying 40 per cent ferric oxide (28 per cent iron) have been smelted, but that with this exception no ores containing over 20 per cent iron are acceptable to zinc smelters. A European smelter would rarely care, says Ingalls, to have more than 10 per cent iron in his charge. In New Jersey the ore smelted at the present time contains 2 to 3 per cent iron, while the same authority says that in Kansas and Missouri probably few smelters carry more than 2.5 per cent iron in their charges.

STANDARD SOLUTIONS AND DETERMINATION OF THE BLANK

The standard ferrocyanide solution contained about 22 grams potassium ferrocyanide and 8 to 10 grams sodium thiosulfate per liter.[5] It was checked every 2 weeks against pure $ZnSO_4.7H_2O$ solution containing 44.000 grams of the pure salt per liter. One cubic centimeter of this solution contained 0.0100 gram of zinc. The indicator used contained 15 gram $UO(NO_3)_2$ in 100 cc. of water.[10]

To test the influence of varying the concentration of the ammonium chloride on the blank, a series of trials was made in which the other factors were kept constant.

TRIAL	NH_4Cl Added Grams	$K_4Fe(CN)_6$ Required Cc.
1	5	0.15
2	10	0.15
3	20	0.15
4	30	0.15
5	40	0.15

* Numbers in text refer to bibliography at end of article.

It is evident that the ammonium chloride can vary over a wide range, so that one can safely use large quantities of ammonium hydroxide and ammonium chloride if necessary in the separation of iron, neutralizing the ammonium hydroxide in the filtrate with hydrochloric acid.

DETERMINATION OF $K_4Fe(CN)_6$ REQUIRED FOR STANDARD ZINC SOLUTION

To a 400-cc. beaker were added 20 cc. of the zinc sulfate solution containing 0.2000 gram zinc from a pipet, 5 cc. concentrated hydrochloric acid (specific gravity 1.19), 10 grams ammonium chloride, and water to 250 cc. The temperature was maintained between 60° and 70° C. during titration. The potassium ferrocyanide was added slowly, not faster than 10 cc. per minute, with constant stirring. Too rapid addition may give a false end point, so that too little potassium ferrocyanide is used. When the titration is carried out as described the precipitate at first produced is greenish or bluish white. After most of the potassium ferrocyanide required has been added, the precipitate becomes quite flocculent and settles fairly quickly. About 0.5 cc. before this end point the solution turns a creamy white, and the particles of the precipitate become much smaller and will settle only after 2 or 3 hours' standing. The change in size of the particles is more readily noticed if the solution is allowed to stand for half a minute without stirring. The potassium ferrocyanide should now be added drop by drop, testing after each. By using a glass tube for stirring three to four drops can be removed for each test. On arriving at the end point, one should wait 2 or 3 minutes to see if the immediately preceding one or two tests develop a color. From the reading decided on as being correct, the blank is naturally to be deducted.

TRIAL	$K_4Fe(CN)_6$ Required Cc.
1	39.50
2	39.70
3	39.55
4	39.55
5	39.65
Average	39.60
Blank	0.15
Net $K_4Fe(CN)_6$ required	39.45

Therefore, 20 cc. ZnSO₄ solution require 39.45 cc. $K_4Fe(CN)_6$ or 1 cc. $K_4Fe(CN)_6$ indicates 0.005070 g. Zn.

SEPARATION OF IRON FROM ZINC BY NH₄OH AND NH₄Cl

A solution of ferric sulfate containing very close to 0.01 gram iron per cubic centimeter was made up by stirring powdered $Fe_2(SO_4)_3.9H_2O$ into warm water faintly acidified with sulfuric acid. The following series of experiments was performed with 20 cc. of this solution and 20 cc. of the standard zinc sulfate—i. e., 0.2 gram of each metal. Precipitation was carried out in a volume of about 150 to 200 cc., the solution being heated to boiling. The solution was filtered hot, using suction, and washed as described in each case. The filtrate was neutralized with concentrated hydrochloric acid and 5 cc. in excess added. Five grams ammonium chloride were then added, the solution made up to 250 cc. and titrated at 60° to 70° C. as before.

(1) Twenty-five cubic centimeters 5 N ammonium hydroxide and 5 grams ammonium chloride were added:

TRIAL	$K_4Fe(CN)_6$ Required Cc.	Zinc Separated Grams	Zinc Present Per cent	Zinc Retained by Fe(OH)₃ Grams	Zinc Present Per cent
1	35.40	0.1794	89.7	0.0206	10.3
2	36.10	0.1830	91.5	0.0170	8.5

The precipitate, which was washed three times with hot water, was very bulky, filling a 9-cm. paper about three-quarters full.

These two trials make it clear that even when very considerable quantities of ammonium chloride and free ammonium hydroxide are present, a single precipitation does not by any means remove all the zinc from the ferric hydroxide.

Experiments on the separation of copper and nickel from iron carried out by the senior author[13] proved astonishingly successful when the solutions were evaporated to 2 or 3 cc., thus making it possible to saturate them with ammonium chloride and make them very strongly ammoniacal without being compelled to employ extravagantly large quantities of these two reagents.

(2) Accordingly, 20 cc. standard zinc sulfate and 20 cc. ferric sulfate were evaporated, with addition of two or three drops of concentrated hydrochloric acid to about 2 cc. Five grams ammonium chloride and 10 cc. concentrated ammonium hydroxide (specific gravity 0.90) were added, the mass was thoroughly worked up with a stirring rod, and 40 cc. of cold water were added. The solution was filtered cold and washed four times with cold water. The filtrate was titrated under the usual conditions.

$K_4Fe(CN)_6$ Required Cc.	Zinc Separated Grams	Zinc Present Per cent	Zinc Retained by Fe(OH)₃ Per cent	Zinc Present Per cent
37.35	0.1896	94.8	0.0104	5.2

Evidently, washing with water alone does not completely remove the zinc from the precipitate. The ferric hydroxide was quite dense, occupying only a fraction of the space required in Experiment 1. Low[11] has also observed this phenomenon, and refers to it in his chapter on the determination of zinc.

(3) Forty cubic centimeters of mixed sulfates and two drops of concentrated hydrochloric acid were evaporated to about 1 cc., worked up with 5 grams ammonium chloride and 5 cc. concentrated ammonium hydroxide, diluted with 25 cc. cold water, filtered, and washed with 50 cc. of cold solution containing 5 grams ammonium chloride and 5 cc. concentrated ammonium hydroxide per 100 cc. of solution.

$K_4Fe(CN)_6$ Required Cc.	Zinc Separated Grams	Zinc Present Per cent	Zinc Retained by Fe(OH)₃ Grams	Zinc Present Per cent
39.25	0.1994	99.7	0.0006	0.3

In order to obtain a confirmatory check on the zinc retained by the precipitate, the ferric hydroxide was dissolved in concentrated hydrochloric acid, precipitated with concentrated ammonium hydroxide, filtered, and washed with ammonium chloride–hydroxide solution.

$K_4Fe(CN)_6$ required, 0.10 cc.
Zinc present, 0.25 per cent (0.0005 gram)

The precipitate produced on addition of the potassium ferrocyanide was just discernible.

(4) This was carried out exactly as in (3), except that the precipitate was washed with 100 cc. of cold solution containing 5 grams ammonium chloride and 5 cc. concentrated ammonium hydroxide.

TRIAL	$K_4Fe(CN)_6$ Required Cc.	Zinc Separated Grams	Zinc Present Per cent	Zinc Retained by Fe(OH)₃ Cc.	$K_4Fe(CN)_6$ Required for Zinc Retained by Fe(OH)₃ Grams	Zinc Present Per cent
1	39.35	0.1996	99.8	0.10	0.0005	0.25
2	39.40	0.1998	99.9	0.05	0.0002	0.1
3	39.35	0.1996	99.8	0.05	0.0002	0.1
4	39.45	0.2000	100.0	0.00	0.0000	0.0
5	39.40	0.1998	99.9	0.05	0.0002	0.1
6	39.50	0.2002	100.1	0.00	0.0000	0.0
7	39.35	0.1996	99.8	0.00	<0.0005	<0.25

Before titrating the filtrate containing this trace of zinc in Trial 2, hydrogen sulfide was bubbled through the ammoniacal solution. No precipitate could be detected.

In Trials 4, 5, 6, and 7, the precipitate was washed eight to ten times with the ammoniacal wash solution.

On testing the precipitate from Trials 4 and 6 for zinc in the usual way with potassium ferrocyanide, no precipitate could be detected, even on standing 1 hour. In Trial 5 a faint precipitate was observable.

Titration to determine the zinc retained by the washed ferric hydroxide in Trial 7 gave the same figure as for the blank—viz., 0.15 cc. potassium ferrocyanide. There was produced a faint precipitate of zinc ferrocyanide; comparing this nephelometrically with the precipitate produced by 0.5 mg. zinc, it was found to be distinctly smaller.

These seven trials prove conclusively that as much as 0.2 gram zinc can be separated from 0.2 gram iron by a single precipitation. The error, if any, lies within the error inseparable from the titration itself. The precipitate of ferric hydroxide must, however, be thoroughly washed with ammonium chloride–hydroxide solution. The dense character of the ferric hydroxide renders this operation easy and rapid if a gentle suction is applied.

(5) These separations were carried out exactly as those recorded under (4), except that the precipitate was filtered hot and washed with hot ammonium chloride-hydroxide solution of the concentration already given.

Trial	$K_4Fe(CN)_6$ Required Cc.	Zinc Separated Grams	Zinc Present Per cent
1	39.40	0.1998	99.9
2	39.30	0.1996	99.8

When tested for zinc with potassium ferrocyanide, the washed ferric hydroxide gave a faint white precipitate in each case after standing 15 minutes. This indicates only a small fraction of a milligram of zinc.

Evidently the method works satisfactorily both hot and cold.

(6) The following separations were carried out exactly as those recorded under (4), using in each trial 100 cc. of wash solution containing 5 grams ammonium chloride and 5 cc. concentrated ammonium hydroxide.

Trial	Zinc Taken Grams	Iron Taken Grams	$K_4Fe(CN)_6$ Required Cc.	Zinc Separated Grams	Zinc Taken Per cent
1	0.2000	0.3	39.55	0.2002	100.1
2	0.4000	0.2	78.95	0.4000	100.0
3	0.2000	0.1	39.50	0.2000	100.0
4	0.2000	0.4	39.35	0.1996	99.8

In Trial 1 the wash solution was hot; in Trials 2, 3, and 4 it was cold. The washed ferric hydroxide in Trial 2 contained enough zinc to give a faint precipitate of zinc ferrocyanide on 2 hours' standing. The precipitate was much smaller than one produced by 0.5 mg. of zinc. Zinc could not be detected in the washed ferric hydroxide from Trial 3, but in Trial 4 a faint test was obtained.

It is evident that 0.2 gram of zinc can be completely separated from as much as 0.4 gram of iron in one precipitation by the foregoing simple procedure.

When such a large quantity as 0.4 gram iron was present, the most satisfactory technic was found to be the following:

To the zinc-iron solution in a beaker or casserole add a few drops of concentrated hydrochloric acid and evaporate to about 5 cc., taking care to avoid local baking. Then take the vessel in the hand and swirl the contents while continuing the evaporation over a small flame, until the volume is reduced to about 2 or 3 cc. While still warm add 5 grams ammonium chloride and work up the mass with a stirring rod. Add 10 cc. concentrated ammonium hydroxide, break up lumps, add about 25 cc. cold water, and filter on a 7-cm. paper in an 8-cm. Büchner funnel. Wash back the bulk of the precipitate into the beaker or casserole, using the ammoniacal wash (5 grams NH_4Cl + 5 cc. concentrated NH_4OH made up to 100 cc.) and transfer again to the filter. Wash six to eight times on the filter, consuming about 100 cc. of the ammoniacal wash liquid in all. Neutralize the ammoniacal solution with concentrated hydrochloric acid, adding about 5 cc. in excess, dilute to about 250 cc., and titrate at from 60° to 70° C. in the manner already described.

A powerful suction packs the precipitate on the paper too tightly, and hence should be avoided. A suction equivalent to about 76 mm. of mercury works very satisfactorily, and with it the whole operation of filtering and washing should not require more than about 5 minutes. When handling smaller quantities of iron, say 0.1 to 0.2 gram, an ordinary funnel is quite satisfactory, but with larger quantities the precipitate packs in the apex of the paper.

Separation of Zinc from Aluminium

Upon separating zinc from aluminium, a small amount of aluminium passes into the filtrate owing to the slight solubility of aluminium hydroxide in solutions strongly alkaline with ammonia, but not enough dissolves to interfere with the subsequent titration of zinc. A test determination gave 4 mg. aluminium in the filtrate.

A solution containing very nearly 0.01 gram aluminium per cubic centimeter was made from $Al_2(SO_4)_3.18H_2O$, a few drops of sulfuric acid being first added to the water.

(7) Twenty cubic centimeters of standard zinc sulfate and 20 cc. of the aluminium sulfate were treated exactly as in Experiment 4.

Trial	$K_4Fe(CN)_6$ Required Cc.	Zinc Separated Grams	Zinc Present Per cent	$K_4Fe(CN)_6$ Required for Zinc Retained by Al(OH)₃ Cc.	Zinc Retained Grams	Zinc Present Per cent
1	39.25	0.1990	99.5	0.15	0.0008	0.4
2	39.40	0.1998	99.9	0.00	0.0000	0.0
3	39.40	0.1998	99.9			

The washed aluminium hydroxide was tested for zinc exactly as described in Experiment 3.

The aluminium hydroxide formed in the concentrated ammonium hydroxide saturated with ammonium chloride, like the ferric hydroxide formed under the same conditions, is much denser than that produced in the usual way. In Trial 2 zinc could not be detected in the washed aluminium hydroxide. In Trial 3 a faint precipitate of zinc ferrocyanide appeared.

Zinc can evidently be separated from aluminium without difficulty in one precipitation, when as much as 0.2 gram of each metal is present, by ammonium hydroxide and ammonium chloride. The precipitate of aluminium hydroxide appears to require somewhat more washing than the ferric hydroxide.

(8) To compare Demorest's method[9] with that of the writers, they proceeded exactly as in Experiment 4, except that they used 5 grams powdered ammonium carbonate in place of 5 cc. concentrated ammonium hydroxide.

The wash solution also contained 5 grams ammonium carbonate per 100 cc. in place of 5 cc. concentrated ammonium hydroxide. Using 20 cc. of standard zinc sulfate and 20 cc. aluminium sulfate.

$K_4Fe(CN)_6$ Required Cc.	Zinc Separated Grams	Zinc Present Per cent
38.45	0.1950	97.5

Care was taken to prevent loss through effervescence when adding hydrochloric acid to the filtrate. It is evident that ammonium carbonate, though effective, does not give quite so satisfactory a separation as concentrated ammonium hydroxide.

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10—Nissenson, "Die Untersuchungsmethoden des Zinks."
11—Low, "Technical Methods of Ore Analysis."
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13—Ardagh and Broughall, *Can. Chem. Met.*, **7**, 198 (1923).

Gas Hazards

Warning as to the deadly hazards of gas in unventilated rooms and garages is again sounded by the Bureau of Mines. Seldom a day passes at this season of the year but the press records the death of one or more persons by asphyxiation in their homes or garages. It should never be forgotten that in burning natural gas carbon monoxide may be given while in the exhaust from an engine this gas is practically always present in exceedingly dangerous amounts.

Many house heaters have no flues for carrying off the waste gases, which then pass into the rooms. If all windows and doors are closed, the effect of these gases sooner or later becomes apparent on the occupants, who become dull and sleepy, and sometimes die. If a gas heater without a flue is used, a window should be partly open all the time—that is, up a half inch or so. Even heaters with flues should be in well-ventilated rooms. Never go to bed with a heater burning and the windows and doors closed. If the engine of an automobile must be kept running while making repairs, the garage must be ventilated. Never crawl under a car when the engine is running, no matter how good the ventilation. If it is desired to sit in an automobile with the engine running, the garage must have proper ventilation. Another hazard of exhaust gas is that of sitting in a tightly closed automobile, on a highway or elsewhere in the open, with the engine running. The car may be fitted with a leaky heater, through which the exhaust gas gets into and concentrates in the car, or else the exhaust from the muffler in some manner gets into and accumulates in the car. Publications bearing upon this subject may be obtained free from the Bureau of Mines, Washington, D. C.

The Assay of Zinc Ores[1]

Use of Powdered Magnesium for Removing Copper and Lead

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THE standard zinc sulfate and potassium ferrocyanide solutions, as well as the conditions for titration, were those described in detail in the preceding article.

The reason for substituting metallic magnesium for the metallic aluminium recommended by earlier investigators lies in the fact that, although the presence of aluminium salts does not affect the blank determination, it does very seriously affect the figures obtained when zinc is present, as the following experiments very clearly show:

(1) *Effect of Aluminium Chloride on Titration of Zinc by Potassium Ferrocyanide.*

Effect on blank. Conditions same as in earlier determination of blank as described in the preceding paper

$AlCl_3$ Grams	$K_4Fe(CN)_6$ Required Cc.
3	0.20
5	0.20

Effect of adding aluminium chloride to 20 cc. standard zinc sulfate

$AlCl_3$ Grams	$K_4Fe(CN)_6$ Required Cc.
3	43.05
5	45.30
5	45.95
None	39.45

(2) *Effect of Magnesium Chloride on Titration of Zinc by Potassium Ferrocyanide.*

Effect on blank. 12 grams $MgCl_2.6H_2O$ added

$K_4Fe(CN)_6$ Required Cc.
0.20
0.15
0.15

Effect on titration of zinc. 20 cc. standard zinc sulfate

$MgCl_2.6H_2O$ Grams	$K_4Fe(CN)_6$ Required Cc.
1	39.50
5	39.40
10	39.40
30	39.45
30	39.40

It is evident that even large quantities of magnesium chloride do not interfere in the potassium ferrocyanide titration.

If, then, metallic aluminium is used to remove copper, lead, etc., the aluminium itself must be removed before the zinc present can be titrated by potassium ferrocyanide as this titration is usually carried out. On the contrary, if metallic magnesium is used to precipitate copper, lead, etc., it need not be removed prior to the titration of the zinc.

(3) *Precipitation of Copper and Lead by Magnesium Followed by Titration with Potassium Ferrocyanide.* To 20 cc. standard zinc sulfate were added 1 gram $CuSO_4.5H_2O$ (approximately 0.25 gram copper), 0.5 gram lead chloride (approximately 0.375 gram lead), and 3 cc. concentrated hydrochloric acid. The whole was diluted to about 75 cc. and heated to boiling. Magnesium powder was then added cautiously to the covered beaker, little by little, until the copper and lead had been completely precipitated. Small additions of the hydrochloric acid to the almost boiling solution were also made from time to time as required. This took about 5 minutes. The solution was then neutralized with ammonium hydroxide and, after adding 5 cc. concentrated hydrochloric acid and 10 grams ammonium chloride,

diluted to 250 cc. It was then heated to 70° C. and titrated without filtering. The figures show that the precipitated copper and lead carry down an appreciable amount of zinc.

$K_4Fe(CN)_6$ Required Cc.	Zinc Separated Grams	Zinc Present Per cent
38.65	0.1960	98.0

On standing 5 minutes longer with vigorous stirring, more zinc entered the solution.

$K_4Fe(CN)_6$ Required Cc.	Zinc Separated Grams	Zinc Present Per cent
39.20	0.1988	99.4

The end point obtained in this way was somewhat blurred by the small particles of metal and possibly by a little copper having gone into solution.

(4) This experiment was a repetition of (3), but the precipitated metals were washed by decantation, then on the filter with warm hydrochloric acid (5 cc. concentrated hydrochloric acid diluted to 100 cc.).

$K_4Fe(CN)_6$ Required Cc.	Zinc Separated Grams	Zinc Present Per cent
36.95	0.1874	93.7

The metallic precipitate was boiled with 10 cc. concentrated hydrochloric acid for 5 minutes. Any copper left undissolved was now in a very finely divided state. The solution was diluted to about 75 cc., treated as before with magnesium powder, the copper and lead filtered off, and the zinc titrated as above.

	$K_4Fe(CN)_6$ Required Cc.	Zinc Separated Grams	Zinc Present Per cent
	2.05	0.0104	5.2
TOTAL	39.00	0.1978	98.9

It is evidently a difficult task to prevent loss of zinc in the precipitated copper and lead.

(5) *Repetition of* (4). The precipitated copper and lead were washed three times by decantation with the dilute hydrochloric acid. They were then boiled with 8 cc. concentrated hydrochloric acid for 5 minutes. Some copper was not dissolved. The copper and lead were reprecipitated, washed several times by decantation and then twice on the filter with the dilute hydrochloric acid. The combined filtrates were titrated as before.

$K_4Fe(CN)_6$ Required Cc.	Zinc Separated Grams	Zinc Present Per cent
39.30	0.1992	99.6

Evidently magnesium can be used satisfactorily to remove copper and lead, but it is necessary to filter off the precipitated metals, boil them with hydrochloric acid, and reprecipitate with magnesium in order to separate the zinc completely. The powdered magnesium must be as free as possible from iron. If traces of iron are present, no more magnesium should be used than absolutely necessary. One must also guard against traces of copper going into solution as a result of oxidation or through the use of too concentrated hydrochloric acid.

(6) *Effect of Lead on the Titration of Zinc by Potassium Ferrocyanide.* Seaman[7,*] claims that lead interferes; Lenher

* The reference numbers refer to the bibliography at the end of the preceding paper.

and Meloche[3] declare it is without influence. It seemed to the writers that these contradictory statements might have resulted from working with different concentrations of hydrochloric acid. To test this the following series was run on 20 cc. standard zinc sulfate containing 2 grams lead chloride (approximately 1.5 grams lead) and varying amounts of hydrochloric acid in 250 cc.

Concd. HCl Cc.	$K_4Fe(CN)_6$ Required Cc.
1	45.10
3	44.90
6	39.60
7	39.45
10	39.40

These experiments make it evident that when the amount of concentrated hydrochloric acid falls below 7 cc. in 250 cc. of solution, high results for zinc will be obtained when lead is present, but by increasing the concentrated hydrochloric acid present to from 7 to 10 cc. in 250 cc. of solution, correct results can be obtained for zinc even when large amounts of lead are present.

Conclusions

(1) Aluminium does not affect the blank in the usual potassium ferrocyanide titration, but results obtained for zinc in the presence of aluminium are high under the usual conditions of carrying out the titration.

(2) Magnesium chloride, even in large quantities, does not interfere with the titration of zinc by potassium ferrocyanide.

(3) Powdered magnesium may be used with advantage to precipitate copper and lead in hydrochloric acid solution. In order to separate the zinc completely, however, the precipitated metals must be filtered off, boiled with concentrated hydrochloric acid, and reprecipitated with magnesium. The magnesium should be as free from iron as possible, and one must also guard against any copper going back into solution.

(4) Correct results for zinc by titration with potassium ferrocyanide can be secured in the presence of lead, provided the hydrochloric acid present amounts to from 7 to 10 cc. of concentrated hydrochloric acid in 250 cc. of solution.

Suitability of Various Solvents for Extracting Vanilla Beans[1]

Part II

By J. B. Wilson and J. W. Sale

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T HE 95 per cent ethyl alcohol, 91 per cent isopropyl alcohol, U. S. P. ether, U. S. P. acetone, and 99.5 per cent carbon tetrachloride were removed from the extractive matter by heating under diminished pressure, and the extractive matter was dissolved in 65 per cent ethyl alcohol.[2] The extracts obtained in this manner and those made directly (without removal of the solvents) with 65 per cent ethyl alcohol and alkaline 65 per cent ethyl alcohol were analyzed. In the course of the main investigation several methods of analysis have been compared.

The quantity and solubility of the total extractive matter obtained by extracting Mexican, Bourbon, and Tahiti vanilla beans, and Tonka beans with 65 and 95 per cent ethyl alcohol, alkaline 65 per cent ethyl alcohol, 91 per cent isopropyl alcohol, U. S. P. ether, U. S. P. acetone, and 99.5 per cent carbon tetrachloride, were reported in Part I of this article. In continuing this investigation vanilla and tonka extracts prepared in various ways have been analyzed.

Methods of Analysis

Vanillin, lead number, color insoluble in amyl alcohol (Marsh's reagent), and coumarin were determined according to the Methods of Analysis of the Association of Official Agricultural Chemists.[3] The vanillin was determined also by the method of Folin and Denis[4] and the lead number by the method of Wichmann.[5] Specific gravity and alcohol (by volume) were determined by means of the pycnometer, the alcohol in the distillates from the Wichmann lead numbers.

In the determination of ash, a 25-cc. sample was used in place of 10 cc., as described in the official methods. The ash was digested on the steam bath for 15 minutes with 25 cc. of distilled water. The solution was then filtered and the residue washed thoroughly with hot water. The filter paper

was then returned to the dish and the dish ignited in the muffle, cooled, and weighed. After the addition of a few drops of methyl red indicator the solution of water-soluble ash was titrated with 0.1 N sulfuric acid. Alkalinity of water-insoluble ash was determined by adding 10 cc. 0.1 N sulfuric acid to the insoluble ash, heating for a few minutes on the steam bath, cooling, and titrating back with 0.05 N potassium hydroxide solution, using methyl red as indicator. The two solutions remaining from the titration of the water-soluble and the water-insoluble ash were united, made alkaline with ammonia, then acid with nitric acid, boiled and filtered. The phosphoric acid was determined volumetrically in the filtrate.

Two determinations of acidity were made, one after diluting 10 cc. of the extract with 180 cc. of 50 per cent alcohol by volume, and the other by diluting 10 cc. with 180 cc. of water. In each case the titration was made with 0.1 N potassium hydroxide solution, using phenolphthalein as indicator. Blank determinations were made and subtracted from the results of the titration. The color of the extracts after precipitation with lead acetate was determined by means of the Lovibond tintometer.

Discussion of Data

The results obtained by these methods are given in Table I Only a small proportion of the total extractive matter obtained with ether, acetone, and carbon tetrachloride is soluble in 65 per cent ethyl alcohol, the solvent selected as a standard of comparison.[2] The data in Table I confirm the opinion that the extractive matter obtained with ether, acetone, and carbon tetrachloride, contains much less of the desired flavoring constituents—that is, vanillin and resins—than that obtained with the other solvents. The data in Table I show also that

[1] Presented before the Division of Agricultural and Food Chemistry at the 66th Meeting of the American Chemical Society, Milwaukee, Wis., September 10 to 14, 1923.

[2] This Journal, **15**, 782 (1923).

[3] Assoc. Official Agr. Chem., Methods, **1919**, p. 197.

[4] This Journal, **14**, 670 (1922); see also Leach, "Food Inspection and Analysis," 4th ed., p. 922.

[5] This Journal, **13**, 414 (1921).

TABLE I—ANALYSIS OF VANILLA AND TONKA EXTRACTS

Solvents	Specific Gravity	Alcohol by Volume, %	Vanillin A.O.A.C. Method, %	Vanillin Folin and Denis Method, %	Coumarin A.O.A.C. Method, %	Lead Number A.O.A.C. Method, %	Lead Number Wichmann Method, %	Residual Color Red	Residual Color Yellow	Ratio Red to Yellow Extract[b]	Ratio Red to Yellow Filtrate	Color Insoluble in Amyl Alcohol Marsh Reagent, %	Acidity Alcohol (50% Vol.) Cc 0.1N/100	Acidity (ume) Cc 0.1N/100	Acidity Water Cc 0.1N/100	Acidity Due to Vanillin (Calcd.) Cc 0.1N/100	Acidity Due to Constituents Other than Vanillin Cc 0.1N	Ash Total G/100 Cc	Ash Water-Sol. G/100 Cc	Ash Water-Insol. G/100 Cc	Alkalinity Total Cc 0.1N/100	Alkalinity Water-Sol. Cc 0.1N/100	Alkalinity Water-Insol. Cc 0.1N/100	P_2O_5 Mg/100 Cc
Mexican																								
Ethyl alcohol, 95%[a]	0.9052	50.2	0.16	0.14	0.01	0.122	0.176	0.8	3.4	4.8	4.2	1.7	28	25	18	10	18	0.091	0.079	0.012	4.2	3.8	0.4	1.0
Isopropyl alcohol, 91%[a]	0.9071	49.4	0.15	0.14	0.01	0.075	0.176	0.8	2.6	7.0	3.2	1.7	24	24	15	10	15	0.061	0.052	0.009	3.8	3.0	0.8	0.8
Ether, U.S.P.[a]	0.9010	49.3	0.14	0.11	0.02	0.041	0.071	0.2	0.8	—	3.0	1.7	12	12	3	9	3	0.018	0.016	0.002	0.2	0.15	0.0	0.3
Acetone, U.S.P.[a]	0.9034	49.3	0.14	0.12	0.02	0.070	0.123	0.8	2.6	8.8	3.0	None	22	4	13	9	13	0.022	0.013	0.009	1.9	—	0.0	1.1
Carbon tetrachloride, 99.5%[a]	0.9009	52.3	0.08	0.08	0.01	0.037	0.025	0.2	0.6	2.0	4.4	8.3	5	3	—	5	—	0.004	0.004	0.000	0.2	0.2	0.0	2.2
Ethyl alcohol, 65%	0.9159	46.8	0.18	0.17	0.02	0.653	0.859	1.4	6.2	3.6	0.7	8.3	42	30	30	12	30	0.360	0.310	0.050	33.2	24.0	9.2	28.2
Alkaline 65% ethyl alcohol	0.9132	49.0	0.09	0.11	0.01	0.780	1.052	12.0	8.0	3.0	—	—	9	6	3	6	3	0.692	0.636	0.056	89.7	77.7	12.0	2.4
Bourbon																								
Ethyl alcohol, 95%[a]	0.9059	50.7	0.23	0.22	0.02	0.176	0.290	1.4	4.0	4.2	2.8	3.4	32	28	17	15	17	0.080	0.069	0.011	5.2	3.4	1.8	14.5
Isopropyl alcohol, 91%[a]	0.9086	48.6	0.19	0.22	0.01	0.126	0.127	0.6	4.2	5.0	3.7	3.4	28	25	16	12	16	0.056	0.048	0.008	4.1	2.5	1.6	1.8
Ether, U.S.P.[a]	0.9008	50.8	0.22	0.18	0.01	0.042	0.227	0.4	1.6	—	2.7	None	20	18	14	13	14	0.009	0.003	0.006	0.2	0.6	1.6	0.5
Acetone, U.S.P.[a]	0.9040	49.4	0.18	0.20	0.02	0.104	0.194	0.2	—	10.6	3.0	1.7	27	26	13	14	13	0.015	0.014	0.001	1.2	—	0.6	0.9
Carbon tetrachloride, 99.5%[a]	0.9048	47.4	0.14	0.15	0.02	0.033	0.055	0.2	0.2	—	1.0	None	24	10	9	9	9	0.004	0.000	0.004	0.0	—	0.0	0.9
Ethyl alcohol, 65%	0.9198	46.8	0.24	0.23	0.02	0.569	0.698	10.0	9.0	5.0	0.5	6.9	41	36	25	17	25	0.250	0.199	0.051	26.2	16.0	10.4	15.9
Alkaline 65% ethyl alcohol	0.9169	47.1	0.11	0.12	0.02	0.589	0.723	12.0	8.0	2.8	—	7.4	9	4	—	7	—	0.484	0.439	0.045	69.2	58.8	10.4	2.2
Tahiti																								
Ethyl alcohol, 95%[a]	0.9047	51.3	0.13	0.14	0.02	0.209	0.318	1.0	4.0	6.4	4.0	0.4	26	22	17	9	17	0.093	0.083	0.010	9.5	6.5	3.0	3.5
Isopropyl alcohol, 91%[a]	0.9085	48.6	0.14	0.12	0.04	0.187	0.253	0.2	0.4	4.0	3.4	1.7	22	14	13	9	13	0.075	0.062	0.013	7.2	5.0	2.2	3.1
Ether, U.S.P.[a]	0.9017	49.3	0.12	0.11	0.04	0.013	0.092	0.4	1.8	—	2.5	None	15	23	6	6	6	0.004	0.002	0.002	0.4	—	0.0	1.3
Acetone, U.S.P.[a]	0.9051	—	0.13	0.07	0.04	0.108	0.238	None	None	5.2	4.2	1.9	23	4	14	9	14	0.045	0.039	0.006	2.1	2.1	0.0	1.6
Carbon tetrachloride, 99.5%	0.9041	42.8	0.09	0.14	0.03	0.001	—	1.0	4.2	3.1	0.6	3.7	4	30	None	6	None	0.004	0.002	0.002	0.2	—	0.0	18.5
Ethyl alcohol, 65%	0.9182	47.3	0.15	0.12	0.03	0.533	0.701	8.6	4.8	6.5	—	7.4	33	None	23	10	23	0.244	0.196	0.048	28.5	18.1	10.4	2.1
Alkaline 65% ethyl alcohol	0.9203	—	0.13	0.12	0.06	0.766	0.832	8.6	4.8	0.6	—	10.0	2	—	—	7	—	0.695	0.650	0.045	90.7	82.3	8.4	2.1
Tonka																								
Ethyl alcohol, 95%[a]	0.9010	51.1	0.02	....	0.21	0.000	0.028	0.2	0.6	0.6	3.0	None	6	6	—	—	—	0.013	0.007	0.006	0.8	0.8	0.0	1.3
Isopropyl alcohol, 91%[a]	0.9047	50.2	0.04	....	0.22	0.003	0.031	0.2	0.8	2.0	4.0	None	4	4	—	—	—	0.011	0.004	0.007	0.8	0.4	0.0	1.5
Ether, U.S.P.[a]	0.9024	50.5	0.08	....	0.23	0.019	0.042	None	None	None	—	None	2	2	—	—	—	0.004	0.000	0.004	0.2	0.2	0.0	1.1
Acetone, U.S.P.[a]	0.9019	50.7	0.08	....	0.22	0.008	0.031	None	None	None	—	None	1	—	—	—	—	0.005	0.003	0.002	0.6	0.2	0.0	1.7
Carbon tetrachloride, 99.5%	0.9017	61.4	0.07	....	0.23	0.000	0.010	None	None	None	—	17.2	10	10	—	—	—	0.003	0.003	0.000	0.6	0.2	0.0	12.9
Ethyl alcohol, 65%	0.9118	61.3	0.10	....	0.23	0.131	0.183	0.4	2.4	3.3	3.0	17.2	None	—	—	—	—	0.137	0.114	0.023	12.8	11.4	1.4	12.9
Alkaline 65% ethyl alcohol	0.9141	—	0.09	....	0.22	0.578	0.388	0.4	2.6	2.5	6.5	10.0	None	None	—	—	—	0.480	0.459	0.021	64.4	59.6	4.8	1.4

[a] Beans were extracted with the solvents as listed, the solvents were evaporated off, and the extractive matter was dissolved in 65 per cent ethyl alcohol.
[b] Calculated from data in Tables I and II of Part I of this article.
[c] Based on figures obtained when extract was diluted with 50 per cent alcohol.
[d] Doubtful end point.

the extracts made with 65 per cent ethyl alcohol contain more vanillin, possess greater acidity from acid constituents other than vanillin, and have higher lead numbers, as determined by both the official and Wichmann methods, than the extracts made with 95 per cent ethyl alcohol, isopropyl alcohol, ether, acetone, or carbon tetrachloride. They have also the largest quantity of color, both red and yellow, the highest ash content, and the highest phosphate content.

When potassium carbonate is added to the 65 per cent ethyl alcohol, the vanillin content and acidity are lowered; the lead numbers, by both official and Wichmann methods, are increased; the color, especially the red, is increased; and the phosphate content is decreased. Tables I and II in Part I showed that when potassium carbonate was employed the total extractive matter and total extractive matter soluble in 65 per cent ethyl alcohol were somewhat higher. Dean and Schlotterbeck[6] found that alkali (1) did not affect the vanillin content, (2) increased lead number values, (3) increased the color of the extracts, and (4) impaired the flavor of the extracts. They employed a menstruum of 50 per cent alcohol with an alkali content ranging from 0.04 to 0.4 per cent based on weight of extract, whereas in this laboratory 100 grams of finely divided beans were mixed with 6 grams of potassium carbonate and extracted three times with 200 cc. of 65 per cent alcohol, the final volume being 1 liter. A conclusion as to the advisability of employing alkali will be reserved until the flavor and aroma of the various extracts have been compared.

The vanilla extracts showing the largest quantity (8.3 per cent) of color insoluble in Marsh's reagent are those made from Mexican beans by extraction with 65 per cent alcohol and with alkaline 65 per cent alcohol. The specific gravities of extracts made by means of the same solvent from the several kinds of beans show only slight differences.

The Wichmann lead numbers are about one-third higher than those obtained by the official method in the case of all extracts made by direct extraction with 65 per cent alcohol and with alkaline 65 per cent alcohol, except that of Tahiti beans. When the beans are extracted with 95 per cent alcohol, the Wichmann lead numbers are about one-half higher; when the extraction is made with acetone they are about twice as high. Attention is called particularly to the low lead numbers with all extracts except those having a menstruum of 65 per cent alcohol and of alkaline 65 per cent alcohol. Apparently, the lead number represents water-soluble constituents rather than resins. This has not been emphasized heretofore so far as the writers are aware, although previous investigators have observed that slightly higher lead numbers were obtained when weak alcohol solutions were employed. Usually, however, all the menstruums that they used contained sub-

stantial percentages of water and the effect on the lead number was not so marked as in the case of the writers' experiments, in which five of the menstruums contained only a very small proportion of water.

The two methods for vanillin agree very well, the largest differences being 0.03 and 0.04 per cent in extracts from Mexican beans and Bourbon beans, respectively, which were made with ether. After the ether solution of vanillin had been washed with 2 per cent ammonia and evaporated, some residue, which was weighed and reported as coumarin, remained. This residue, which had no odor of coumarin and was slightly colored in most cases, was probably a resinous material. The largest quantities were found in Tahiti bean extracts. Of the residues obtained in the analyses of the Tonka extracts, reported under the heading "vanillin," the highest (0.10 per cent) was found in the extract made with 65 per cent alcohol. These residues likewise had no odor of vanillin and gave no test with ferric chloride.

The extractive matter soluble in 65 per cent alcohol, reported in Table II, Part I, was determined by evaporating a measured quantity of the extract in a vacuum oven after mixing with sand. It was thought that less vanillin would be lost by this procedure than by the official method for the determination of total solids in vanilla extract. However, when 10 cc. of a standard vanillin solution containing 20 mg. of vanillin dissolved in 65 per cent alcohol (by volume) were evaporated in the vacuum oven under the same conditions, a residue of only 1.2 mg. remained, showing that nearly all the vanillin had been volatilized.

An experiment was conducted to determine whether losses of vanillin occurred when the several solvents were removed under diminished pressure. Quantities of vanillin were dissolved in 95 per cent ethyl alcohol, 91 per cent isopropyl alcohol, U. S. P. ether, U. S. P. acetone, 99.5 per cent carbon tetrachloride, and 95 per cent ethyl alcohol containing vanilla resins. In the case of each of these solutions 100 cc. were measured into double-necked distilling flasks and the solvents were removed at 70± mm. pressure. When dry, the vanillin remaining in the flasks was dissolved in 95 per cent alcohol and diluted to 100 cc. (Solutions a, b, c, d, e, f). Fifty cubic centimeters of the solution of vanillin in carbon tetrachloride and of the solution of vanillin in ether were allowed to evaporate spontaneously to dryness, and the residue was dissolved in 95 per cent alcohol and diluted to 50 cc. (Solutions g and h).

The original solutions of vanillin in those solvents that are miscible with water (ethyl alcohol, isopropyl alcohol, acetone, and the ethyl alcohol containing vanilla resins) and Solutions a, b, c, d, e, f, g, and h were treated as follows:

Five cubic centimeters of solution were added to several hundred cubic centimeters of distilled water in a volumetric flask of 500 cc. capacity. Enough distilled water to make 500 cc. was added and the solution was thoroughly mixed. Five cubic centimeters of each solution were then withdrawn into a 50-cc. volumetric flask, 5 cc. of sodium tungstate–phosphomolybdate reagent were added, and after 10 minutes the volume was made up to 50 cc. with a saturated solution of sodium carbonate. After the precipitate had been allowed to settle for half an hour, the solutions were filtered through dry filters.

A comparison between the original solutions and those from which the solvent had been removed under diminished pressure was made in a Duboscq colorimeter. The percentages of vanillin recovered were as follows: from 95 per cent ethyl alcohol, 99.9 (duplicate 98.2); from 91 per cent isopropyl alcohol, 98; from U. S. P. ether, 99; from U. S. P. acetone, 98.3; from 99.5 per cent carbon tetrachloride, 95.6; and from the alcohol containing vanilla resins, 98.5 (duplicate, 98.5).

Since these recoveries are practically complete except in the case of carbon tetrachloride, it is probable that the differences in the vanillin contents of the various extracts are due to the action of the solvent in question rather than to any loss sustained in its removal. When making up the solutions the weighed amount (3 grams) of vanillin was dissolved in about 160 cc. of the solvent. The entire amount dissolved except in the case of carbon tetrachloride. The undissolved portion was filtered off before measuring out the quantity used in the experiment, after which 50 cc. of the solution were allowed to evaporate spontaneously, final drying being accomplished by leaving the vanillin in a sulfuric acid desiccator for 72 hours. The residue remaining (0.780 gram) showed a solubility of 1.56 grams of vanillin in 100 cc. of carbon tetrachloride. This low solubility probably accounts for the small quantity of vanillin in extracts made with carbon tetrachloride as solvent.

The investigation is being continued to determine the relative values of the extracts from the standpoint of aroma and flavor, and also to determine whether or not a substantial advantage can be obtained by a preliminary extraction of the beans with carbon tetrachloride, followed by a second extraction with dilute ethyl alcohol. The data so far obtained indicate that this procedure will result in the production of a high-grade extract by the use of a smaller quantity of ethyl alcohol than is ordinarily employed.

All-Glass Apparatus for Automatic Evaporation of Water Samples[1]

By G. A. de Graaf

Public Service Electric Co., Irvington, N. J.

THE apparatus shown in the accompanying figures has been found quite satisfactory for the evaporation of large samples of water in small dishes, without attention.
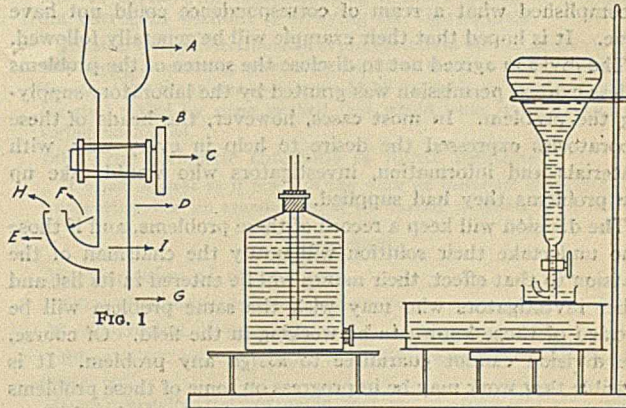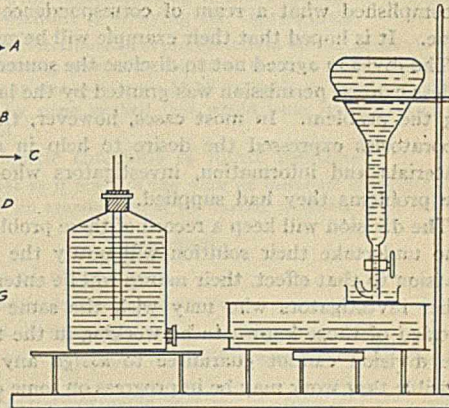

Fig. 1

Fig. 2

The part A, Fig. 1, is ground to fit the neck of an ordinary volumetric flask. The flask is filled to the mark, the stopper inserted, and the flask inverted over the dish with the stopcock C closed. The stopcock is opened cautiously and the adjustment of height so made that the point I, which determines the level of water in the dish, is at a suitable height. The stopcock is then opened wide. At the close of the evaporation the lower part of the tube is washed carefully with a small amount of distilled water. In the absence of steam an electric hot plate has been used for heating a water bath provided with the usual automatic level and overflow device. Stoppage of the water has resulted in loss of samples when left evaporating over night. This has been avoided by use of an aspirator bottle (Fig. 2) with the level in the bath determined by the position of the lower end of the open tube in the bottle.

A List of Research Problems in Chemistry[1]

By J. E. Zanetti

DIVISION OF CHEMISTRY AND CHEMICAL TECHNOLOGY, NATIONAL RESEARCH COUNCIL, WASHINGTON, D. C.

THE list of research problems here presented is intended to call the attention of investigators to pressing questions which need solution, rather than to stimulate new recruits to the field of research with inspiring problems. Only a very few are capable of that. Much can be accomplished, however, to forward the interests of research by calling attention, from time to time, to the lack of certain information that is desired, not only by the industries, but by investigators in general. At least, coöperation of effort may thus be secured.

These problems were supplied from various sources. The editor of International Critical Tables found in the compilation of his tables numerous gaps as well as contradictory and insufficient data. By direct correspondence with some investigators he has secured their services in solving some of his problems, but the supply of unsolved ones is still large. The Mellon Institute of Industrial Research kindly supplied from its files a number of problems awaiting solution. Directors of research of some of the largest industrial laboratories have contributed a very large number to this list. Some were supplied by individual investigators.

It is not claimed that this list gives a representative set of research problems from the chemical industry in general. Industrial laboratories are naturally cautious and are loath to let it be known what line of work they may be pursuing. It was felt, and experience proved the assumption to be correct, that a circular letter asking for problems would meet with little response; hence resort was had to direct personal appeal. By explaining to some of the heads of industrial laboratories the purposes of the Division of Chemistry and Chemical Technology, their coöperation was secured and as usual a few minutes' talk accomplished what a ream of correspondence could not have done. It is hoped that their example will be generally followed.

The division agreed not to disclose the source of the problems unless express permission was granted by the laboratory supplying the problem. In most cases, however, the heads of these laboratories expressed the desire to help in every way, with materials and information, investigators who would take up the problems they had supplied.

The division will keep a record of these problems, and if those who undertake their solution will notify the chairman of the division to that effect, their names will be entered in its list and other investigators who may wish the same problem will be notified of those known to be working in the field. Of course, the division cannot guarantee to *assign* any problem. It is possible that work may be in progress on some of these problems and that specialists may know of others that have already been solved. It is requested that in such case the division be notified, so as to avoid duplication of effort.

Physical Chemistry

1—Boiling point and vapor pressure curve of aluminium.
2—Boiling point and vapor pressure curve of alkyl carbonates.

Dimethyl carbonate, diethyl carbonate, dipropyl carbonate, iso and normal propyl carbonate, iso and normal butyl carbonate, isoamyl carbonate.

3—Boiling point and vapor pressure curve of ethyl benzene.
4—Vapor pressure curve of benzoic acid.

Vapor pressure over range of 100° to 180° C.
5—Vapor pressure curve of certain chlorides, such as of copper, zinc, gold, and silver.

6—Vapor pressure curve of formic acid.
7—Vapor pressure curve of hydrocyanic acid.

Vapor pressure, solid and liquid, vapor pressure of system hydrocyanic acid–water.

8—Boiling point and vapor pressure curve of magnesium.
9—Vapor pressure of mixed acids.

Specially interested in composition: actual sulfuric 56.00, actual nitric 22.3, nitrosyl sulfuric 5, and water 16 per cent.

10—Vapor pressure curve of pure silver.
11—Vapor pressure curve of salicylic acid.
12—Vapor pressure relations of metal and alloys.

Very few data on the vapor pressure relations of metals and alloys are available. For example, it would be interesting to know the effect of copper on lowering the vapor pressure of magnesium, and this might be carried through the complete series of compositions from pure magnesium to pure copper, and similar vapor pressure equilibrium diagrams for the system aluminium–copper would be not only very interesting but useful. Such work as this would be more or less pioneering and would represent a very creditable investigation when completed.

13—Equilibrium diagram of iron–carbon–silicon system.

The iron–carbon–silicon system is pretty accurately known so far as the liquidus is concerned, fairly well known as to the solidus, but imperfectly investigated with respect to the A_1 and A_2 transformations. An accurate survey of these unknown areas up to 4 or 5 per cent of silicon and at least up to 2 per cent carbon would be most valuable.

14—Equilibrium diagram of ternary system iron–carbon–metal.

Other ternary systems of iron–carbon and one other element would also be of importance. Further, the effect of relatively small additions of a fourth element to the iron–silicon–carbon system would have much value.

15—Study of the systems (*a*) water and potassium and sodium carbonates, (*b*) water and potassium and sodium bicarbonates, (*c*) water and potassium and sodium hydroxides, (*d*) combinations of water with three or more of the foregoing components.

Each of these systems should be studied in the light of the phase rule. The method of investigation of this problem would be analogous to that described in the paper by Blasdale on mixtures of sodium and magnesium chlorides and sulfates, This Journal, **13**, 164 (1920).

16—Free energy relation of certain aluminium compounds.

There is need for accurate data on the free energy relations of aluminium carbide, aluminium nitride, aluminium sulfide, and aluminium fluoride. In connection with the heat of formation of aluminium nitride, a recent statement [*C. A.*, **17**, 667 (1923)] gives the heat of formation as 62,000 calories per gram molecule of aluminium nitride. This is very much lower than the figures previously given by Serpek, who has determined a value of about 116,000 calories. A correct figure is of some importance, and it would be desirable to have another set of determinations, preferably by a different method.

17—A general study of the nature of colloidal solution in nonaqueous non-ionizing solvents.

The phenomena of colloidal solutions in aqueous media are fairly generally understood and are explained in terms of the ionic hypothesis. Comparatively slight attention has been paid to the nonaqueous solutions, some of which, of course—as, for instance, nitrocellulose—are of very great technical importance.

18—Fundamental study that will throw light on the structure of gels in nonaqueous solvents.
19—Heat of combustion of ethyl benzenes.
20—Heat of formation of cementite.
21—Heat of reaction $FeO + SiO_2 \longrightarrow FeSiO_3$ and $MnO + SiO_2 \longrightarrow MnSiO_3$.

Present values are for $FeO.SiO_2$: LeChatelier, 10 600 gram calories; Vologdin, 5905 gram calories; $MnO.SiO_2$: Le Chatelier, 5400 gram calories; Vologdin, 7725 gram calories; $FeO_2.SiO_2$: Hofman, 22,236 gram calories; Vologdin, 20,133 gram calories.

22—Index of refraction of alkyl carbonates.

Dimethyl carbonate, diethyl carbonate, dipropyl carbonate, iso and normal propyl carbonate, iso and normal butyl carbonate, isoamyl carbonate.

23—Index of refraction of ethyl benzenes.

24—Latent heat of vaporization of salicylic acid.

25—Latent heat of vaporization of phthalic anhydride.

26—Latent heat of fusion of salicylic acid.

27—Latent heat of fusion of phthalic anhydride.

28—Melting behavior of potassium fluoride.

There appears to be some uncertainty as to precisely what happens when potassium fluoride melts and as to how this melting temperature is affected by the presence of other salts or of water; and it seems desirable that more definite knowledge on this point should be secured.

29—Melting point of m-cresol.

Two melting points for m-cresol are found in the literature, one group of investigators giving values in the neighborhood of 10° C., and the other in the neighborhood of 4° C. What is the correct value? Or, are both values possibly correct, owing to the existence of two crystalline forms? This information is particularly desired by the International Critical Tables.

30—Moisture transfer rate through solids.

Wanted, value $\frac{dw}{dx}$ where w = per cent water and x = distance.

31—Melting point of acetylsalicylic acid.

There is a wide difference in melting points of the various makes of acetylsalicylic acid on the market and considerable discussion in the literature as to correct melting point. It would be desirable to have this point checked up on acetylsalicylic acid, with which particular attention has been paid to obtain an absolutely pure product.

32—Solubility of certain gases in steel 1500° to 1600° C.

Gases carbon dioxide and carbon monoxide especially desired.

33—Solubility of potassium cyanide.

Solubility in water and alcohol at various temperatures.

34—Solubility of sodium cyanide.

Solubility in water and alcohol at various temperatures.

35—Solubility of metallic soaps in various vegetable oils.

Reliable figures for the solubility of different kinds of soaps in the ordinary vegetable oils. The metallic soaps of lead, manganese, etc., are of great practical interest in the paint and varnish trade; and copper, iron, lead, and perhaps zinc soaps, which might occur as contaminations in refined edible oil, as well, of course, as the sodium, potassium, and, to a less extent, ammonium soaps, which are produced in the refining of these oils, interest the edible oil refiner.

36—Solubility of silver in distilled water.

37—Specific gravity of alkyl carbonates.

Dimethyl carbonate, diethyl carbonate, dipropyl carbonate, iso and normal propyl carbonate, iso and normal butyl carbonate, isoamyl carbonate.

38—Specific gravity of hexamethylenetetramine.

39—Specific gravity concentration tables with temperature coefficient for the system hydrocyanic acid–water.

40—Specific heat of asphalts.

41—Specific heats of ferrous oxide and manganese oxide from 1500° to 1600° C.

42—Investigation of the reason why the presence of nitrogen tetroxide in nitric acid so greatly hastens its action on metals.

This could probably be attacked best from the standpoint of the oxidation potential of nitric acid containing various amounts of oxides of nitrogen. The method would be similar to that outlined in papers by Moore, J. Am. Chem. Soc., **35**, 333 (1913), on the oxidation potential of aqua regia, which proved that aqua regia does not dissolve gold, platinum, etc., because it is a more powerful oxidizing agent than nitric acid or because of the action of the free chlorine present, but rather that the solvent effect is due to the removal of the platinum, gold, etc., ions to form complex ions, thus removing the reaction products from the field of action. The applicability of such information is obvious in problems involving, for example, the resistance of materials to the action of nitric acid.

43—A method of estimating the degree of wetting of solids by liquids.

We know that there are differences in degree of wetting, the only qualitative measure of that, at present, being the angle of contact between liquid and solid. Some better method, particularly as to the wetting of fine powders by liquids, would be useful.

44—A physico-chemical study of the system morphine–water.

This should include the determination of the freezing point-solubility diagram for the system and the vapor pressure diagram for the hydrated crystals. The information in the literature is very discordant. Apparently, the hydrated crystal substance decomposes when heated, but melting points are given which differ by as much as 20° C. The situation in regard to this system is so bad that the U. S. Pharmacopœia gives no data at all.

45—Viscosity of hydrocyanic acid solutions.

ELECTROCHEMISTRY

46—Condensers—study of certain alloys for condenser plates.

A study of the alloys of tantalum and aluminium to make condenser plates or the combination of asymmetric film-forming metals to produce good condenser anodes.

47—Conductivity, electrical, of metals and alloys above fusing point.

48—Copper plating.

Use of barium cyanide in copper plating; current efficiency at low concentrations and the effect in lowering sludge.

49—Electroplating of rarer metals.

Electroplating of the rarer metals, such as tantalum, titanium, zirconium, etc.

50—Films—composition of condenser films.

Composition and thickness of condenser films (found in various asymmetric film-forming metals of the electrolytic anodes). Chemical rather than physical methods to be used.

51—Can a cell similar to the oxyhydrogen cell be made to work with nitrogen and hydrogen?

If so, the fixation of nitrogen as ammonia could be made to liberate energy rather than requiring preliminary heating and compression as at present. The natural method of attack would be the employment of various electrode materials which might "catalyze" the change of molecular nitrogen to the ionic form.

52—Equilibrium of the cyanide zinc-plating bath.

Our knowledge of the ion concentrations in solutions such as are used for zinc plating leaves much to be desired. An investigation of the equilibria involved would yield useful information. It is not impossible that work along these lines has already been started, but a number of different equilibria are involved here, and it would not really matter if more than one person should tackle the general problem.

53—Effect of the surface of the base metal upon the character of the electrodeposit.

It is known that the character of an electrodeposit is affected by the metal on which the deposit is made, but there appears to be little definite information as to the why and wherefore of this effect.

54—A method of estimating the degree of adherence of electroplated films on metal.

No information seems to be available as to why some electroplated films adhere so much better than others. Some definite information on this matter would be very desirable. This problem is clearly closely related to No. 53.

55—A method of electroplating a steel spring to protect it from corrosion without destroying its "springiness."

If a steel spring is electroplated to protect it from corrosion, its character as a spring is seriously affected by reason of the fact that it absorbs hydrogen. For many purposes it would be desirable to be able to protect the steel spring by some method that would leave its properties as a spring unaffected.

56—True dielectric constants of dilute solutions.

It would appear as if much of the work on dielectric constants is not trustworthy, and an examination of the matter promises to be useful.

CORROSION

57—Corrosion of copper.

Effect of impurities in copper and its rate of corrosion in sea water.

58—Corrosion of copper.

Effect of sea water on copper coils with brazed joints, silver-soldered joints, etc.

59—An accelerated corrosion test on (a) iron, (b) zinc-coated iron, (c) nickel-coated iron.

We cannot have too much work upon types of accelerated corrosion test and intercomparisons between these, and the behavior of metals in actual use under various circumstances.

60—Characterization of surface films on metals by optical, electrical or other means.

It is becoming fairly clear that a very important factor in corrosion is the precise character of the first film that is formed upon the metal. Hitherto, however, there has been no method of characterizing these surface films, and it appears as if we might soon learn much more about the phenomena of corrosion if we had some method of differentiating these films.

61—The study of the inhibiting effect of sodium silicates and other silicates on the corrosion of metals.

It has been known for some time that sodium silicate will completely inhibit, within certain concentrations, the action of sodium hydroxide upon aluminium. About 0.5 per cent of sodium silicate will prevent action of a 1 or 2 per cent solution of sodium hydroxide which normally will

react vigorously with aluminium. The action of even a 5 per cent solution of sodium hydroxide is greatly lessened by the addition of 0.5 per cent of sodium silicate. The phenomenon probably involves the production of a protective coating of insoluble aluminium silicate, but there are many reasons to believe that the mechanism is not quite so simple and that a number of colloidal phenomena are involved. It is known that sodium silicate plays an important role in inhibiting the corrosion of iron and steel. In the case of nickel, sodium silicate will inhibit the action of sodium hypochlorite on this metal, which is vigorously attacked by the hypochlorite alone. Undoubtedly, this same action takes place in the case of other metals. A thorough study of this action not only would have great scientific interest, but would find considerable industrial application.

Inorganic Chemistry

62—Alloys of alkaline earth metals.

The alloys of the alkaline earth metals are becoming of commercial importance and a comprehensive study of their properties would be of great value.

63—Beryllium—large scale production of.

64—Production of metallic gallium and its substitution for mercury where used as an amalgamating agent.

65—Preparation of pure metallic barium (and strontium).

An examination of the literature indicates no method of preparation of pure metallic barium or strontium. It would be desirable to know how to prepare these in a pure state.

66—Production of and uses for thulia and thulium salts.

Thulia has interesting properties. On carefully heating thulia a beautiful carmine-colored light is given off, which changes as the temperature is raised, becoming yellow and then almost white.

67—A broader study of liquid ammonia and liquid sulfur dioxide as solvents with reference to commercial applications.

68—The commercial production of and uses for tantalum and columbium metals which possess high acid-resisting properties.

Organic Chemistry

69—Aceto-acetic ester. Keto-enol equilibrium.

In the condensation of the ethyl ester of aceto-acetic acid with aniline only about one-half of the ester is converted to the anilide. What influence on this reaction may be attributed to the tautomeric forms of the ester? Can the equilibrium between the enol and keto forms be varied advantageously? What other factors influence the condensation?

70—Anthraquinone—sulfonation of.

(a) Vapor phase sulfonation.

(b) Sulfonation with sulfur trioxide using liquid sulfur dioxide as a medium.

71—Formaldehyde—mechanism of its polymerization on storing.

Establishment of the relation between the amount of formic acid formed by oxidation and the velocity and extent of polymerization. Study of the use of small amounts of effective negative catalysts to inhibit oxidation and subsequent polymerization if this be the course of the reaction.

72—Indicator test paper.

The comprehensive study of indicator test papers for the determination of hydrogen-ion concentration, including (1) sensitivity, (2) methods of preparation, (3) development of new indicator papers, particularly a paper for the range covered by litmus and also one to cover the range between litmus and Congo red.

73—Rate of coupling of dye intermediates.

Methods of determining relative rates of coupling of dye intermediates and the establishment of the necessary constants for the more important ones. The data should be sufficient to enable one to predict which of a given pair of intermediates would couple more rapidly under a given set of conditions.

74—A study of the reduction of aldehydes and ketones having the structure $R - \underset{\text{C}}{\overset{\text{H}}{|}} = \underset{\text{C}}{\overset{\text{H}}{|}} - \underset{\text{C}}{\overset{\text{H}}{|}} = O$ to the corresponding alcohol.

Examples—cinnamic aldehyde, citral, benzylidine acetone.

75—The study of Friedel and Crafts' synthesis or its modifications when using compounds like ethylene chlorohydrin or ethylene oxide.

Example—Preparation of phenylethyl alcohol from benzene and ethylene chlorohydrin.

76—Development of an economic process of making m-cresol.

m-Cresol is important in the preparation of methylcoumarin and thymol.

77—Structure of metallic derivatives of dithiocyanic acid and perthiocyanic acid.

The discussion of these compounds in Beilstein indicates that most of the work on them is quite old and apparently has never been critically considered. Determination of their structure might prove an interesting study. There are apparently a number of related compounds the constitution of which is assumed on rather slender grounds, and a careful study of a few of these might clear up considerable territory.

78—A general study of the possible synthesis of organic compounds from carbon and lime (via acetylene).

79—Preparation of pure salts of phenol.

Calcium phenolate, sodium phenolate, copper phenolate, aluminium phenolate, magnesium phenolate, barium phenolate, etc.

Cellulose and Nitrocellulose

80—Adsorption by nitrocellulose—studies of.

81—Nitrocellulose—nature of camphor-nitrocellulose complex.

82—Nitrocellulose—preparation and study of properties of pure nitrocellulose.

Preparation and study of properties of pure nitrocellulose of exact chemical composition—for example, cellulose pentanitrate.

83—Nitrocellulose—study of solvent power of anhydrous solvents.

84—What relation does a so-called "solvent," a "colloiding agent," or a "softener" bear to nitrocellulose when one or all of these substances are in combination with nitrocellulose?

Is the relation chemical or physical or both? Almost as many hypotheses have been advanced to explain this relation as there are possibilities, but there is a great dearth of data from which any of them could be judged. If the relation or relations could be found, methods of determining these relations quantitatively would probably be found also, and this would lead to more definite plans of search for improved solvents, etc. It might be desirable to confine this study to nitrocellulose, because this substance has properties that lend it to investigation at normal temperatures.

85—The colloidal chemistry of cellulose derivatives, especially cellulose esters and ethers.

Our knowledge of the remarkable properties of these materials is confined almost wholly to their applications in the arts, where most of the development work has been empirical. Their systems have been classified under the general heading of colloidal solid solutions by scientific writers, who refer to them in texts on colloid chemistry only in connection with the use of collodion for the preparation of dialyzing bags. It seems remarkable that materials of such wide application should have been avoided so long, when a clear understanding of the fundamental reasons for their properties is obviously necessary to a complete and scientific development of them in the future.

86—A study of new reactions of cellulose.

Paints and Varnishes

87—Paints—heat radiating.

Paints to be used on heat-conducting surfaces to aid in heat dissipation rather than as a heat insulator. Investigation of thin, protective oxide finishes on metals.

88—Reflective coefficient of pigments.

Determination of the reflective coefficient in the ultra-violet of various commercial pigments, such as are used in paints and varnishes.

89—Method of estimating adherence of japan films to metals.

Japan films adhere well to some metals and not to others, and the degree of adherence seems to depend upon the character of the surface of the metal, and therefore upon its previous treatment. It would be very desirable to have some method that would give us a convenient measure of this degree of adherence.

90—Influence of temperature upon the qualities of japan and paint films.

A more definite knowledge would be desirable as to the effect of baking temperature upon the properties of japan or paint films, and, indeed, as to precisely what happens during this baking process.

Rubber

91—Study of behavior of pigments in rubber.

Comprehensive and thorough study of the behavior of pigments in unvulcanized rubber and during and after vulcanization, including further correlation between average particle size and reinforcing effect, orientation of the particles in the mass, particle shape, degree of dispersion of the particles, flocculation, undispersed aggregates, forces of adsorption of adhesion between dispersed particles and the rubber matrix, particle size of uniformity, etc. This study will require the skilled use of the microscope.

92—Study of plasticity of unvulcanized rubber.

Study of the plasticity of unvulcanized rubber and resolution of this property into reliable values for its two components, mobility and "yield value." Present instruments and methods for the measurement of plasticity in rubber apparently do not measure "yield value." The

investigation should compare various commercial raw rubbers, study the effect of mechanical working (milling), "softeners," accelerators, rubber "solvents," and mineral compounding ingredients on the component true physical properties embodied in the concept of *plasticity*.

93—Determination of solubility in rubber.

Determination of the solubility in rubber (true solution) of various substances commonly used in the compounding of rubber, including, of course, sulfur (to confirm recently published data), organic accelerators, waxes, pitches, asphalts, vegetable oils, factice, paraffin, etc. Such an investigation would throw a great deal of light on the behavior of these substances in acting as "softeners" and increasing the "tackiness" of degree of disaggregation of unvulcanized rubber in the mixing operation prior to vulcanizing.

94—Investigation of aging or "perishing" of vulcanized rubber.

An exhaustive investigation of the aging or "perishing" of vulcanized rubber and the development of "tackiness" in raw rubber, including the influence of oxidation, "depolymerization" of disaggregation, combined sulfur temperature, anti-oxygens, vulcanization accelerators, and compounding ingredients. Such a study must necessarily consider the *chemical mechanism of aging*.

95—Study of changes in principal physical and mechanical properties of rubber.

Study of the changes in the principal physical and mechanical properties of rubber, both unvulcanized and vulcanized, which accompany changes in temperature. Should include tensile properties, extensibility, resistance to rupture by extension or impact, rigidity or "hardness," resilient energy capacity, permanent or supermanent deformation following stress, density (coefficient of cubical expansion), etc.

96—Chemical relation of rubber, gutta-percha, balata, etc.

Little seems to be known as to the precise chemical relationship of these substances, and any information upon the fundamental chemistry of them would therefore be useful.

97—Direct determination of rubber in vulcanized rubber goods.

There seems to be no good method for directly determining rubber in vulcanized rubber goods. Such a method, if it can be developed, would be very useful.

98—Effect of copper (or other metallic) salts upon the deterioration of rubber.

It is known that various metals and metallic salts act catalytically in destroying the usefulness of rubber. Further information along this line would be welcome.

99—Diffusion of sulfur through rubber in relation to the phenomenon of blooming.

Apparently, little work has been published as to the rate of diffusion of sulfur through rubber and the relation between this rate, the amount of sulfur in the rubber, and the phenomenon of blooming on the surface of the rubber.

PAPER

100—Method of estimating the acidity of paper.

It is not certain that the methods now used for estimating the acidity of paper give correct results, owing to the possibility of preferential adsorption by the paper. Further examination of this question therefore is desirable. The acidity of paper used for electrical insulating purposes is an important consideration.

Commercial Invert Sugar[1]

Its Manufacture and Uses

By Stroud Jordan

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There are few manufactured products containing sucrose which do not also contain notable amounts of invert sugar, either from intentional addition or from unintentional production in process of manufacture. Invert sugar is a valuable addition to any diet on account of the ease with which it is assimilated, and as a moisture holder it is the equal of glycerol. Its small cost and the simplicity of its preparation make of it an indispensable product for confectioners, bakers, tobacco manufacturers, preservers, and canners. General historical data, patent references, methods of preparation, and some of its more general uses are given in the accompanying article.

THE first plant for the production of invert sugar was established by Busy Bee, Ltd., and his product was intended for home consumption. As its use became more general, supply would not meet demand and the only method available was the raising of more bees. One often finds that an increase in production by natural means is not efficient; this was the case with bee raising, for the bees consumed entirely too much of their own product. Under such circumstances man turns towards duplication, either from natural sources or by artificial means, but natural sources were not promising and have never been developed, while production of artificial honey and honey substitutes has gained remarkable headway in the last fifty years.

Honey contains, for the most part, equal parts of dextrose and levulose, along with small quantities of formic and other acids and the extractive matter peculiar to the plants, flowers, and fruits from which the honey has been gathered. Since dextrose and levulose constitute the major portion of honey, the investigator usually attempts to duplicate this portion first. If dextrose and levulose alone were used for honey substitutes, they would offer no perceptible advantage over a straight sucrose-water solution, for the actual honey character is due to small amounts of perfume and flavor which have been gathered by the bee and without this flavoring material no saccharine matter will bear the slightest resemblance to honey in taste.

[1] Presented before a meeting of the New York Section of the American Chemical Society, October 5, 1923.

HISTORICAL DATA

It was early observed that when sucrose was heated with certain fruit juices it did not grain out, or such action was noticeably retarded. Such observations led to a systematic examination, and in each case where graining was retarded or stopped the juice was found to be distinctly acid in character. In juices deficient in acid little or no change took place. Lemon juice may be taken as an example of the former and fig and citron juices as examples of the latter, but the real nature of the change which took place was not understood until Dubrunfaut heated 700 grams of sucrose in a 10 per cent aqueous solution with 14 cc. of hydrochloric acid for 12 hours at 60° C., and then separated dextrose and levulose from the resulting solution. This experiment was carried out in 1830, but the name was not appended to the product until after Biot discovered that a plane of polarized light when passed through an aqueous sucrose solution turned to the right but that after the same solution had been heated with acids the light was turned to the left. This phenomenon was noted in 1836, and the product was called inverse or invert sugar, while the process was called inversion of sucrose.

About 1843 Mitscherlich found that it was not necessary to use so much acid in the inversion of sucrose, and that as little as 0.01 to 0.10 per cent of a strong inorganic or organic acid would cause as nearly a complete inversion as could be carried out, provided the solution was kept at a sufficiently high temperature for the proper length of time. Dubrunfaut found out later, about 1856, that the use of tartaric, phosphoric, or oxalic acids

in about 0.01 per cent concentrations would cause inversion, that there would be no secondary reaction such as is produced by strong mineral acids, and further that the resulting mass would assume the consistency of grained honey if allowed to stand for a time in a cool place. In 1885 Herzfeld made a study of the inversion of sucrose in aqueous solution and used small quantities of citric, tartaric, and other organic acids. He heated the sucrose solution with the acid to approximately 230° to 235° F., but found that such heats would caramelize the sugar and produce a dark yellow color. In his treatise, published about 1887, he describes methods for the production of invert sirups and their uses in making wine, in brewing, and in preserving fruits, notably those deficient in acids. The method recommended for the production of invert sugar was to make an aqueous solution of sucrose containing 75.00 per cent of sucrose, add 0.11 per cent of tartaric acid, and maintain the solution at a boiling temperature until it acquired a golden yellow color. The product was intended to look like honey and to be used in the blending of strong heather and linden honeys, whereby they became more palatable.

PATENT REFERENCES

Colored invert sirups are easy to make, for the levulose formed will begin to caramelize if the solution is not cooled immediately after the reaction has finished. To keep the sirup white requires immediate cooling, and this fact was covered by Wohl and Kohlrepp, who patented a process for the production of invert sugar by the action of 0.045 per cent of tartaric and 0.06 per cent of citric acid on an 80 per cent aqueous sucrose solution, at a temperature of 100° to 110° C. At the end of the reaction the product was rapidly cooled, and the device forms a part of British Patent 16,540, issued to the inventors in 1889. Another patent covering a similar process was issued by the U. S. Patent Office, bearing number 1,181,086 and dated April 25, 1916. This patent is essentially the action of 0.07 per cent of citric acid on an approximate 75 to 80 per cent aqueous sucrose solution, heated from 99° to 103° C. for about one hour and then at 111.5° C. for a short time, after which 0.14 per cent of gum arabic is dissolved in water and added. The solution is then well skimmed and suddenly cooled by an umbrella-shaped cooler, which is described in and forms a part of the patent.

British Patent 25,340, issued November 10, 1906, covers the preparation of invert sugar sirups by the precipitation of the bases from the salts normally present in high-ash sugars by the addition of hydrofluoric acid and using the liberated acids to invert and bleach the sirup. A later patent to the same inventor, British 5900, November 9, 1914, covers the addition during inversion, of carbon, having a low acid-soluble ash, and then filtering. Oxygen or air is bubbled through to agitate, either before or after filtering.

In the manufacture of confections or containers with invert sugar centers, British Patent 17,637, July 29, 1909, covers the preparation of a shell of glucose by molding and then filling with invert sugar and subsequently capping with glucose. This is made for transportable forms and presumably covers the preparation of liquid confections.

Perhaps the most interesting and unique patent covering the preparation of invert sirups from raw sugars was issued December 8, 1909, and bears British Patent 28,742. It consists in first making a small quantity of invert sirup from pure sucrose and water by the action of a small quantity of acid, and using this sirup to wash raw sugars in a centrifugal machine, whereby the molasses jacket around the crystals is removed, leaving a washed sugar which may then be used for inversion. The resulting inverted sugar sirups are again used to wash the next batch of raw sugar, and this subsequently is inverted, giving a sirup of a pleasing yellowish brown color and desirable raw sugar taste. The use for such material would probably be in the blending of molasses or as a table sirup, just as it is made.

Still another unique patent covers the preparation of invert

sugar in 20 per cent concentrations of raw sugar in aqueous solution, by passing through an electric current of the proper voltage and amperage at the same time heat is applied to the solution. The mineral salts are split and the liberated acids cause hydrolysis. It is not necessary to resort to such measures as just described if the sucrose content of the raw sugar employed is 96 per cent or better and if the ash value of the sugar is kept at the lowest possible point. Small quantities of citric or tartaric acids will invert such sugars, and the extra acid employed will be used up eventually in forming compounds with the bases that are combined with weak acids. The resulting solution will have a very nice taste and the acidity will not be excessive. Until the alkalinity of the ash, as lime, has been thoroughly neutralized, or rather, until a sufficient quantity of citric or tartaric acid has been used to replace the weak acids in the raw sugar employed, the inversion will rarely exceed the inverting power of the calcium salt of the acid employed. This means that the total inversion in high-ash sugars will be due to the weak acids liberated, which is almost negligible, and to the solubility and subsequent ionization of the calcium salt or other salts present. To illustrate this fact a hot 75 per cent solution of a raw sugar containing approximately 1 per cent ash was made up with water. This solution was divided into five parts and to each part was added 1.5, 3, 4, 8, and 12 ounces of tartaric acid per hundredweight of sugar and each part heated at 111° C. for 30 minutes. In each case the resulting solution showed a very slight variation from +50.0° V. on a normal sugar weight basis. The inversion in each case was practically the same.

Many other processes and patents are in existence for the preparation of invert sugar and sirups, but they all depend upon the action of an acid, salt, or enzyme in an aqueous solution, whereby the sucrose is split into dextrose and levulose after it has combined with one molecule of water in the reaction. On long boiling in aqueous solution and at a sufficiently elevated temperature, sucrose will gradually break down and assume an acid character. Such solutions will invert without the addition of other materials if the heat is continued long enough.

METHODS OF PREPARATION

In the preparation of invert sugar sirups by the invertase method, there is the drawback of having to keep the solution at a nearly constant temperature, and the sucrose concentration is seldom in excess of 20 per cent, generally lower, which does not compare very favorably with the higher concentration employed in the acid inversion. In most cases where invert sirups are employed, a concentration of 80 per cent sugars in the sirups is necessary, and to make such a sirup by the invertase method will require the use of a vacuum pan to concentrate the finished product, which cuts down very materially the actual poundage to be made. Invertase is required in some cases, for a slight trace of acidity will sometimes work havoc with a product, and in such instances this method is indicated for the production of the invert sirup. As an example of the effect of small quantities of acid in a fondant or cream, 0.12 per cent of tartaric acid, introduced as a 50 per cent aqueous solution and at an average room temperature (75° F.) and kept for 6 months, showed an increase in reducing sugars equivalent to 8 per cent of invert sugar.

Methods in which mineral acids are used will go very well if color is of no moment and if the presence of such acids is not objectionable. These acids make a very inferior product, as they have to be neutralized with sodium bicarbonate and this introduces mineral matter into the sirup, causing it to become yellow much quicker when heated to high temperatures. The taste of such sirups does not compare with the taste of sirup made by the action of small quantities of citric or tartaric acid.

COMMERCIAL MANUFACTURE

The equipment required is small and common in most places requiring such a product. A steam-jacketed copper or enameled

kettle of sufficient capacity, with an attachment for running cold water and steam through the jacket, is the simplest and least expensive form. If a cooling system such as is employed in the manufacture of cream or fondant is available, a better and whiter product is obtained. The kettle should be equipped with a suitable stirrer, preferably of the propeller type, which should be kept in motion at all times. Fifteen to 20 revolutions per minute will be found sufficient.

On a 1000-pound producing basis, 750 pounds of sucrose, 250 pounds of water (approximately 30 gallons), and 10 ounces of tartaric or 13 ounces of citric acid are used. The sucrose is dissolved in the water by stirring while the heat is being raised to the boiling point. The acid, dissolved in a small quantity of water, is added to the sugar and water before the heat is applied and the whole mixture is heated until it boils gently and is held at incipient boiling for 30 minutes. The sirup is then run out and passed through the cooler, or, if the cooling type kettle is to be employed, the steam is shut off and cold water run through the jacket, keeping the sirup in constant motion all the time cooling is in progress. The finished product should weigh 950 pounds, and if the consistency of grained honey is desired, it is seeded with dextrose crystals, chilled thoroughly, and allowed to stand in a cool place for a few days. If the sucrose content which remained unchanged during the process does not exceed 2 per cent, and if the total sugar solids show 80 per cent, then the graining will not be slow in beginning.

The cost of 100 pounds of invert sugar sirup will be the cost of the sucrose used plus a small charge for acid, labor, and steam. The larger the individual batch the smaller the poundage charge for "overhead" will be. It was customary at one time, however, for manufacturers of invert sugar sirups of an approximate 80 per cent sugar solid content to charge 55 points in excess of the price for sugar, on sirup poundage. It must be remembered that the manufacturer has to absorb barrel cost, filling, and perhaps haulage to the point of shipment, and then make a profit in addition—all of which is eliminated if one makes his own product.

If it is desired to invert raw sugars, one should use 96 per cent raws or better and four times the quantity of acid required in the process using standard granulated sugar. It will also be found advisable to boil the sugar and water before adding the tartaric or citric acid solution and to skim the solution well. In this manner some of the trash and mineral matter is removed and a better inversion takes place. If a specially mild sirup is desired, enough calcium carbonate may be added to combine with most of the free acid and the sirup boiled a few minutes after the inversion has finished. The calcium salts will settle out on standing, if they are in sufficient quantities to give trouble.

Uses of Invert Sugar

There are two distinct uses for this product, which may be called direct and indirect needs. Wherever the use of sucrose alone causes the product to become hard and gritty from the presence of crystals, this defect may be overcome by partial inversion or by incorporating a small percentage of invert sugar with the sucrose; this is a direct need. If it is necessary to hold moisture in a product, invert sugar may be used, but it will not replace glycerol in all such cases. As a softener and moisture-holder this may be called an indirect need, for sweetness is not of prime importance. It is well to point out that invert sugar will not replace glycerol where a softening and lubricating effect as well as the holding of moisture is necessary, for it does not have the striking-in power of glycerol and instead of being a lubricant it is gummy and sticky, although it will hold 15 per cent moisture under most conditions.

In the preparation of certain infant and invalid foods invert sugar has been and is still used. Results show that more invert sugar is assimilated than either milk sugar or maltose. Tests carried out in infant feeding, by determining the amount of sugar which is eliminated, show more invert sugar being assimilated than milk sugar, maltose, or sucrose. This is a sort of pre-digested sugar, and in the same shape the stomach has to prepare sucrose, by the action of acid juices and enzyme action, before assimilation.

The baking trade uses a considerable amount of invert sirups to keep its products soft and to prevent checking. In this connection it is interesting to note that Austria allowed up to 5 per cent of rye, barley, or other flour to be replaced by invert sugar during the war period, with exceptionally pleasing results. It was later advocated in Germany as a fat substitute and was prepared for this purpose by inverting with a mixture of tartaric acid and calcium and sodium chlorides. The reason given for the addition of calcium and sodium chlorides was that it required more salt to offset the added sweet taste than was required where no such addition had been made.

The preserving and canning trades seldom require the addition of invert sugar sirups, for fruit juices will generally attend to all inversion required. In such cases as have been mentioned, notably figs and citron, where the normal acidity is deficient, invert sugar or an acid must be added, or the time-honored recipe of our grandmothers, which calls for a slice of lemon in pear, fig, and citron preserves, adhered to. This is a very common direction in recipes for home preserving and, besides causing inversion of sucrose, the lemon adds somewhat to the resulting flavor.

Fountain sirups and true fruits require little invert sugar, except in such cases as have been mentioned. The need for this material is very apparent when artificial or imitation extracts are used in conjunction with "simple" sirup. To keep such sirups from graining the ratio of invert to sucrose of two to one is effective in most cases.

In confectionery the use of invert sugar is and has been universal for some time. There are few products using pure sucrose where a percentage of invert sugar is not used in the preparation or an acid or acid salt is not used in the cooking process. In the so-called liquefying centers and other self-softening confections, the action is due to slow inversion caused by acids, acid salts, or enzymes. In other cases where confections tend to get short with age, one will find that invert sugar, used in small quantities, will retard and sometimes inhibit such action.

The tobacco industries consume quite a yearly poundage, but as a general rule they prepare their own invert sirups. Their saving in cost averages one dollar per hundred pounds when compared with the outside suppliers' price; moreover the tobacco industries generally use raw sugars for inversion. The use of invert sugar has saved the tobacco industries many dollars on the glycerol they have been able to eliminate, but it must not be understood that this was a direct need for glycerol which invert sugar replaced. By substituting invert sugar for a large portion of the sucrose used, crystallization and attendant hardening disappeared and with it the need for glycerol. Invert sugar is used by the tobacco manufacturers as a "casing" for some cigaret tobaccos to hold the short tobacco with the long and to keep moisture in the tobacco at the same time. Its widest application is to the manufacture of plug and pipe-smoking tobaccos and for the heavy dips used on highly sweetened and flavored cigaret tobaccos. The tobacco industries consume enormous quantities of invert sugars yearly, perhaps more than any other industry.

Invert sugar has been and still is used as a source of levulose and dextrose. It would seem that the hydrolysis of starch should furnish the necessary amount of dextrose, and inulin from tubers, such as the dahlia, artichoke, and chicory, should furnish the necessary amount of levulose. Processes are said to be in vogue on the European Continent for the preparation of a levulose sirup of good quality from the Jerusalem artichoke and the dahlia bulb. Many other materials will yield invert sugar and therefore dextrose and levulose, but their use is worth only passing mention. It is possible to recover 33 per cent of

dextrose hydrate from well-grained invert sugar by the simple process of centrifuging and washing, but the drawback to this process is that the invert sirups will not always crystallize. If such a proposition could be handled, the resulting sirup, rich in levulose, would most surely have a ready market and command a good price.

Conclusion

No quantity of invert sugar is too small for the individual user to make at a saving. The process is simple and the product

easily handled. If, however, it is desired to purchase this material under any of its fancy names, as it appears on the open market, the specifications as laid down in This Journal, 9, 757 (1917) should be strictly adhered to. It is useless to buy sirup as invert sugar which does not contain as much sucrose inverted as is chemically possible, and this may be set as within 2 per cent of the total sucrose present in a sirup at the start, if pure sucrose has been used. Buy invert sugar and you can mix whatever amount of sucrose you may desire with it, but make the supplier sell invert sugar and not an invert and sucrose mixture.

Standard Methods for Determining Viscosity and Jelly Strength of Glue

Adopted by the National Association of Glue Manufacturers, Atlantic City, N. J., October 10, 1923

PART I

(A) Preparation of Sample

1. Subdivision of Sample—Sheet and flake glue should preferably be reduced to at least 4 mesh, finer if in the judgment of the operator it appears necessary, so as to minimize weighing errors and to shorten the soaking period.

2. Concentration and Quantity of Solution—Samples are made up in duplicate at a concentration of 12.5 per cent by weight. Since a minimum of 100 cc. of solution at 60° C. is required for the viscosity determination, 15 ± 0.05 grams of commercially dry glue are weighed out and transferred without loss to the standard container (described in C-2), and 105 ± 0.25 grams of distilled water at approximately 15° C. are added while the glue is being thoroughly stirred with a thin metal rod. A metal rod is preferable to one of glass, since small glue particles will not adhere to the former when it is wet. If the end of the rod is pointed, particles in the corner of the container can be reached. The container is now closed with the perforated stopper.

3. Soaking Temperature—The samples are then placed in a cooler, ice box, or other compartment held at a temperature of 10° to 15° C.

4. Soaking Period—In view of the variableness in subdivision and grade of glue samples, the committee does not consider it advisable to fix the exact length of the soaking period. It must, however, be long enough to soften the glue thoroughly. Soaking over night is sufficient for all glues. It has been demonstrated that shorter time is permissible for some samples, but such a change in procedure should only be made in the light of experience justifying same.

5. Procedure for Melting of Samples—In order not to crack the thick-walled containers they should be placed for a few minutes in water of 20° to 30° C. before being put into the melting bath. The sample is then placed in the melting bath, the temperature of which is not allowed to exceed 70° C., and brought to a temperature of 62° C. as determined by an accurate thermometer placed in the glue solution and carrying one of the stoppers described but with a small perforation off center. The stopper originally closing the container is placed aside until after the viscosity determination has been made, when it is again used to close the bottle.

The time required to bring the sample up to temperature should not exceed 15 minutes and, having attained the required temperature, there should be no delay in transferring the sample to the viscosity pipet. After closing the container with the stopper carrying the thermometer and before reaching the final temperature, the solution must be made thoroughly uniform, preferably by swirling the container a number of times. Any motion

that will produce violent agitation of the solution should be avoided.

In order to keep the supply of samples to the pipet continuous, several samples will have to be in the process of melting at the same time. Moreover, they should leave the bath in the same order that they entered it so that all samples will have been subjected to as nearly identical thermal conditions as possible. The maximum number of samples present in the bath at any one time will depend largely upon the speed with which the subsequent viscosity determinations are made. A short trial will determine the correct number. Samples of low-grade glues heat through more rapidly than the more viscous high-grade ones and can be brought to temperature faster than the latter. The time required to make the viscosity determination varies in the same direction; hence the number of samples in the melting bath at any one time becomes fairly constant.

(B) The Viscosity Determination

1. Viscometer—The committee recommends the adoption of the pipet form of viscometer for glue solutions. The particular form of pipet distributed to members of the association was designed after the Bloom viscosity pipet, which has been in use at the laboratory of a large packing company for the past five years (Fig. 1). A slight modification of the bulb portion of the pipet was made to secure better drainage. This type of viscometer furnishes a rapid and, when used under proper conditions, a sufficiently accurate means of determining the viscosity of glue and gelatin solutions.

2. Temperature Control—The pipet is jacketed with water held at a temperature of 60° ± 0.2° C. by an electrical heating device. Approximately complete immersion of the heating element is desirable, and can be accomplished by the insertion of variable external resistance in series with the heating element. A centigrade thermometer graduated in 0.1 degree is used to determine the temperature of the glue liquor after its introduction into the pipet.

3. Stop Watch—A watch graduated in fifths of a second and checked for accuracy should be used. It is recommended that the watch be of the type that runs continuously when wound, and not of the type whose whole mechanism is set in motion when the stem is pressed, as it has been observed that there is a lag in the time recorded due to this acceleration of the mechanism.

4. Assembling and Setting up Viscosity Apparatus—The assembling and setting up of the viscosity apparatus is described in the circular sent out with each set. A few additional suggestions may be added here. If the water jacket when fixed in position is not held firmly by the upper ring, the ring should be covered with a piece of rubber tubing slit lengthwise and of

thick enough wall to prevent furthur play of the bottle in the ring clamp. This precaution serves to prevent the breakage of the pipet at the capillary end. A rubber stopper (No. 13) cut to a thickness of $^1/_4$ inch (6 mm.) makes a better support for the lower end of the pipet, since it is more flexible than cork and will not become leaky on use. The water-jacket drain tube may also be used for the introduction of the compressed air when this is used for agitation of the bath. Small sections of rubber tubing slipped over the jaws of the buret clamp used to hold the upper part of the pipet in position will make a snug fit and thus reduce the chances of snapping off the capillary end. The end of the capillary tube should extend approximately $^1/_{16}$ inch (2 mm.) beyond the rubber stopper. Care should be taken that the viscometer is in a vertical position and that it is not held in position under strain. The water in the jacket must be agitated so that not more than 0.2° C. difference in temperature exists between any two points of the bath while the determination is being made.

5. CALIBRATION OF THE VISCOMETER—This is fully discussed in the circular accompanying the apparatus.

6. THE VISCOSITY DETERMINATION—The sample, prepared as directed in Section A, is transferred to the pipet as quickly as possible without entrapping air. Enough of the solution is poured into the viscometer to bring its level about 1 cm. above the upper mark on the pipet while a finger of the free hand closes the capillary end. The residual liquor is left in the container and the latter placed on the iron stand directly under the exit tube. The special centigrade thermometer furnished with the apparatus is placed in the pipet and slowly lowered and raised until it registers and maintains the temperature of 60.0° C. when its bulb is about midway between the top and bottom of the bulb of the pipet. The thermometer is then removed and the level of the solution adjusted to the upper mark. When not in actual use the thermometer should be placed to nearly its full length in water having a temperature slightly above 60° C. It should, of course, be wiped dry before use. The time required for the 100 cc. of solution to pass through the capillary tube of the viscometer is obtained by simultaneously starting the watch and withdrawing the finger from the end of the tube and then stopping the watch when the level of the solution has reached the lower mark on the pipet. The container is then closed with the original perforated stopper and the sample used for the jelly strength determination. After each determination and also before using after the apparatus has been idle for any length of time, the pipet is washed out with about 25 cc. of water heated to 62° C. and allowed to drain thoroughly. When not in use the funnel end of the viscometer should be covered to prevent the entrance of foreign matter.

The viscosity is to be expressed in millipoises calculated according to the formula appearing on the certificate of calibration accompanying each pipet and as described in the circular. The viscosity range of ordinary commercial glues is approximately 30 to 165 millipoises.

(C) JELLY STRENGTH DETERMINATION

1. GELOMETER—The committee recommends the adoption of the Bloom gelometer (Association Style A) as the official instrument of the association for making the jelly test of glues and gelatin (Fig. 2). It has been found to give duplicate results under identical conditions, is easy of operation, and capable of exact duplication in construction, particularly of fundamental parts.

2. CONTAINER FOR THE JELLY—The container recommended is an extra wide mouthed bottle of the following specifications:

Capacity	150 cc.
Diameter of body:	
Inside	59 mm.
Outside	66 mm.
Height over all	85 mm.
To take rubber stopper No. 9.	

Bottles showing a variation of more than 1 mm. in average internal diameter from these dimensions shall be rejected. The

tapered stopper is cut in half and the upper portion is perforated by plunging a red-hot, 1-inch brad through it at the center. The upper half of the stopper is used to obtain a snug fit in the neck of the bottle and the air vent prevents the stopper from being blown out during the melting and heating of the sample. It is not necessary to emphasize that the containers and stoppers must be clean and dry.

3. METHOD OF CHILLING GLUE SOLUTIONS—The sample from the viscosity determination in the tightly stoppered container is allowed to cool in air to approximately 45° C. The finger is then placed over the perforation in the stopper and the container inverted several times to mix in the water that has condensed on the walls of the bottle and the under side of the stopper. The container is then placed in a constant temperature chill bath for not less than 16 nor more than 18 hours at 10° ± 0.1° C. The committee wishes to call attention to the importance of the temperature variation of the chill bath. Unless the bath controls the temperature within the limits prescribed above, it will be necessary to use "standards" and thus make relative and not absolute tests.

4. DETERMINATION OF JELLY STRENGTH—The determination of the jelly strength of the sample is made with the Bloom gelometer, adjusted to give a 4-mm. depression and to deliver shot at the rate of 200 grams per 5 seconds when the clam-shell arm E_4 rests upon dog D_2 and 800 grams of polished No. 12 chilled lead shot are in Hopper I. Specific directions for making these adjustments accompany each instrument. All determinations are made from the dog D_2, the results to be recorded in grams required to produce the 4-mm. depression as prescribed above.

(D) CHILL BATH

The chill bath developed by F. S. Williams is a great step in advance of previous apparatus used by members of the association, and is recommended for adoption in general form and principles by this committee. Only a few members have thus far been supplied with the chill bath, and the apparatus has been in use only a short time. If further experience and continued use indicate the desirability of modification of the mechanical details, this can readily be accomplished.
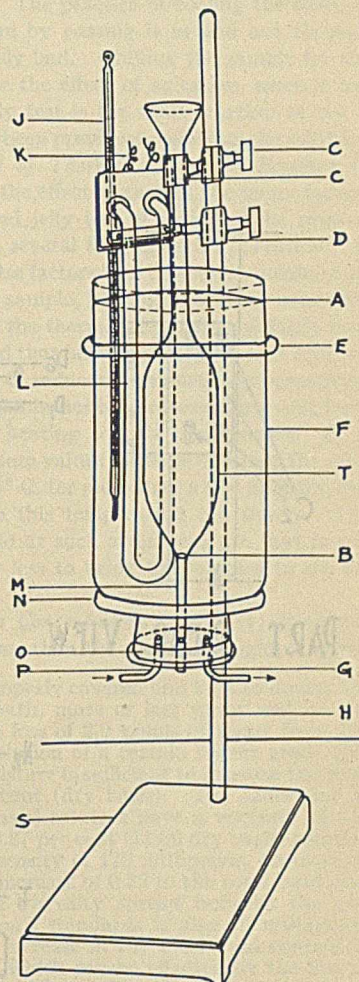

FIG. 1—STANDARD VISCOSITY PIPET

A—Upper etched line
B—Lower etched line
C—Clamp supporting pipet
D—Clamp supporting heating element
E—Ring clamp supporting water bath
F—Water bath (5-pound bottle, bottom cut off)
G—Drain tube
H—Iron support
J—Thermometer
K—Terminals to heating element
L—Heating element
M—Capillary efflux tube
N—Ring supporting water bath
O—Rubber stopper
P—Compressed air connection for agitation
S—Iron stand
T—Calibrated viscosity pipet
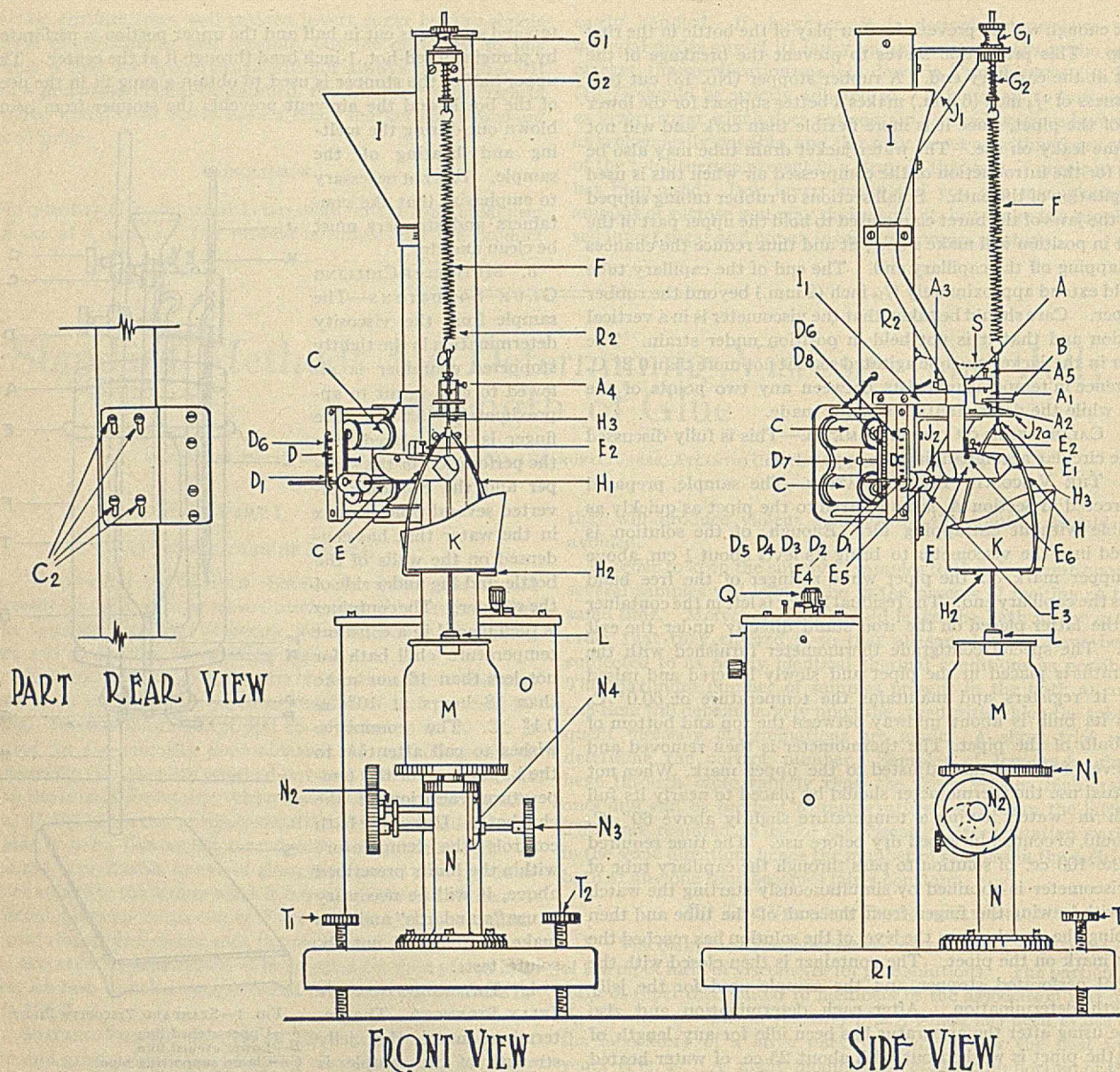
PART REAR VIEW   FRONT VIEW   SIDE VIEW

FIG. 2—BLOOM GELOMETER

A—Brass contact point bracket
A₁—Upper contact point
A₂—Lower contact point
A₃—Wood fiber support for A
A₄—Set screw to hold adjustment screw in position
A₅—Adjustment screw for A
B—Pure silver disk (⅝ inch diameter and ¹/₁₆ inch thick)
C—Electromagnet
C₂—Adjustment screws for adjusting pitch of clam cut off E
D—Guide bar of automatic shot control mechanism
D₁, D₂, D₃, D₄, D₅—Lower dog
D₆—Upper dog
D₇—Hair spring coil to keep D₃ in position
D₈—Soft iron bar supporting dogs D₁ to D₆
E—Clam-shell spout
E₁—Stationary clam-shell jaw
E₂—Adjusting screws to regulate closure
E₃—Weight
E₄—Clam-shell arm
E₅—Set screw to clamp weight to clam-shell arm
E₆—Bearing on which cut-off mechanism turns
F—Spiral spring (No. 6 steel music wire)
G—Adjustable support for spring F
G₁—Thumb screw nut
G₂—Tension spring

H—Suspended pan and pan arm for shot receiver, etc.
H₁—Pan arms
H₂—Pan
H₃—Rod attached to pan arms supporting disk B
I—Shot hopper with delivery tube
I₁—Bracket to hold lower end of shot delivery tube
J₁—Upper supporting bracket attached to frame support R₂
J₂—Lower supporting bracket attached to frame support R₂
J₂ₐ—Guide arm attached to J₂
K—Shot receiver
L—Plunger (12.7 mm. in diameter)
M—Test bottle
N—Elevating platform base
N₁—Platform
N₂—Rack and pinion elevating mechanism
N₃—Fine adjustment on rack and pinion
N₄—Brake shoe on adjustment arm of N₃
O—Battery box and batteries
Q—Electrical switch
R₁—Base of gelometer
R₂—Pillar of gelometer
S—Fine copper wire coil making contact across from suspended
      disk to binding post on support
T₁, T₂—Leveling screws

PART II

(A) FACTORS INVOLVED IN PREPARATION OF SAMPLE THAT AFFECT PHYSICAL PROPERTIES OF RESULTING SOLUTION

(a) Quantity of Water Absorbed by Glue during Soaking Period.
It has been shown by numerous investigators that the viscosity of emulsoids, such as gelatin solutions, is a function of the size of the particles (micellae) of the gelatin-rich phase. The size of these particles (micellae) is in turn dependent, among other factors, on the extent to which they have become solvated. If the time factor is unlimited, then the degree of subdivision of the dry sample is no longer of influence and the solvation of the gelatin is controlled largely by the temperature, the pH, and the degree of ionization of the gelatin salt.

If the amount of water absorbed by gelatin in the cold predetermines the extent to which the colloidal gelatin particles

are solvated in the resulting sol at 60° C., it becomes necessary to follow rigidly a definite set of conditions for this period of imbibition.

It is well known that heating the gelatin swollen in the cold results in expelling some of the water absorbed by the particles at the lower temperature, but to what extent this occurs is not known, nor do we know whether the amount of unexpelled solvent is proportional to that originally held or is independent of it.

Among the factors that control the extent to which gelatin absorbs water in the cold will be found several over which the glue tester has no control, whereas others are amenable to exact regulation. Among the former are those resulting from the history of the product during manufacture, such as (1) grade or quality of sample, (2) pH of liquor, and (3) thickness of flake and degree of subdivision of sample, if ground. Among the latter factors are (4) temperature of water, (5) pH of water, (6) degree of subdivision of dry glue when in sheet or flake form, and (7) length of soaking period.

A brief discussion of these factors may not be out of place here.

(1) That the amount of water absorbed by glues in the cold is dependent upon the grade of the product is too well known to require comment.

(2 and 5) The pH of a solution measures the activity of the acid or base present in the system. It is not synonymous with the terms "acidity" or "alkalinity," since these measure the available or total amount of acid or base. Not all the acid or base present in a solution is in a reactive condition at any given instant; the pH, however, gives a measure of the active portion. The units on the pH scale extend from 0 to 14, the range 0 to 7 is acid to water, that from 7 to 14 is alkaline, while 7 represents the neutral point. Gelatin can play the role of both acid and base, its neutral or isoelectric point being at a pH value of 4.7. Recent work by J. A. Wilson and his co-workers indicates that the isoelectric point of gelatin may be at pH 7.7 instead of at 4.7, or that 4.7 may be the isoelectric point of the sol form and 7.7 of the gel form. This work requires confirmation, and more investigation of the region between pH 4.7 and pH 7.7 is necessary. The minimal water absorption and consequent swelling occurs at the isoelectric point and maximal at 3.0 to 3.5 and 10 to 11.

(3 and 6) The rate at which water is absorbed by glues is a function of the surface area exposed to the action of the water. For a given weight of glue the surface area increases with diminishing thickness of flake and with decrease in the size of the ground samples. Therefore, a given degree of absorption will be attained by a certain glue in a period that varies inversely with the subdivision of the dry product. The committee has found that glues even of low grade, ground to such a degree that 75 per cent passes a 10-mesh sieve, give the same viscosity and jelly strength when soaked for 3 hours at 8° to 10° C. as when soaked for 24 hours at the same temperature. Similar information on coarse products has not been obtained.

(4) It is a well-known fact that glue swells more in cold than in warm water. From the observation that gelatin gives off heat (5.7 calories per gram) on swelling, one would predict this behavior and conclude that the lower the temperature—down to the freezing point of water—the greater the swelling, provided ample time is allowed for the system to reach equilibrium. If the time is limited this conclusion is not borne out by the observed facts, since the initial rate of absorption at, say 25° C., is much greater than at 10° C. Owing to the possible influence that the degree of absorption in the cold may have on the degree of hydration of the colloidal particles of the sol at 60° C., it will reduce the number of variables if a temperature range of 10° to 15° C. is adopted for the soaking process. Inasmuch as 10° C. is to be the standard temperature for jelly tests, the same room or compartment can be used to secure a constant temperature for the imbibition period, even though the rate of absorption and swelling is much less than at room temperature.

(7) Since the time required for a given sample of glue to absorb the practical maximum of water is dependent upon factors, some of which are inherent in the product as received and hence are not under the control of the glue tester, the committee thinks it best to make the official soaking period a maximum.

(b) *Agitation of Solution.* It has been demonstrated repeatedly that the viscosity of glue solutions is lowered by vigorous mechanical agitation. It is therefore necessary to avoid undue agitation of the sample during the melting and subsequent heat-

ing to 62° C. The observed lowering of the viscosity by the passage of the glue solution through the capillary viscometer is probably due to the same cause. Because of this fact any standard viscosity pipet must be filled from the top and not by suction through the capillary end. The practice of cooling the solution to the required temperature by passing it in and out through the capillary end is obviously bad. Chilling the sample for the jelly test appears to reverse the effect of agitation, since it has been observed that the jelly test is the same whether or not a viscosity determination has been previously made on the solution.

(c) *Length and Intensity of Thermal Treatment Received in Melting Bath.* In general, the effect of each of the many factors influencing the viscosity and jelly test of glues will be proportional to the time that the several factors are in operation. If the resultant effect of all these factors is to be even approximately comparable from sample to sample, it is absolutely essential that the length and intensity of the thermal treatment be fairly constant. It has been observed that heating a 12.5 per cent solution of high-grade gelatin at 60° C. reduces the viscosity progressively with time. At the end of 30 minutes it is reduced 2 per cent from that obtained by quickly heating to this temperature. It is obvious, then, that if maximum values are to be obtained the solutions must not be held at 62° C. for more than a few minutes, nor should they be brought to this temperature too slowly. The melting bath should be held at such a temperature that it will require only 15 minutes or less to bring the samples to the required temperature.

(d) *Effect of Variation in Concentration Due to* (1) Evaporation, or to the addition of less than the required weight of water.

Unless the container is properly covered and kept so during the time it is in the melting bath, more or less water will be lost through evaporation. The loss of 2.9 grams of water from 100 grams of a 12.5 per cent solution of a certain higher grade glue containing 11.7 per cent moisture is sufficient to increase the total solid content by 0.32 per cent (dry basis). The same glue in 12.5 per cent (11.04 dry basis) solution gave a viscosity of 155 millipoises at 60° C. A 12.87 per cent (11.36 dry basis) solution of the same glue gave a viscosity of 170 millipoises, an increase of 15 millipoises due to an increase of 0.32 in the total solid content of the solution. The viscosity spread between the two highest grades of association's standards is also 15 millipoises. Therefore, a 0.11 per cent increase in the total solid content of 100 grams of this solution, which can be effected by the loss of about 1 gram of water, will increase the viscosity of the sample by one-third of a grade. Higher grade glues will show a greater increase, while low-grade ones will show less, for the same change in total solids.

(2) Addition of more than required weight of water to dry sample.

A decrease of 0.11 per cent (dry basis) in the total solid content of 100 grams of the above solution will lower the viscosity by one-third of a grade. This decrease in solids can be effected by the addition of 1 gram of water.

(3) Error in weighing out sample.

Making a plus or minus error of 0.12 gram (dry basis) on 12.5 (11.04 dry basis) grams will respectively increase or decrease the viscosity one-third of a grade.

(4) Change in moisture content of sample.

It was stated above that the change of 0.11 per cent in the total solid content of 100 grams of an originally 12.5 per cent solution (11.04 dry basis) will alter the viscosity by one-third of a grade. This change in the solids will result from a gain or loss of 0.88 per cent in the moisture content of the sample originally containing 11.7 per cent.

(B) Factors Affecting Viscosity of Glue Solutions

The term "viscosity" is used in the foregoing methods in a somewhat unrestricted sense. The committee is aware of the possibility that plastic and not viscous flow is the property being determined, especially, for example, when determining the viscosity of an opaque or "painted" glue. Solutions of glue and gelatin in water belong to that class of colloidal solutions known

as emulsoids. The viscosity of emulsoids has been found to depend upon the following factors: (a) concentration, (b) temperature, (c) the pH value of the solution, (d) degree of dispersion of the colloid, (e) degree of hydration of the colloid, (f) solution history of the sample (thermal treatment, age of solution, extent of mechanical agitation of solution, etc.), (g) addition of foreign substances, (h) inoculation or seeding with other colloids of different solution age. With the possible exception of the two last named, all of the above are involved in each viscosity determination of glue and gelatin solutions. Occasionally the last two may be involved. It is difficult to say at this time just what degree of control is necessary in the case of each of these factors that are amenable to regulation. Temperature and solution history are the only factors absolutely under the control of the glue tester. As long as the moisture content of the glue has changed but little, the concentration factor may be included. A brief survey of the influence of the above-mentioned factors may help one to appreciate their relative importance to glue and gelatin testing.

(a) For dilute solutions (1 per cent or less) the relation between viscosity and concentration of glue is practically linear, but as the concentration is increased the curve changes from a straight line to a curve of increasing slope. The higher the grade of the glue the sooner this departure occurs and the steeper the slope at corresponding concentrations. The effect of change in the moisture content of the sample resulting in a change of total solid content of the solution has already been discussed.

(b) The influence of temperature variation on the viscosity depends largely on the temperature at which the determination is made. The higher this temperature the smaller is the change per degree. The tolerance is of course greater the lower the quality of the glue. The magnitude of the temperature tolerance for 12.5 per cent glue solutions at 60° C. has not been determined by the committee for the apparatus and method recommended, nor are there any published data that will give an approximate idea of it. The concentration, temperature, type of viscometer, and general procedure recommended by the committee differ so widely from those used by workers in other fields that it would not be safe to draw conclusions by analogy.

(c) It has been shown by numerous investigators that the viscosity is a function of the pH value of the solution. The pH-viscosity curves for low concentrations exhibit two maxima, one higher than the other. The former is located on the acid side of the isoelectric point of gelatin at a pH = about 3.0, the other on the alkaline side at a pH = about 11.5. At the isoelectric point the viscosity is a minimum. The influence of the pH of the solution on the viscosity of glues of all grades determined by the association's method has not been determined by the committee. In the laboratory of one member of the committee, preliminary work on solutions of 12.5 per cent shows no maximum viscosity on the acid side and a very decided one on the alkaline side for high-grade gelatin by the association's method.

(d) In regard to the importance of the factor (d), Bogue[1] makes the following statement:

Of the many factors which influence the viscosity of emulsoids the degree of dispersion is probably of greater importance than any other with the exception of concentration and temperature. It is, in fact, highly probable that the influence of many if not all of the other factors affecting viscosity is brought about through changes in the size of the particles of the dispersed phase (the micellae).

It appears that there exists a range in the size of the particles—the colloidal zone of dispersion—wherein the viscosity reaches a maximum value. Solutions in which the average size of their particles is outside of this range have lower viscosity. Whether this "degree of maximum colloidality," as it is called, is of significance in glue and gelatin control work has not been determined by the committee.

(e) Since the degree of dispersion is dependent upon the extent to which the colloidal particles have become solvated or hydrated, this factor attains considerable importance. It has been discussed in Section A.

(f) The effect of the method of preparing the solution on the subsequent viscosity has been referred to in Section A. The lowering of the viscosity by mechanical agitation and by passing the solution through the viscometer has been discussed. The explanation advanced by colloid chemists to account for these facts is that the solution tends to assume a certain structure under a definite set of conditions and that this structure is al-

tered or destroyed by such treatment. Heating gelatin sols at temperatures above 40° C. decreases rather than increases the viscosity as the age of the sol is increased.[2] This decrease in viscosity is not necessarily due to chemical decomposition, but, as stated in the literature, to a physical change in the structure of the sol, since by chilling for several days the solutions recover their original value in some cases.

(g) The presence of soluble acids, bases, salts, and nonelectrolytes alters the viscosity. The extent of the influence of electrolytes depends on the amount and type of electrolyte present in solutions of definite pH value. The extensive and painstaking researches of Jacques Loeb on the addition of acids, bases, and neutral salts to solutions of originally isoelectric gelatin and of known pH value are the basis for a plausible theory of the behavior of protein solutions.

Since the amount and nature of the electrolytes present in glues is not usually under the control of the glue tester, any variation in the viscosity due to this cause cannot be charged to the method of testing.

(h) Although the inoculation or seeding of a gelatin solution with one greater in age increases the viscosity, this factor is operative only at temperatures below 40° C. and hence cannot influence viscosity determinations made according to the association's method.

As already stated, the influence on the viscosity of the above-discussed factors has been determined by numerous investigators using a variety of methods of procedure and sources of gelatin. Whether the factors other than concentration and temperature have any important influence on the viscosity as determined by the association's methods is a problem of the future.

(C) Factors Affecting the Jelly Strength

Many factors influence the resistance to deformation exhibited by a given sample of gelatin. Among these may be mentioned (a) concentration, (b) temperature, (c) pH value, (d) solution history of the sample, (e) rate of chilling solution, (f) inside dimensions of the container, (g) effect of plunger area, (h) depth of depression, (i) nature of jelly surface, (j) time factor in making the jelly strength determination. In general, most of these factors have greater influence the higher the grade of the glue. A brief discussion of these factors follows.

(a) Effect of Variation in Concentration Due to (1) Evaporation or the addition of less than the required weight of water.

The loss of 2.9 grams of water from 100 grams of a 12.5 per cent solution of a certain high-grade glue is sufficient to raise the jelly test from 379 to 397 grams at 10° C. or by 18 grams. The spread between the association's two highest glue standards is about 18 grams at this temperature; hence the loss of 1.0 gram of water from 100 grams of the solution will increase the jelly test one-third of a grade.

(2) Addition of more than the required weight of water to the dry sample.

The addition of 3.0 grams of water to 100 grams of a 12.5 per cent solution (11.04 dry basis) of the high-grade glue decreases the jelly strength by 13.5 grams. Thus an increase of 1.4 grams of water per 100 grams of the solution will decrease the jelly strength one-third of a grade.

(3) Error in weighing out sample.

A negative error of 0.17 gram (dry basis) or a positive one of 0.12 gram (dry basis) on 12.5 grams, respectively, decreases or increases the jelly test one-third of a grade.

(4) Changes in moisture content of sample.

The gain of 0.11 per cent (dry basis) in the concentration of the glue is equivalent to the loss of 0.85 per cent, and the loss of 0.15 per cent (dry basis) in the concentration is equivalent to the gain of 1.3 per cent in the moisture content of a sample of the high-grade glue having an original moisture content of 11.7 per cent. Therefore, these changes in moisture content are sufficient to change the test of the sample one-third of a grade.

(b) Effect of Temperature on the Jelly Test. The higher the grade of glue the higher the total solid content of the jelly; the smaller the diameter of the cylindrical container and the smaller the depth of jelly (below a certain minimum value), the greater will be the temperature coefficient of the jelly strength. In

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[1] "The Chemistry and Technology of Gelatin and Glue," p. 190.   [2] Davis and Oakes, J. Am. Chem. Soc., 44, 464 (1922).

other words, a given small variation in the temperature of the jelly under test produces a greater variation in the results the higher the concentration and grade of glue and the smaller the depth and diameter of the jelly. Three of the four variables mentioned are fixed in the method presented—viz., concentration, diameter and form of container, and depth of jelly—the latter being automatically determined by the volume of solution made up. Under these conditions a variation of $\pm 1.0°$ C. from $10.0°$ C. will decrease or increase the jelly strength of high-grade glues about 15 to 20 grams, and proportionately less for lower grade ones. The foregoing discussion assumes a constant value for the area of plunger and the depression. The temperature $10°$ C. has been adopted to conform with the generally accepted theory that above this temperature and below about $40°$ C. gelatin in water exists in two forms—a "gel" or solid, and a "sol" or liquid—which are in equilibrium with one another, the amount of gel form increasing as the temperature is lowered below $40°$ C.

(c) *Effect of the pH Value of Solution.* In a series of experiments conducted by Davis and Oakes[3] with the view of determining the effect of the pH of the solution on the jelly strength, it was found that a maximum value was obtained in the region of pH = 8.0. Subsequent, and as yet unpublished, work carried out in the laboratory of one of the committee confirms this point of maximum jelly strength for solutions of 12.5 per cent concentration. Starting on the acid side at a pH = 1.0, the jelly strength increases gradually with the pH until the maximum is reached. After that the jelly strength falls rapidly until after a pH = 11.0 is reached, when the sample no longer jells at $10°$ C. over night in 12.5 per cent solution.

(d) *Solution History of Sample.* Whether the length and temperature of the soaking period or the time taken to melt the swollen glue and the maximum temperature reached have any influence on the jelly strength does not seem to have been determined by any one, so far as the committee is aware at this time. As stated in Section A, the results of coöperative work by the committee on five samples covering the whole range of the association's grades showed that 3 hours' soaking of the ground glues gave the same jelly strength as did 24 hours' soaking. The time required for complete soaking of 4-mesh pieces has not been investigated by the committee.

(e) *Rate of Chilling Solutions.* It has been noted in the laboratory of one of the committee that the jelly strength is apparently a function of the rate of chilling when the total time of chilling is about 16 hours. Jellies that have been rapidly cooled to $10°$ C. gave a higher test than those cooled slowly to this temperature, both samples having been chilled for a total of 16 hours.

(f) *Inside Dimensions of Container.* Recent work published by Sheppard and Sweet[4] shows the influence of the ratio of the diameter of the plunger to that of the jelly; also the effect of the depth of the jelly on the jelly strength. These investigators conclude from their results that the diameter of the jelly should be at least four and a half times that of the plunger in order to avoid the effects due to the container wall. They also conclude that the depth of the jelly should be 5 cm. or more if the influence of the bottom of the container is to be negligible. The concentrations of the jellies used in their experimetnal work varied from 1 to 10 per cent.

With the container and conditions recommended above not enough difference in the jelly strength of a high-grade glue was found for jellies of 40, 45, and 50 mm. depth to make any practical difference in the test. The depth of the jelly in the association's method is about 40 mm. For greater depressions than 4 mm. greater depths of the jelly would be required to be independent of the bottom of the container.

The average variation of the inside diameter of ten of the standard containers chosen at random was ± 0.3 mm. When negative

this variation will increase the test of a high-grade glue about 2 grams, and if positive it will decrease it about 1 gram. It is evident, therefore, that the ordinary variation in the diameter of these blown bottles is well within the allowable tolerances.

Theoretically, the diameter of the container should be very large and the depth of the jelly should not be below a certain minimum value if the effects of the wall and the bottom of the container are to be negligibly small. A container of such dimensions is not practical, however, since it requires too large a quantity of sample of dry glue. Since duplicate results can be obtained with a container of smaller dimensions by adhering strictly to definite conditions, the committee choose the container that gives, with the 120 grams of solution, a practical width with a depth of about 40 mm.

Some idea of the influence of the container wall was gained from the following experiment: A number of jellies of constant diameter (72 mm.) and varying depth were tested before and after removing from cylindrical containers. The jelly strength was always lower when supported only on the bottom, the difference being greater the greater the depth of the jelly. For a 30-mm. depth the decrease was about 8 per cent and for an 80-mm. depth it was about 33 per cent of the value obtained in the container.

(g) *Effect of Plunger Area.* Other things being equal, the jelly test increases with increase in the area of the plunger. For this reason it is essential that the diameter of the plunger be standardized. The committee recommends that the standard plunger of the Bloom gelometer be circular in cross section and 12.7 mm. (0.5 inch) in diameter.

(h) *Depth of Depression.* The jelly strength increases with increase in the depth of depression, and it therefore becomes necessary to fix the magnitude of this factor. The committee recommends a 4-mm. depression as one giving a practical spread at the standard concentration, temperature, and dimensions of the container.

(i) *Nature of Jelly Surface.* Too rapid chilling causes a reticulation or corrugation of the jelly surface, which leads to uncertain and fictitious results. The jelly surface must also be perfectly level or lower results will be obtained, since the entire surface of the plunger will not be acting for the full 4-mm. distance. Too much care cannot be used to obtain a proper level, as only a slight tilt from the horizontal will throw off the results.

Foam should not be allowed to exist near the center of the surface after the sample has been placed in the chilling bath. The presence of foam at the spot where the plunger must rest prevents accurate setting at the initial position and results in low values for the jelly test, since a portion of the 4-mm. depression is made against the resistance of the layer of foam.

(j) *Time Factor in Making Jelly Strength Determination.* Several experiments have been carried out with the view of determining what influence, if any, the time required to add the load of shot has on the value of the jelly strength of a given sample. The samples chosen were the association's No. 1 and No. 11 grades. The results obtained point clearly to the fact that with the Bloom gelometer the time factor is negligible with glue jellies within the Grades 1 to 11. Another fact clearly brought out was that the load producing the 4-mm. depression is a function of the rate of flow of shot, being greater the faster the flow. This variation in the jelly strength of a given sample is due largely to the variable weights of shot in mid-air at the instant the flow of shot is cut off, the calculated and observed differences agreeing very well.

In view of these facts, the committee recommends that all jelly strength determinations be made from the dog D_2, the latter being adjusted so that 200 grams of shot are delivered in five seconds.

F. L. DeBeukelaer
J. R. Powell
E. F. Bahlmann
          Committee

[3] This Journal, **14**, 706 (1922).
[4] *J. Am. Chem. Soc.,* **45**, 571 (1923).

AMERICAN CONTEMPORARIES

A Close-up of Professor Bailey

THIS is the year in which Professor Edgar Henry Summerfield Bailey completes fifty years of teaching, forty of them spent as professor of chemistry of the University of Kansas.

For the chemist who has distinguished himself in research there are honors, rewards, and even popular applause if the achievement is spectacular. For the technical chemist who makes a valuable invention there are more tangible compensations. But for the chemist who devotes his best energies to teaching and is never tempted to neglect his students by the lure of lucre or the lust of fame there are no rewards and little recompense except the gratitude, too often unexpressed, of the thousands he has trained to a love of truth and inspired with the impulse to pursue it beyond the horizon of human knowledge. If some philanthropist would provide a fund to give a big, round gold medal to great teachers, I think it might do as much to advance science as another research foundation. Anyhow, something should be done to restore to the teacher some of his former prestige, for otherwise good teaching seems likely to become one of the lost arts, since the younger generation not only neglects but despises it.

The research problem that interested Professor Bailey most was what could be made out of the raw material that was dumped into his classroom every fall. Some of it was very rare and his means were limited. When I came to the Kansas State University in the later eighties the departments of chemistry and pharmacy were housed in a small building which had been constructed out of a remnant that had, through some accident, been left over from a legislative appropriation—$35,000, if I remember right. Professor Bailey attended to everything, laboratory and lectures, elementary and advance classes, research and commercial work, with no help but "student assistants"— and you know what that means. So do I, because I was one of them. I had been admitted to the university as a "special student" with the rank of "conditioned subfreshman" pursuing an "elective course"—if you know what that means. Scholastic laws were elastic in those days, fortunately for me. Of course, nowadays no respectable university would let in a fellow in my fix, so I would never had had a chance at an education if I had been born later. Neither would Ed Franklin, last year the honored President of the AMERICAN CHEMICAL SOCIETY, since he was even more irregular in academic classification than I, and only cleared up his entrance requirements the month before he was graduated. Ed was "the assistant in chemistry" when I entered the university and exercised my freedom of election by taking sophomore chemistry on the start.

I had not been in the laboratory more than a week when Professor Bailey in one of his flying trips stopped at my desk to say:

"There is a Science Club meeting tonight. Did you get an invitation to come?"

I said yes, that a chap named Vernon Kellogg had asked me. "Aren't you coming?"

"I guess not. I don't know anybody there."
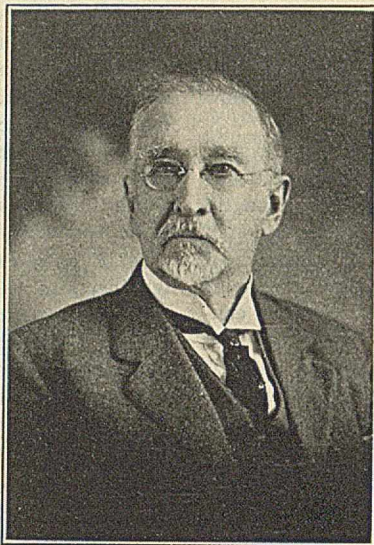
E. H. S. BAILEY

"Better come. Good way to get acquainted. There will be doughnuts and sweet cider and Professor Snow is going to talk." So I went and joined the Science Club; but I soon found that I was expected to do more than listen and eat. A few weeks later Professor Bailey hailed me again.

"We are going to have some brief biographies of distinguished scientists at the club. You are down for Faraday next."

"But I do not know anything about him."

"Look him up. There is a life of him in the library. And get out his three volumes on 'Experimental Researches in Electricity.'"

I do not know that my ten-minute talk on Faraday did anybody else any good, but I got two things out of it that are of use to me today. I got an interest in the history and personalities of science, and I learned that to get the best material for an article one should go to the source.

Professor Bailey was always expecting his students to do things that they did not think they could do. He would get them by degrees to wade in deeper than they thought and before they knew it they were swimming. One day he called me into his office and laboratory (which were the same) and showed me some queer stones on the table.

"This is a new find of meteorites from Kiowa County. If you will help me analyze them we will get out a joint paper on them for the Kansas Academy of Sciences."

I was, of course, quite willing to oblige him in this way, but protested that I knew nothing about meteorites.

"You will find a lot about meteorites in Silliman's Journal. Better run through the whole set." Professor Bailey was a loyal Yale man.

I did find a lot about them—also a lot of volumes. I was growing discouraged about getting through them when Professor Bailey appeared with another suggestion.

"Better make a card index of all the analyses while you are about it, so we will have them handy. I will pay you 25 cents an hour for it."

Now this was a curious coincidence, for board at our students' club had jumped from $2.25 to $2.40 a week and I was wondering whether I would have enough money to last out the year. But, of course, Professor Bailey could not know anything about that, for I had never told him.

About the same time, Professor Bailey set a lively youngster by the name of Case to analyzing the coals of Kansas. This started a line of investigation that developed into a comprehensive survey of the natural resources of the State—and it started E. C. Case on a career of research that has landed him in a chair of paleontology at the University of Michigan.

Professor Bailey could never be kept within the bounds of conventional chemistry. He was especially interested in food, cooking and preserving, which in those days was not generally regarded as properly the province of the chemist, but has since become one of its most important branches. Food is the subject of his latest book, which shows that in the thirty-five years since there has been no flagging of his interest or failing of his powers.

Next to food he had a fondness for poisons, and whenever the contents of a murdered man came in for analysis he would call some of us boys into his room to show us, with some pride on his part and much profit on ours, how he had prepared the tests for presentation in court, and tell us how to meet a lawyer's cross examination.

Not content with analyzing foods and poisons, he began to wonder why sugar is sweet and strychnine is bitter. Not content to wonder, he began to experiment. This led him into the field of psychology, but he did not stop for that. So for several years any boy or girl who came into the building was likely to be called in to taste or smell of rows of bottles containing distilled water and other things more or less agreeable. This was pioneer work in a field that has been largely left uncultivated until recently, the relation of chemical composition to taste and odor.

A new tariff law created a sudden demand for sugar chemists, and Professor Bailey put a few picked students through an extemporized course of what is now called "intensive training" and sent them off to Louisiana plantations for the season. Franklin was the first to go, and Professor Bailey astonished me by telling me that I was expected to take his place while he was down South. I was scared at the idea, for it is a ticklish thing to try teaching for the first time on one's own schoolmates. But Professor Bailey explained that Franklin's leaving in the midst of the term had put him in an embarrassing position, from which he hoped I would help him out. Of course, being put in that way I could not refuse him the favor. Nor did I refuse him when a year later he offered me the position of chemist in the University of Wyoming where I stayed for thirteen years. We boys had to work awful hard to keep him from realizing the mistake he had made in putting us in positions too big for our ability. We knew he would feel bad if he found out.

Professor Bailey is a Presbyterian and a homeopathist. This is an unusual combination for, as Dr. Oliver Wendell Holmes showed long ago, homeopathy and Unitarianism naturally go together. I did not follow Professor Bailey into homeopathy, but I did into Presbyterianism. Whenever I went to his house he used to give me *The Independent* to read, and I became so attached to it that when I left I subscribed for it and got to writing for it and later became literary editor of it for seventeen years. So I owe to him, not only my first job of teaching, but my second job of editing.

All this sounds very egotistical. "I" appears in it as often as "Bailey." But I do not mean it that way. What I mean is that what Professor Bailey did for me—and I am not telling a tenth of it—he has been doing for other fellows for fifty years. All over the country you will find "Bailey's boys," in universities and factories, engaged in teaching, research, or industry, and they will all tell you the same story—of the peculiar personal interest that Professor Bailey took in their individual welfare, how he found for them the work they were most fitted to do, and how he headed them toward promising careers. And how unselfishly and tactfully he did it all, always giving them full credit for a "joint" piece of research; always slipping behind them and pushing them forward when it came to honors and rewards. That is why he is loved by so many, and that is why no one will ever be able to estimate what has been his service to science.

EDWIN E. SLOSSON

John M. Francis—1867 to 1924

DIED, January 8, 1924, at his home in Detroit, Mich.—Dr. John M. Francis.

With this simple statement there will come to every man who knew him a sense of personal loss, for he had, to a remarkable degree, the faculty of establishing bonds of sincere friendship between himself and almost everyone with whom he came in contact. The personality of a man is that which we remember when details of his achievements are forgotten, and yet it is fitting that a brief review of Dr. Francis' life should be presented here.

Born in the little town of Jacksonville, Ala., October 25, 1867, his early life was such as falls to the lot of the average active boy in a small town, but the early bent of mind toward an interest in all phenomena of nature persisted through his entire life in a love for the outdoors and in the pursuit of science.

Graduating from the University of Alabama, he taught there for a short time and then took up some further studies at Johns Hopkins University. From here he went, in 1892, to Detroit, entering the Analytical Department of Parke, Davis & Company, and shortly afterwards becoming head of this department. During succeeding years he did much to develop the efficiency and usefulness of this department, and in 1905 the scope of his work was greatly increased and he was appointed to the newly created position of chief chemist—a position which in turn, as was characteristic of him, he developed to a very great extent. He was bigger than any single niche to which he might be assigned, and the influence of his keen mind and striking personality was felt in many circles other than that of his immediate work.

JOHN M. FRANCIS

Throughout the course of his life he was actively identified with many matters pertaining to pharmaceutical and medicinal chemistry. He was a member of the Revision Committee of the U. S. Pharmacopœia, was chairman of the Committee on Chemical Research on Medicinal Substances of the National Research Council, was actively identified with work of the American Chemical Society and the American Pharmaceutical Association for many years, and gave much valuable service to the Scientific Section of the American Drug Manufacturers' Association.

He was for many years an elder and clerk of the session of the Jefferson Avenue Presbyterian Church in Detroit.

He possessed clarity of thought and directness of speech, along with a thoughtful consideration of the views and opinion of other men, which led to frequent calls upon his wise counsel. He had no patience with anything that savored of sham or subterfuge, but would go to unusual lengths to be of any help or service to all whose efforts sprang from sincerity of purpose.

A lover of nature in every form, he was an ardent fisherman and hunter, and found a perpetual joy and relaxation from the cares of a busy life in a most unusual flower garden.

No man can be greater than the motives that inspire him, but oftentimes his achievements are more honored than the man himself. Dr. Francis achieved distinction in scientific circles and success in business, but his highest honor will be from those who knew him best and had come to understand the greatness of his soul.

FRANK O. TAYLOR
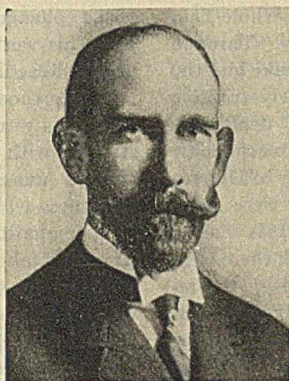
Jacques Loeb—1859 to 1924

THE life and character of Jacques Loeb were so indissolubly united with his work that they can never be separated. His was one of those rare minds whose fiery quest for the truth brushed aside and subordinated all other interests. It is difficult to think of him otherwise than in his laboratory surrounded by a mass of experimental data or striding up and down as he turned over and over in his mind some difficult problem, inspecting it from all angles in the attempt to find the point which could be subjected to experimental test. The test of direct experiment was one of the striking characteristics of his work. Any suggestion of verbalism or the slightest lack of logical clearness in a discussion or scientific paper would call forth a burst of impatient criticism. It was in devising and carrying out experimental tests of his ideas that his genius reached its greatest heights. He did not believe in conquering an obstacle by laying siege with laborious and painstaking experiments, but preferred to spring upon it from some totally unexpected angle and decide the issue with a simple but marvelously ingenious experiment. To the chemist this method was at times disconcerting. A reviewer of one of his books remarked, "Some of the methods would curdle the blood of an analytical chemist." They furnished results which answered the question, however, and that was to him the essential point. Like Faraday, he had at times the uncanny gift of knowing the truth before the work was done. He would sometimes say, "I know what it is. The question is, how to prove it." And yet a single trustworthy experiment would cause him to give up at once a theory he had upheld with the greatest enthusiasm.

An indefatigable worker, for many years he had not rested even a day, from his experiments. His publications of over three hundred papers and many books covered the whole field of biology and extended into chemistry and psychology. Through them all may be traced the love of truth for its own sake and the insistence on a basis of experimental fact. His early training was medical, and his first book, "Brain Physiology," dealt with the instincts and will from a purely objective and mechanistic viewpoint. It was an attempt to place the philosophy of Diderot and D'Alembert on a scientific basis. The views were revolutionary and were, of course, met with opposition. It is characteristic that he turned to simpler experiments in which there were no disturbing factors. Such material was furnished by the reactions of lower animals to light and other stimuli. Loeb insisted that these responses were purely mechanical and were governed by the ordinary laws of physics and chemistry, and he proceeded to prove this thesis by a series of brilliant experiments. He showed that an animal would go to the light even though it starved while food lay near it but away from the light. He showed that these animals and plants obeyed the Bunsen-Roscoe law—that if the intensity of the light were doubled half the exposure would bring the same response. These and innumerable other experiments have laid a firm foundation for his "Tropism Theory."

The theory of electrolytic dissociation led him to the belief that the ions are intimately connected with the properties of living matter. The classical experiments on artificial parthenogenesis stand as a monument to the correctness of the idea. He showed in these startling experiments that by suitable treatment with acids and salts certain unfertilized eggs could be caused to develop. In this way the chasm between dead and living matter was partially bridged and a great advance made in the problem to which he devoted his life.
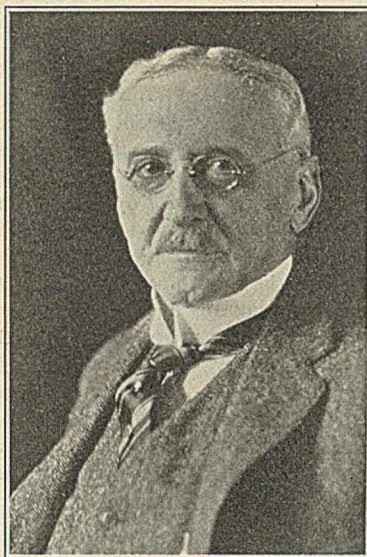
Loeb then took up the work on balanced salt solutions. Certain eggs can develop in distilled water and sea water, but die immediately in a solution of any one salt, even sodium chloride. He worked out in detail the exact relation between the various salts necessary for normal development, and was able to show that it is due to the small amount of calcium in our blood that our muscles do not twitch continuously. But the problem was still too complicated for complete solution, and he turned again to a simpler case, the properties of colloids, which resembled in many ways those of living matter. Here again his remarkable experimental ability enabled him to show that a theory derived by Donnan from the laws of classical chemistry sufficed to bring order out of chaos, and it became possible to have a clear, logical explanation for the most striking properties of prtoeins and colloidal solutions in general. Simultaneously with this work a long series of intricate experiments on the laws governing regeneration in plants was also led to a successful and simple solution. Nothing could better show his tireless energy and unique ability for experimental work.

Like all original workers, Loeb was frequently criticized. His disregard of details and impatience for results left him open to criticism on minor points, while his enthusiasm led him occasionally to venture farther than others were willing to follow. His insistence on quantitative experiments and frequently caustic criticism of anything suggesting verbalism antagonized many of his colleagues. These are minor points and will be forgotten while his work as a whole will always stand as a record of remarkable achievement.

But to those who knew him well the man himself stands even above his work; when at work, a forceful, striking personality, striving with tireless energy after the truth; to his friends a kindly, unassuming gentleman. The same simplicity and directness which characterized his work were striking points of his personality. He preferred the simplest equipment for his office and laboratory, and was most at home in his laboratory at Woods Hole surrounded by innumerable dishes of sea water in which his experiments were being carried on.

Doctor Loeb possessed a charm of manner which was unusual and called forth an immediate response from those who met him. The table at which he sat at luncheon was always a coveted place, for the conversation was sure to be brightened by some characteristic discussion of current work or by a whimsical elaboration of some quaint idea. To his many younger friends he was a constant source of inspiration and sympathetic advice. They appealed to him all the more readily since his never-failing enthusiasm and idealism kept him always young.

John H. Northrop

NOTES AND CORRESPONDENCE

Gas-Tight Stirrer

Editor of Industrial and Engineering Chemistry:

In the November issue of THIS JOURNAL there appears on page 1134 a description of a gas-tight stirrer, closely resembling a type described by me some two years ago.[1] As I have had considerable experience with such stirrers I venture to point out that there are certain disadvantages attaching to the type illustrated in your journal, which do not apply to the stirrer in the accompanying drawing.
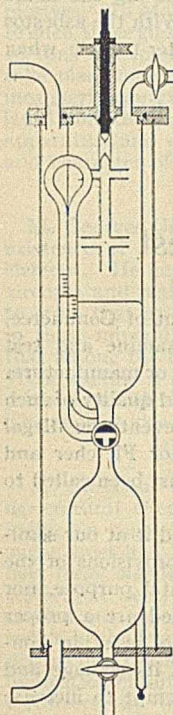
In my experience the use of a parallel shaft kept gas-tight by a packing gland leads to excessive friction with a resulting increase in the power required to drive the stirrer. In the type shown by the accompanying drawing the shaft is provided with a conical shoulder which exactly fits the conical bearing, so that when the pulley is screwed onto the other end of the shaft it enters a similar cone and thus draws the two cones into close contact. This secures a gas-tight bearing without the use of any packing gland.

The second point is that in the figure described by Holm a long length of steel shaft and the packing gland are exposed to whatever gas may be in the flask. This means that if corrosive gases are being used the metal parts will be quickly attacked. It will be seen that this difficulty is overcome in my stirrer by making the lower part of the glass stirrer conical, and grinding it into contact with a corresponding outer cone on the bearing, so that nothing but glass or ebonite comes in contact with the gas or liquid in use.

These small changes make all the difference between a stirrer which will give much trouble in operation and one which will run for long periods without attention.

H. G. Becker

15, York Road
Rathmines
Dublin, Ireland
December 4, 1923

[1] *Proc. Roy. Dublin Soc.*, **16**, 334 (1921).

. . . .

Editor of Industrial and Engineering Chemistry:

In reply to Mr. Becker's letter, we first wish to point out that the problem of securing a gas-tight seal is quite different from obtaining a seal against a liquid, such as is the case in the inverted type of stirrer he uses.

We have not been seriously hampered by any of the objections voiced, but realize that with highly corrosive gases and liquids objections may be raised to almost any apparatus that is not made wholly of glass. The form and material of such an apparatus is best determined by the nature of the work in question.

George E. Holm
George R. Greenbank

Research Laboratories, Dairy Division
Bureau of Animal Industry
Washington, D. C.
January 8, 1924

Amino Acid Distribution in Proteins of Wheat Flours

Editor of Industrial and Engineering Chemistry:

I would like to point out that the problem on "Amino Acid Distribution in Proteins of Wheat Flours," which R. J. Cross and R. E. Swain discuss in THIS JOURNAL, **16**, 49 (1924), had already been discussed by M. J. Blish in THIS JOURNAL, **8**, 131 (1916). Cross and Swain make no reference to this paper, but their findings are essentially identical with the findings of Blish.

R. A. Gortner

University of Minnesota
St. Paul, Minn.
January 9, 1924

. . . .

Editor of Industrial and Engineering Chemistry:

Dr. Gortner is entirely right. Proper reference to the paper by Blish should have been made in our paper. The paper by Blish was entirely overlooked by us in our review of the literature. This may have been due in part to the fact that the review of the paper in *Chemical Abstracts* makes no mention of the analysis of proteins of different varieties of wheat, but deals wholly with other points brought out in the investigation.

R. J. Cross
R. E. Swain

Stanford University
California
February 1, 1924

Professional Protection

Editor of Industrial and Engineering Chemistry:

During the past eighteen years I have had inquiries from a number of consulting chemists, which indicated that other men in actual practice had had experiences similar to my own.

I have in mind the fact that consulting chemists are continually promoting sales for the builders of machinery and equipment, without receiving from them any financial recognition. This matter of "professional protection" is of considerable importance and it is queer that mention of it should have been omitted from codes of ethics issued by chemists.

In the professions of architecture and engineering there are, I believe, well-established practices. The advertising brokers seem to have adopted the 15 per cent commission as the basis of their business, and clients are informed that any publicity medium (magazines, etc.) that does not grant a 15 per cent commission to the advertising broker throws the burden of the commission on the client, and the client is then called on to pay definitely 15 per cent to the broker.

The consulting chemist who promotes the sale and use of a certain appliance, machine, or apparatus, or who instals laboratories for clients is properly entitled to recognition in a substantial way. The client should know that a 15 per cent protection is accorded the consulting chemist and the client should further know that this 15 per cent does not have any influence on the price.

Consulting chemists, many of them, have come to me and said that one machine builder offered the following plan:

A machine is offered for sale direct to the consumer for, say, $1000. If this machine is recommended to the consumer by a consulting chemist, the machine builder will add 15 per cent

to the price, or will add any amount that the consulting chemist wants. In this case the price would be $1150 if purchased at the suggestion of a consulting chemist and $1000 if purchased direct.

In such a case the machinery builder is not paying anybody a commission for his sales promotion work, but he is showing the consumer that the consulting chemist is making the client pay for this sales promotion work.

This state of affairs has now reached the point where the machinery builders should be promptly and courteously called to account, and I hope that there will be a free discussion in our journal. We do not hope to receive the answer that the machinery builders are making possible the publication of our SOCIETY journal.

FREDERIC DANNERTH

NEWARK, N. J.
January 23, 1924

Information on Colloid Chemistry

Editor of Industrial and Engineering Chemistry:

About a year ago [THIS JOURNAL, **15**, 321 (1923)] I asked for assistance in preparation of a comprehensive book on "Colloid Chemistry, Theoretical and Applied," and I am glad to say that over one hundred and fifty of the best men of all countries have promised contributions to it, thus insuring its international character. Papers have already been received from the following:

CANADA	GERMANY	SWEDEN
F. E. Lloyd	F. Emslander	C. Benedicks
W. H. Martin	H. Freundlich	UNITED STATES
CZECHOSLOVAKIA	R. Lorenz	E. E. Ayres, Jr.
G. Georgeivics	H. Lüppo-Cramer	C. Barus
ENGLAND	P. Prausnitz	G. Bouyoucos
E. F. Armstrong	H. Schade	M. M. McCool
S. C. Bradford	R. Zsigmondy	H. J. Creighton
A. E. Dunstan	HOLLAND	W. P. Davey
W. B. Hardy	N. Waterman	E. I. Fulmei
D. Jordan Lloyd	JAPAN	H. A. Gardner
E. J. Mardles	T. Hagiwara	R. A. Gortner
H. R. Procter	S. Utzino	H. N. Holmes
FRANCE	JUGOSLAVIA	J. U. Lloyd
A. Lumiere	M. Samec	G. D. McLaughlin
A. Mary	MEXICO	H. N. Spencer
S. Leduc	A. L. Herrera	M. Toch
	RUSSIA	E. C. Washburn
	L. Gurwitsch	F. Zerban

Many others are either in the mail or will soon be—e. g., from:

M. Ascoli	E. Hatschek	A. B. Searle
W. D. Bancroft	W. H. Herschel	S. E. Sheppard
H. Bassett	D. D. Jackson	P. Scherrer
W. H. Bragg	P. S. Landolt	G. Storm
E. F. Burton	R. E. Liesegang	J. Traube
G. Bredig	D. T. MacDougal	W. E. S. Turner
W. Clayton	L. Michaelis	P. P. von Weimarn
J. Duclaux	Sven Oden	R. Willstatter
H. Handovsky	Wo. Pauli	P. Wislicenus

An enormous range of topics is being covered, including technology, agriculture, biology, and medicine. Thus there are papers on cancer, tuberculosis, concretions (gallstones, calculi, etc.).

If any of the readers of THIS JOURNAL can send me reprints of papers germane to the book, or suggestions as to points that they would like to have included or discussed, I shall appreciate it and make the best use I can of the information. I am looking for all the coöperation I can get to make this book a compendium of our present knowledge of colloid chemistry, so that it may be of the widest possible use, not only to chemists, but also to manufacturers, biologists, physicians, and many others.

JEROME ALEXANDER

50 EAST 41ST ST.
NEW YORK, N. Y.
February 13, 1924

Device for Sodium Flame

Editor of Industrial and Engineering Chemistry:

May I call attention to the fact that the device for a sodium flame described by Dolid, THIS JOURNAL, **16**, 53 (1924), is similar to one that has been listed for a number of years by one of the large chemical apparatus supply companies? The method is very satisfactory as long as the asbestos wick does not become clogged. The wick can, of course, be easily replaced if necessary.

Another method, for which apparatus is also listed, utilizes an aspirator of special design by means of which the salt solution is drawn in a fine spray into the gas which feeds the flame. This method is more satisfactory than the other for two reasons: it operates satisfactorily as long as there is solution in the reservoir, and there is no difficulty from contaminating the flame with salts that are not supposed to be there. With the asbestos wick it is almost impossible to avoid the latter trouble when salts other than those of sodium are used.

PAUL E. KLOPSTEG

CENTRAL SCIENTIFIC COMPANY
CHICAGO, ILL.
January 8, 1924

Register Your Protest

Editor of Industrial and Engineering Chemistry:

A bill, S. 845, "To authorize the Department of Commerce, by the National Bureau of Standards, to examine and test manufactured articles or products for the owner or manufacturer thereof, to issue a certificate as to the nature and quality of such manufactured articles or products, and to prevent the illegal use of such certificate," introduced by Senator Fletcher and referred to the Committee on Commerce, has just been called to our attention.

We have read this bill carefully and discussed it at our semiweekly conference. We cannot see that the provisions of the proposed law will serve any useful governmental purpose, nor do we believe that the services to be provided are a proper governmental function. It is not designed to assist in conserving the health of the nation or to protect its coinage and precious metals. It looks to be rather an attempt to increase greatly the force of the Bureau of Standards with no corresponding benefit to the public at large. Furthermore it seems to trespass greatly upon the field of activity of the many thousand chemists who are employed by the better type of manufacturer or who are maintaining commercial laboratories throughout the country. It is our belief that it is time to call a halt in the aggressive and almost universal tendency toward unnecessary and irksome paternalism on the part of many of our legislators.

We hope that our fellow chemists will see the merits of our position and that they will be cognizant of what is impending and take such action as they properly may to prevent Senate Bill 845 from becoming a law.

CHARLES G. WOODS

EKROTH LABORATORIES
NEW YORK, N. Y.
February 14, 1924

Calendar of Meetings

American Chemical Society—67th Meeting, New Willard Hotel, Washington, D. C., April 21 to 25, 1924.

American Electrochemical Society—Spring Meeting, Philadelphia, Pa., April 24 to 26, 1924.

National Fertilizer Association—Kenilworth Inn, Asheville, N. C., week of June 9, 1924.

5th Congress of the International Union of Pure and Applied Chemistry—Copenhagen, June 26 to July 1, 1924.

WORLD-WIDE CHEMISTRY

Paris Letter

By Charles Lormand

4 AVENUE DE L'OBSERVATOIRE, PARIS, FRANCE

EXPERIMENTS ON THE PROPAGATION OF SOUND

The experiments recently carried out in Holland on the speed of the propagation of sound have given extremely important results. Therefore, the French Government has decided to repeat these experiments in this country using its stocks of explosives. In May, 1924, at Camp de la Courtine, in the center of France, three gigantic explosions will take place, for each of which 10 tons of explosives will be used. These three explosions will take place fifteen days apart in order to have variations in atmospheric conditions. The time of the explosions will be regulated from the Eiffel Tower. Numerous seismographs, registering apparatus, and observatories will note the direction, intensity, and character of the sound.

NEW SOURCE OF CELTIUM

M. Georges Urbain, who was one of the first to determine the existence of celtium, is hunting for possible deposits of this element. He has recently studied a number of minerals such as zirconia and malacons from Madagascar and Brazil, and is able to state that an appreciable amount of celtium has been found in these minerals. This statement is important since it shows that among the trivalent metals, such as those of rare earths and yttric earths, it is possible to find quadrivalent elements such as celtium, which M. Urbain has detected by the spectroscope. The ancient idea of isomorphism will therefore have to be revised.

FERTILIZER CATALYSTS

M. Stoklasa, who has specialized in research on catalysis in agricultural chemistry, has recently determined the effects of iodine on vegetation. Inspired by the fact that the cultivated sugar beet had its botanical origin in a wild beet, the nautical beet (*betta maritima*), he determined the amount of iodine in the cultivated beet, and then in the laboratory and in the field carried out experiments testing the fertilization of the soil with iodine in the form of potassium iodide. With 1.720 kg. of iodine per hectare in the form of iodide of potassium, and with the same quantities of nitrogen, phosphorus, and potassium as in other fertilizers, he obtained supplementary yields of 80 quintals per hectare. If the amount of iodine is increased to 4 or 5 kg., the sugar content of the beet decreases and the abnormal presence of pentoses such as arabinose is found in the sugar.

M. Stoklasa thinks that iodine should play a part in the photosynthesis of carbohydrates, although he has not been able to demonstrate this in a precise manner.

It is interesting to compare this work with a recent study by M. Freundler, presented at l'Académie des Sciences, in which he compares the iodine content in algae at different times of the day, studying the algae maintained in the light or darkness. Whatever the method of preparation used, whether incineration, extraction with bisulfite, or by osmosis, M. Freundler has established that the iodine is maintained in the greatest proportion in the algae in the dark or when immersed in a saline solution, this solution absorbing the ultra-violet rays. The iodine in the plant should accumulate in the leaves when it is dark and pass into the sea water in the light.

A NEW GAS GENERATOR

As I have pointed out at different times, investigations are going on in France with the hope of replacing the gasoline in motors by fuels of less weight. The Imbert gas generator has recently been tried in an automobile. This generator burns any fuel—coal, coke, anthracite, wood charcoal. It ignites very rapidly and includes as accessory parts an air cooler, which lowers the temperature of the gas from 1400° to 60° C., and a purifier with iron turnings and filings impregnated with oil. The ashes formed by the carbon are well fused and form a cake at the bottom of the generator. The gas produced by this apparatus contains 33 per cent of combustible gas, of which 30 per cent is carbon monoxide. The absence of hydrogen renders it superior to the generators giving water gas, for the variations of hydrogen in such a gas render its use difficult in motors. The Imbert gas

generator using wood charcoal gives, for equal distances, an expenditure one-fourth that when oil is used.

The French automobile industries are beginning to develop the use of this gas generator, which they have begun to use in agricultural motors for tractors and plows.

DIAGNOSTIC CHEMISTRY OF PICTURES

I mentioned more than two years ago the use of radiography for the identification of pictures. MM. Bayle and Kling have perfected other methods of determining whether a picture has been retouched. They use groups of red, blue, green, or white light to light the picture, and they examine the suspected canvas with the spectrometer. The use of these various colors puts in relief the retouchings, scrapings, and changed signatures which constitute a false picture. By employing the ultra-violet ray they make the zinc white and certain varnishes stand out by fluorescence. Finally, by scraping off very small amounts of paint, they have made spectrographic analyses of them, and have been able thus to determine—for example, in a false Renoir, the presence of a cadmium yellow, when Renoir only used chrome yellow.

February 1, 1924

German Letter

By Walter Roth

CÖTHEN, GERMANY

CHEMISTRY AND ART

Science and the arts are still to a certain degree antagonistic to each other, in spite of the fact that true culture will result from their intimate association. Therefore, everyone should welcome even a slight coördination between the two branches of science as a step in the progress toward their complete harmony. Chemistry, especially, plays a far greater role in the arts than those in the ranks of philosophy, literature, and, particularly, artists want to admit. In the libraries and museums chemistry is already essential in making old or damaged handwritings again legible or in restoring old, worn-out portraits. Moreover, problems such as, for example, what causes the beautiful tone of the Italian master violins, today unattainable, are not solved through round-about trials, but on the basis of chemical knowledge and investigations. Thus, Dr. Ditmar, who has been working for some time on the utilization of rubber latex, has recently shown that the Cremona violin owes its wonderful tone to a wood impregnated with rubber latex from Euphorbia or *Ficus elastica*.

HIGH PRESSURE SYMPOSIUM

The most recent advances in chemical technic depend not so much on new chemical theory as on the designing and perfection of chemical apparatus. The chemical engineer has the leading word in chemical technic today. Therefore, the high-pressure steam symposium at the meeting of the "Vereins deutscher Ingenieure," in Berlin in January, held the greatest for all chemists. At this symposium Dr. Münzinger spoke on the technical and economic principles and prospects of the production and utilization of high-pressure steam, and Professor Goerens discussed materials for boiler construction. With machines combining heat and power and using high-pressure turbines, up to 25 per cent of the heating power of the coal can be utilized to obtain an efficiency which approaches that of the Diesel motor. According to Goerens, 5 per cent nickel steel poor in carbon has been found to be a good boiler material. Exhibits by Director Loch showed that boilers of over 30 atmospheres no longer use rivet joints—seamless rolled or forged boilers being used for higher pressures.

ELECTROLYTIC RECOVERY OF ZINC

Wilhelm Palmaer and A. Wejnarth have been making an exhaustive study of this problem. According to them the use of sulfuric acid or zinc sulfate solution is preferred to the use of hydrochloric acid or zinc chloride solution. By comparing the electrolytic with the electrothermic production of zinc, it is

shown that the first method is far superior from the point of view of power consumption. This is of special importance if no very cheap power is available. The electrolytic method can use poor zinc ores as long as they offer no special difficulties in extraction, while the electrothermal process requires pure ores. On the other hand, for the same production capacity the capital necessary for the electrolytic process is undoubtedly higher than for the electrothermal process. In America and in other countries the electrolytic method has been greatly extended in the last few years, while the electrothermal process is in use only in Sweden and possibly in Norway. According to the experiments described, about half of the zinc content of the solution is precipitated with an average current gain of 75 per cent. The addition of lime, which is sometimes recommended, proved to be unnecessary. As a cathode material aluminium is very suitable, as has already been mentioned in the literature.

Hexeton, a New Camphor Compound

A compound isomeric to the ordinary camphor and easily prepared synthetically, proved to be 3-methyl-5-isopropyl-Δ-2,3-cyclohexane. This compound, which was discovered by the Farbenfabriken vor Friedrich Bayer & Co., in Leverkusen, and was being studied extensively there, as well as in the University of Heidelberg, is a transparent liquid of characteristic odor and bitter taste. According to investigations of Professors Gottlieb, Schulemann, Krehl, and Franz, this new compound, called "hexeton" for short, has the same qualitative effect as camphor, but is from two to four times as strong. Hexeton is readily soluble in water solutions of sodium salicylate to a clear, stable, and sterile liquid, which should be valuable for medicinal purposes, as no harmful effects of its use have as yet been observed.

Mending Platinum Dishes

With the present high price of platinum, the mending of damaged platinum articles frequently has to be considered. For this purpose von Fellenburg recommends soldering with gold. A small piece of fine gold is beaten into a sheet about 0.1 mm. wide and cut into strips about 0.5 mm. wide and a little more than the length of the crack and heated from underneath with the blast. After a few seconds the gold melts and fills the opening. According to one writer this process has only a temporary value, as by frequent heating the gold alloys with the platinum and the crack opens up again. This can be prevented if another thin platinum sheet is laid on the gold sheet and the two together are fused to the dish—then the patch will hold.

German Atomic Weight Commission

This commission, which consists of Professors Honigschmid, Bodenstein, Hahn, and Meyer, has recently published its report of the July, 1922, to November, 1923, public dissertations on the atomic weight determinations. In the tables given out by this commission the "practical atomic weights for 1923" have been changed as follows: gallium 69.72 instead of 69.9; lanthanum 138.9 instead of 139; silicon 28.06 instead of 28.3.

To the dispute that has arisen in the chemical world over hafnium and over the nomenclature of the two components of what was formerly called ytterbium, the commission states that for the element with the atomic weight 72, the name hafnium is accepted, and for the elements with the atomic weights 70 and 71, the names ytterbium and cassiopeium, respectively. The commission has, furthermore, arranged isotope tables of the common chemical elements corresponding to the state of research on October 1, 1923. According to these tables more than one kind of atoms has been detected in the following: lithium, boron, neon, magnesium, silicon, chlorine, argon, potassium, calcium, titanium (?), iron (?), nickel, copper, zinc, gallium, germanium, selenium, bromine, krypton, rubidium, silver, tin, antimony, xenon, and mercury (?). According to this table the greatest number of isotopes—that is, nine—is attributed to xenon.

January 29, 1924

The Locust as an Industrial Raw Material—Good progress is being made by the South African Locust Products Company making fertilizers, poultry foods, etc., from locusts. It appears that numerous inquiries have been received from Australia, America, and Europe, and that a much larger factory is to be opened at Johannesburg, in addition to the existing one, and another at Capetown (which latter will probably deal with the export demand).

Washington Letter

Paper and Pulp Committee Meets

How to help the United States Department of Agriculture work out its forestry program for the nation was discussed at a recent gathering in Washington of prominent paper and pulp manufacturers who were invited by Secretary of Agriculture Wallace to form an advisory committee to meet with him and with representatives of the Forest Service. The committee voted immediately to lend its efforts toward better forestry and utilization of wood, and to aid in the development of a national forestry program. The committee will assist the department particularly in studying the local methods for growing timber suitable for pulpwood and better manufacturing processes. One of the most urgent forest problems, according to the advisory committee, is for governmental agencies and the paper and pulp industry to work together to determine how much timber is available for paper making in the chief manufacturing regions, how long the supply of timber will last, and how to handle and protect the forests so as to keep them permanently productive.

The value of scientific research in forestry problems and the utilization of wood were emphasized. One of the definite accomplishments of the meeting was the decision to have small groups of timberland owners act in an advisory capacity to the Federal Forest Experiment Stations at New Orleans, La., Asheville, N. C., Amherst, Mass., St. Paul, Minn., and to the Forest Products Laboratory at Madison, Wis.

Samuel T. Dana, director of the Northeastern Forest Experiment Station, and Raphael Zon, director of the Lake States Forest Experiment Station, discussed the work of their stations relative to growing pulpwood. The main producing regions of timber best suitable for pulpwood lie within the territory covered by these two Forest Service Stations.

Pasteur Exhibit Now in Washington

The American Pasteur exhibit prepared by the Department of Agriculture and displayed at the American Museum of Natural History, New York City, in December, 1922, in honor of the centenary of the birth of Louis Pasteur, has been awarded the *diplome de grande prix* by the Exposition Internationale de Pasteur at Strasburg. This exhibit illustrated all Pasteur's world-famous experiments in fermentation, as well as his work on anthrax, chicken cholera, and rabies. Apparatus exactly like that employed by Pasteur was reproduced by the Bureau of Chemistry and arranged in such orderly sequence that one could follow each successive step of the great discoveries. John S. Buckley, of the pathological division of the Bureau of Animal Industry, furnished the material showing the experiments on rabies, etc. The exhibit of the Bureau of Chemistry has been returned to Washington and reassembled in the east gallery of the old National Museum.

Tariff Commission Happenings

All argument before Justice Siddons, of the Supreme Court of the District of Columbia, on the petition of the Norwegian Nitrogen Products Company for a writ of mandamus to compel the Tariff Commission to disclose to the petitioner the production costs and other information submitted by the American Nitrogen Products Company in the investigation of sodium nitrite, was completed on January 31, 1924. Trial briefs have been filed, but as yet no decision has been handed down.

A hearing on phenol was held in the office of the commission on January 24, and was closed on the same date, thirty days having been given for the filing of briefs. Oral argument in the case was waived. The hearing on cresylic acid set for the same date was postponed until January 25, and then, upon request by the applicants for a decrease in duty, was further postponed until February 14, at which time representatives of the Insecticide and Disinfectant Manufacturers' Association, the applicants for the reduction in duty, did not appear. Representatives appeared in the interest of cresol, U. S. P., however. Members of The Barrett Company appeared in opposition. Thirty days were given to file briefs. In response to a petition for a lowering in the duty on cottonseed oil, the commission has announced a public hearing for March 5. Another hearing which is attracting a great deal of interest is that announced for March 7, having to do with vegetable, animal, and fish oils, including herring, menhaden, whale, olive, coconut, cottonseed, soy bean, and peanut oils, tallow, oleo oil, and oleostearin. Field work will not be undertaken until after the preliminary hearing.

English Technologists Visit America

As the result of an agreement recently effected between the British Home Office and the Department of the Interior for the exchange of technical information to prevent mine accidents and to promote mine-safety conditions, R. V. Wheeler, professor of fuel technology at Sheffield University and director of the Eskmeals Testing Station, Cumberland, England, W. R. Chapman, scientific assistant to Dr. Wheeler, and Henry Walker, deputy chief inspector of mines for the British Government, have come to the United States to observe the progress of research work here. Mr. Chapman will be detailed to the Pittsburgh Experiment Station of the Bureau of Mines for an indefinite period.

The visiting technologists, after attending the meeting of the American Institute of Mining and Metallurgical Engineers in New York, will visit Washington, Pittsburgh, Chicago, Schenectady, and other cities, where inspections of various research laboratories and industrial plants will be made. The experimental coal mine of the Bureau of Mines, near Pittsburgh, and certain of the larger bituminous coal mines in Illinois will be visited. The party will be escorted by George S. Rice, chief mining engineer of the Bureau of Mines, who recently returned from a protracted study of European mining conditions, and at whose suggestion the agreement for an exchange of technical information was effected.

Motion Picture Films Available

A series of vivid and striking educational motion picture films, depicting the mining, preparation, and utilization of the various mineral materials, is made more readily available to the public through a new system of distribution, arranged by the Department of the Interior, by which the many industrial films made by the Bureau of Mines may be obtained through State or sectional centers of distribution.

Nearly a hundred educational films have been prepared in the past few years by the Bureau of Mines in coöperation with industrial concerns. The demand for these films by educational institutions and civic bodies has become so great that the original plan of centralized distribution from the Pittsburgh Experiment Station of the Bureau of Mines has become inadequate. A selected list of the best of these films is now made available at twenty-seven coöperating agencies located in the different States. The films relate to coal, petroleum, sulfur, iron, asbestos, zinc, marble, copper, natural gas, and other minerals. A series of films depicts most vividly such industrial processes as the manufacture of oxygen, the making of fire-clay refractories, the manufacture of automobiles, the method of compressing air, the quarrying of limestone, etc. Other films illustrate dangerous and safe practices in mining, efficiency in the combustion of coal, the utilization of water power, and the operation of a gasoline motor.

The following is a list of State distribution centers, to which interested persons should apply for information:

University of Arkansas, Fayetteville, Ark.
University of California, Berkeley, Calif.
Department of Visual Education, Los Angeles County Public Schools, Los Angeles, Calif.
University of Colorado, Boulder, Colo.
University of Florida, Gainesville, Fla.
Bureau of Visual Instruction, Chicago Board of Education, Chicago, Ill.
State University of Iowa, Iowa City, Iowa
Iowa State College, Ames, Iowa
Indiana University, Bloomington, Ind.
University of Kansas, Lawrence, Kan.
State Normal College, Natchitoches, La.
University of Michigan, Ann Arbor, Mich.
State Department of Public Instruction, Lansing, Mich.
University of Minnesota, Minneapolis, Minn.
University of Missouri, Columbia, Mo.
Agricultural and Mechanical College of Mississippi, A. and M. College, Miss.
University of Nebraska, Lincoln, Nebr.
New Jersey State Museum, Trenton, N. J.
State Department of Education, Raleigh, N. C.
Educational Museum, Cleveland School of Education, Cleveland, Ohio
University of Oklahoma, Norman, Okla.
University of Oregon, Eugene, Ore.
Coöperative Extension Work in Agriculture and Home Economics, Brookings, S. D.
University of Texas, Austin, Texas
University of Utah, Salt Lake City, Utah
State College of Washington, Pullman, Wash
University of Wisconsin, Madison, Wis.

Absorption of Nitrogen by Diffusion

The Bureau of Standards has experienced a great deal of difficulty in securing a suitable liquid seal for gas-holders containing very pure hydrogen. Various liquids have been tried, but thus far crude glycerol has proved the most successful. Analyses made of some hydrogen that had been stored in a gasholder over crude glycerol showed that the rate of absorption of nitrogen by diffusion through the glycerol had been at a rate equal to about one-tenth the rate of absorption through machine oil.

This is a great improvement, but is not quite so good as was expected. It is thought that evolution of nitrogen contained in the glycerol may have occurred when it was first placed in the holder, and to check this another analysis will be made to determine whether the rate of absorption has diminished.

February 20, 1924

Tokyo Letter

By K. Kashima

992, Ikebukuro, Near Tokyo, Japan

Japanese Acid Clay

Research on the nature of this clay is now progressing under the direction of K. Ikeda, of the Institute of Physical and Chemical Research.

Clays may be divided into three classes according to their activity with neutral salt solutions and acids. The first is not dissolved by treating with salt solutions and is only slightly dissolved by strong acids; the second is not dissolved by salt solutions, but to a large extent by acids; the third is dissolved to a considerable extent by both reagents. Japanese acid clay belongs to the last class, although it is not much different in composition from common clays. When treated with neutral salt solutions, the positive radicals in the salt unite with the clay particles and the aluminium in the clay goes into solution as the corresponding salt. This reaction is attributed partly to adsorptive action but mainly to double decomposition, and the acidity of the solution is governed by the salt used and the adsorptive and reactive affinities of the clay.

When treated with a 5 per cent oxalic acid solution, the Japanese acid clay is gelatinized to a pasty mass, called "ceramocoll," the degree of gelatinization being practically proportional to the acidity of the clay. The ceramocoll is stable and does not easily coagulate or precipitate. With the proper proportions of clay and solution and proper concentration of the solution, the product has the maximum plasticity, which is due chiefly to the formation of insoluble aluminium oxalate.

The uses of this clay have been considerably extended, and include purification of naphthalene and removal of basic compounds and coloring matters, such as from crude aminophenylarsenic acid.

Dr. Ikeda has succeeded in obtaining the clay in granular form. A pasty mixture of the clay and water is pressed through small holes in metallic plates into prismatic grains about 10 to 15 mm. long and 4 to 9 sq. cm. in cross-sectional area. They are then heated at 150° to 600° C. The product is called "Adsol." When air is circulated through a layer of Adsol and a wet material, the latter is easily dried at low temperature. This drying power decreases in time, but it is renewed by passing air through the layer electrically heated at about 300° C., by means of a special equipment. Because of this property Adsol is used for drying purposes, such as in the drying of foods and for its dehydrating action in the production of ethylene from alcohol.

New Journal

The investigations of K. Honda and his colleagues at the Tohoku Imperial University on the chemistry of iron and allied metals are well known among chemists and engineers interested in these subjects, and they have been published in the Report of the Tohoku Imperial University. For prompt publication of the works of the Metal Research Laboratory, of which Professor Honda is the head, a monthly journal written in Japanese, *Kinzoku Kenkyô* (Researches on Metals), is being published, the first number already having been issued. It contains original papers, lectures, miscellaneous reports, and abstracts of papers on metals, etc. The journal has been looked forward to with much interest by chemists and engineers and should prove very valuable.

January 26, 1924

BOOK REVIEWS

Chemistry of the Rarer Elements. By B. Smith Hopkins. 376 pp. D. C. Heath & Co., Boston and New York, 1923. Price, $4.00.

By "rarer" the author designates all the elements that are little known, either because they are really rare or because they have been neglected from lack of interest or of importance, or have been but recently discovered. Both the selection and treatment are happy. Since more than half of the elements are included, the text is necessarily somewhat encyclopedic in character, but the writer has skilfully avoided monotony, and has succeeded in bringing together the most important and interesting facts bearing on his subject, from widely divergent sources. The task was unquestionably a difficult one, and the writer has rendered a real service in having compiled in a single volume so much of value regarding the rarer elements.

The utility of the book is much enhanced by the fact that Professor Hopkins has gone far outside the bounds of ordinary chemistry in including the topics: Natural Occurrence, Metallurgy, History, and Uses, besides many other special subjects of particular interest for each element. The order of treatment is that of the periodic system, and the elements considered are the rare gases of Group O; helium, neon, argon, xenon, krypton, and niton; lithium, rubidium, and caesium of Group 1; radium, mesothorium, and beryllium of Group 2; the rare earths and gallium, indium, and thallium of Group 3; titanium, zirconium, cerium, and thorium of Group 4; vanadium, columbium, and tantalum of Group 5; molybdenum, tungsten, uranium, selenium, and tellurium of Group 6; and the platinum metals of Group 8.

An authors' index would have been a great convenience in the use of this work as a reference book. Illustrations were wisely omitted. The tabulation, while not abundant, is well done and effective.

S. C. Lind

Colloid Symposium Monograph. Papers and Discussions presented at the National Symposium on Colloid Chemistry held at the University of Wisconsin, June, 1923. Edited by J. Howard Mathews. 419 pages. Published by the Department of Chemistry, University of Wisconsin, Madison, 1923. Price, $2.75.

The remarkable success of this symposium created a demand for a permanent record of the papers and discussion. Many of the papers were general surveys of definite fields. Since most of our colloid chemists were present, the discussion, fully reported in the monograph, is unusually interesting. Dr. Svedberg's part is important, as is his scholarly paper on "Colloid Chemistry Technic."

Proteins receive true Jacques Loeb treatment from J. A. Wilson, who discusses their swelling. It requires 13 pages of the monograph to record the animated comment on the subject. J. H. Mathews and B. W. Rowland offer a report of their research on "The Thermochemistry of Protein Behavior."

Coagulating influences are stressed by E. F. Burton in his paper on "Forces Regulating the Size of Colloidal Particles," and by Thomas and Johnson in their report on "The Mechanism of the Mutual Precipitation of Hydrosols." "The Application of Colloid Chemistry to Some Agricultural Problems," by R. A. Gortner, brings in a clear treatment of hydrophilic colloids in drought-resisting plants. The colloid difference between "strong" and "weak" flours is a feature of this paper.

The pharmacist's interest is attracted by David Klein's paper on "Colloid Problems in the Manufacture of Enzymic and Animal Glandular Products." Martin Fischer's opinions "On the Theory of Lyophilic Colloids and the Behavior of Protoplasm" are followed by a vigorous discussion.

Gel structure, inorganic jellies, and special jellies received attention from H. B. Weiser, E. O. Kraemer, and Harry N. Holmes. Emulsions, rubber, adsorption, catalysis, anomalous osmose, surface films, alloys, photography, collagen, clays, and other topics are presented ably by J. H. Hildebrand, E. B. Spear, H. S. Taylor, F. E. Bartell, R. E. Wilson, Jerome Alexander, S. E. Sheppard, R. H. Bogue, R. Bradfield, and F. L. Browne.

Harry N. Holmes

Stories of Scientific Discovery. By D. B. Hammond. 199 pages. Cambridge University Press, 1923. Price, $2.40.

This is a very interesting book. Mrs. Hammond desired to know something about the lives of real leaders in science. She read with care "the standard biographies of a few of the greatest scientific discoverers and from them produced a series of short sketches, chiefly for the benefit of those whose lives are still over-busy for the study of the fuller originals."

Her labors have been most successful, and as one reads what she submits on Priestley, Lavoisier, Rumford, Falne, Darwin and Wallace, Pasteur, and the Curies, one wishes that she might have included others; but then the book would have been too extended, so she contented herself with these splendid examples.

The book is well composed and the hurried reader is sure to glean a knowledge of the salient points in the life of each individual. However well informed the reader may be on the work of these eminent workers in science, the little book will assist in fixing many points of deepest interest, for there is throughout its pages a loving personal touch, which holds one's closest attention.

If the great public is ever to become conversant with these quiet laborers in the domain of science, it will be largely through the influence of such volumes as Mrs. Hammond has prepared for some of the scientific worthies. May there be more of them.

Edgar F. Smith

Production et condensation de la vapeur. By E. Sauvage. 366 pages, 303 illustrations. J.-B. Baillière & Fils, Paris, 1923. Price, stitched, 35 fr.; bound, 45 fr.

This work bears on its title page the statement that it is a part of an industrial cyclopedia published under the patronage of the French Society of Civil Engineers and the Society for the Encouragement of National Industry. The scope of the book is best illustrated by the table of contents: Fuels, 11 pages; Production of Heat (Furnace Design), 65 pages; Types of Boilers, 115 pages; Boiler Accessories, 64 pages; Condensers, 99 pages. Throughout this book the treatment is purely descriptive. There are practically no discussions of even the simplest theory, or principles of design; neither is there any critical comparison of different designs or discussion of the conditions to which a given design is applicable.

As would be expected, the boilers and accessories described are those common in France. A few illustrations contributed by the foreign branches of large American concerns look familiar, but most of the book describes apparatus not found in this country. The illustrations are excellent, numerous, and the book is printed on paper that does them justice. Fully 50 per cent of the space in the book is taken by illustrations.

Owing to the absence of theoretical discussion, the book will be of no great value to an American engineer, unless one wishes a picture of French practice in the form of an easily read descriptive treatise.

W. L. Badger

Grundlegende Operationen der Farbenchemie. By Hans Eduard Fierz-David. 2nd enlarged edition. 46 illustrations and 1 table. 267 pages. By Julius Springer, Berlin, 1922. Price, $2.40.

The outstanding feature of the book by Professor Fierz-David is that it gives information as to actual factory procedures now being used in the manufacture of dyes and intermediates. The present volume treats of intermediates under the heads of Sulfonations, Nitrations and Reductions, Chlorinations, Oxidations, and Condensations—embracing under these heads 113 pages. The book then devotes 85 pages to the preparation and manufacture of a considerable number of a varied line of dyes. This is then followed by a section on technical details, in which are given many interesting hints with regard to the apparatus employed in the industry together with some notes on the management of a dye industry and an example of the calculation of the cost of a simple dye. The book concludes with 15 pages devoted to analytical methods.

The present edition has quite a little new matter, much of it of considerable technical importance. Notwithstanding the added matter, the present edition contains only 266 pages, while the first edition embraced 323 pages, and this is made possible by the use of a somewhat finer print.

All in all, the book is a very satisfactory one from the point of view of anyone engaged in the dye industry, and it is filled with practical information. The paper and the binding of the present edition are very satisfactory and the typography is excellent.

R. Norris Shreve

The New Physics. (Lectures for Laymen and Others.) By Arthur Haas and R. W. Lawson. 165 pages. E. P. Dutton & Co., New York, 1923. Price, $2.50.

This volume presents in a series of six lectures glimpses of the tremendous accomplishments of modern physics. The discourse throughout is of a narrative turn, entirely free from any mathematical formulas, and particularly interesting in its presentation. While it is impossible to present adequately any of the subjects dwelt upon without the aid of mathematics, the author has, happily, chosen a viewpoint that permits his discursive style to give a very real grasp of the general ideas involved. In the lectures on Theory of Light and Molecular Statistics the material used does not permit of the interesting development which comes in the later lectures. The Electron Theory is of more than average interest, but not until the discussion on The Quantum Theory and The Chemical Elements does the author gain his real stride in interesting presentation. In The Theory of Relativity the author has used—as he has so successfully in the preceding lectures—what comparisons he may to bring the ideas of modern physics more concretely to the layman. If it is deemed necessary that laymen should have such inadequate conception of relativity as they may grasp, then chapters similar to the final one are justified.

W. E. Tisdale

Chemische-Technische Vorschriften. Ein Handbuch der speziellen chemischen Technologie insbesondere für chemische Fabriken und verwandte technische Betriebe enthaltend Vorschriften aus allen Gebieten der chemischen Technologie mit umfassenden Literaturnachweisen. Band III—Harze, Öle, Fette. By Otto Lange. 3rd edition. 796 pages. Otto Spamer, Leipzig, 1923. Price, paper, 45 gold marks; cloth, 50 gold marks.

In reviewing the third volume of this encyclopedic work, little can be added to the general comments made on volumes one and two [This Journal, **15**, 982 (1923); **16**, 105 (1924)]. The present volume covers the general fields of resins, oils, and fats. Of the numerous topics discussed the following may be mentioned: rubber—synthesis, preparation, vulcanization, and substitutes; hard rubber; resins; resin substitutes—phenol condensation products, etc.; varnishes and varnish substitutes; lakes—resin, cellulose ester, rubber, protein, asphalt, dye, etc.; lacquers; gilding and bronzing materials; inks; petroleum and natural gas; asphalts, tars and pitches; lubricants; fats, oils, and waxes—preparation, methods of saponification, bleaching, hydrogenation and sulfonation; soaps and saponins; cosmetics; disinfection, sterilization and decoloring agents; water purification; waste waters; noxious gases, etc. As in previous volumes, most of the references are to patent specifications.

C. J. West

Das Erdöl. By Richard Kissling. Volume V of Monographien aus dem Gebiete der Fett-Chemie. 146 pages. 26 figures. Wissenschaftliche Verlagsgesellschaft, m. b. H., Stuttgart, 1923.

This compend is evidently based upon a work of similar scope written by Dr. Kissling in 1907–8; in fact, it may be looked upon as a revision of his earlier book, although this information is not given by the author. However, it is of less interest to American petroleum chemists than its ancestor at the time of its appearance, because several very much more comprehensive treatises have been published in this country during the past eight years. Moreover, the compound may be likened in character to a petroleum specialist's conception of an abridgment in German of the late Sir Boverton Redwood's standard work. A condensed summary of so much knowledge is of little educational and no technical value, except in countries where the German language is used and where petroleum is of less importance than here and in Great Britain. It may also be regarded as an epitome of certain parts of the very voluminous treatise

of Engler and Höfer, access to which is frequently inconvenient, even in Germany.

The volume contains four sections, as follows: (1) Origin, Chemical Composition, Chemical and Physical Properties, History, Occurrence, Winning, Storage, and Transportation of Crude Petroleum; (2) Working-up and Refining of Petroleum; (3) Uses and Quality of Petroleum Products; and (4) Testing and Evaluation of Petroleum and Its Products. In each part the author presents very concise statements of reported facts of general interest, and he has succeeded in so small compass in giving descriptive information which no doubt makes the volume useful to German students of chemical technology and chemists who are not specializing in petroleum work. While the reviewer does not wish to be critical of this "precis of naphthology," for he is aware of the limitations imposed upon its distinguished author, he finds it necessary to point out that the subjects of refining and testing are given disappointingly cursory treatment, the book being very weak in its consideration of American practice.

W. A. Hamor

NEW BOOKS

Action of the Beater. S. Smith. Translated from the Danish by R. Marx. 212 pp. Technical Section of the Papermakers' Association of Great Britain and Ireland, London. Price, 15 s.

Aerial Haze and Its Effect on Photography from the Air. Monograph No. 4 on the Theory of Photography from the Research Laboratory of the Eastman Kodak Company. 84 pp. D. Van Nostrand Co., New York. Price, $2.50.

Analyse et Essais des Materiaux de Construction: Chimie et Physique Appliquées aux Travaux Publics. J. Malette. 2nd edition. 916 pp. 189 illustrations. Dunod, Paris. Price, 54 fr.

Chemical Calculations. R. Harman Ashley. 3rd edition, revised. 287 pp. Illustrated. D. Van Nostrand Co., New York. Price, $3.00.

Compressor Theory and Practice. Joseph M. Ford. 345 pp. Constable & Co., London. Price, 31 s. 6 d. net.

Course of Instruction in Instrumental Methods of Chemical Analysis. William N. Lacey. 98 pp. Illustrated. The Macmillan Co., New York. Price, $1.50.

Dictionnaires Techniques Illustrés en Six Langues. Les Matières Textiles. Vol. XIV. Alfred Schlomann. 500 pp. Dunod, Paris. Price, 90 fr.

Dizionario di Merceologia e di Chimica Applicata. 4th edition, revised and enlarged. Vol. II. Damiana-Mussena. G. Vittorio Villavecchia. 1679 pp. Ulrico Hoepli, Milan. Price, L. 35.

D. S. Series of Illustrated Dictionaries in Six Languages. Vol. XIV—Raw Materials of the Textile Industry. Constable & Co., London. Price, 20 s. net.

Electrical Handling of Materials. Vol. IV—Machinery and Methods. H. H. Broughton. 354 pp. Illustrated. D. Van Nostrand Co., New York. Price, $12.50.

Honors Courses in American Colleges and Universities. Frank Aydelotte. 57 pp. National Research Council, Washington, D. C. Price, 75 cents.

Institute of Chemistry of Great Britain and Ireland. Report of Conference held at Liverpool, October 18 to 20, 1923.

Photography as a Scientific Implement. A. E. Conrady and others. 557 pp. D. Van Nostrand Co., New York. Price, $9.00.

Physical Chemistry of the Photographic Process. Faraday Society. 94 pp. Faraday Society, London. Price, 12 s. 6 d.

Praxis des Eisenhüttenchemikers. Carl Krug. 200 pp. Julius Springer, Berlin. Price, $14.50.

Publications of the Imperial Mineral Resources Bureau. The Mineral Industry of the British Empire and Foreign Countries. Statistics, 1919–1921. Bismuth. 9 pp. Price, 9 d. Graphite. 16 pp. Price, 1 s. Quicksilver. 15 pp. Price, 1 s. Strontium Minerals. 3 pp. Price, 6 d. H. M. Stationery Office, London.

Pulverized and Colloidal Fuel. J. T. Dunn. 197 pp. E. Benn, Ltd., London. Price, 25 s.

Quantitative Chemical Analysis. Frank Clowes and J. Bernard Coleman. 576 pp. J. and A. Churchill, London. Price, 18 s.

Quantum Theory. E. P. Adams. 2nd edition, revised and enlarged. 109 pp. National Research Council, Washington, D. C. Price, $1.50.

Raw Materials for the Manufacture of Sulfuric Acid and the Manufacture of Sulfur Dioxide. Wilfred Wyld. 571 pp. D. Van Nostrand Co., New York. Price, $10.00.

Recent Developments in Atomic Theory. Leo Graetz. Translated by Guy Barr. 174 pp. Illustrated. E. P. Dutton & Co., New York. Price, $3.50.

Standards and Tests for Reagent Chemicals. Benjamin L. Murray. 400 pp. D. Van Nostrand Co., New York. Price, $2.00.

Thermal Process Time for Canned Food. Charles Olin Ball. 76 pp. National Research Council, Washington, D. C. Price, $1.50.

GOVERNMENT PUBLICATIONS

Notice—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate.

Bureau of Foreign and Domestic Commerce

Annual Report of the Director of the Bureau of Foreign and Domestic Commerce to the Secretary of Commerce for the Fiscal Year Ended June 30, 1923. 170 pp.

Foreign Markets for Paints and Paint Materials with Complete Statistics of United States Exports for 1922 and First Six Months of 1923. W. M. Taylor. *Trade Information Bulletin* 164. 26 pp. Issued December 23, 1923.

German Chemical Industry Notes, November, 1923. *Special Circular* 20, Chemical Division. 4 pp.

Market for Prepared Medicines in Brazil. M. A. Cremer. *Trade Information Bulletin* 165. 14 pp. Issued December 3, 1923.

Markets for Paper and Paper Products in Chile and Peru. Prepared from data furnished by W. E. Embry, C. F. Deichman, Homer Brett, S. E. McMillin, S. R. Thompson, and W. N. Pearce. *Trade Information Bulletin* 168. 21 pp. Issued December 10, 1923.

Tanning Materials Survey. Part I—The Problem of Our Commercial Independence in Tanning Materials. Prepared under the direction of W. J. Page. *Trade Information Bulletin* 167. 18 pp. Issued January 2, 1924.

The Swiss Dyestuffs Industry. Production, Export, and Import Statistics. F. E. Breithut. *Trade Information Bulletin* 175. 16 pp. Issued January 14, 1924.

Bureau of Mines

Analyses of Ohio Coals. M. R. Campbell, J. W. Paul, and others. *Technical Paper* 344. 40 pp. Paper, 5 cents.

An Investigation of Powdered Coal as Fuel for Power-Plant Boilers. Tests at Oneida Street Power Station, Milwaukee, Wis. Henry Kreisinger, John Blizard, C. E. Augustine, and B. J. Cross. *Bulletin* 223. 92 pp. Paper, 15 cents.

Carbon Monoxide Fatalities from Natural-Gas Heaters Investigated by the Bureau of Mines in the Pittsburgh District during the Past Year. G. W. Jones and W. P. Yant. *Reports of Investigations* 2572. 4 pp. Issued February, 1924.

Carbon Monoxide Hazards from House Heaters Burning Natural Gas. G. W. Jones, L. B. Berger, and W. F. Holbrook. *Technical Paper* 337. 31 pp. Paper, 10 cents.

Changes in Specifications for Petroleum Products and Methods for Testing as Applying to Bureau of Mines Technical Paper 323. Recommended by the Technical Committee on Lubricants and Liquid Fuels and Approved by the Federal Specifications Board. 10 pp. Issued January 3, 1924.

Industrial Accidents in the California Oil Fields. H. C. Miller. *Reports of Investigations* 2557. 22 pp. Issued December, 1923.

Oxygen-Oil Explosions. Preliminary Report III. Spontaneous Ignition of Oils in Oxygen under Pressure. S. H. Brooks. *Reports of Investigations* 2555. 4 pp. Issued December, 1923.

Production and Briquetting of Carbonized Lignite. E. J. Babcock and W. W. Odell. *Bulletin* 221. 82 pp. Paper, 20 cents. This bulletin represents work done under a coöperative agreement between the Bureau of Mines, Department of the Interior, and the School of Mines of the University of North Dakota.

The Paraffin Problem in Oil Wells. R. Van A. Mills. *Reports of Investigations* 2550. 11 pp. Issued December, 1923.

Uses of Water in the Oil-Shale Industry with Particular Reference to Engineering Requirements. J. J. Jakosky. With a Chapter on the Sanitation of Oil-Shale Camps. A. L. Murray. *Technical Paper* 324. 57 pp. Paper, 10 cents.

Bureau of Standards

Annual Report of the Director of the Bureau of Standards, Fiscal Year, 1923. *Miscellaneous Publication* 53. 330 pp.

Recommended Specification for Ceramic Whiting. *Circular* 152. 7 pp. Issued December 8, 1923. Paper, 5 cents.

Recommended Specification for Quicklime and Hydrated Lime for the Manufacture of Silica Brick. *Circular* 153. 7 pp. Issued December 27, 1923. Paper, 5 cents.

Recommended Specification for Quicklime and Hydrated Lime for Use in the Manufacture of Sand-Lime Brick. *Circular* 150. 6 pp. Issued December 28, 1923.

Wet Process Enamels for Cast Iron. R. R. Danielson and H. P. Reinecker. *Technologic Paper* 246. 41 pp. Issued December 19, 1923. Paper, 10 cents.

Congress

Arsenic. Letter from the Secretary of the Interior transmitted in response to Senate Resolution 64, agreed to December 17, 1923, containing information prepared by the United States Geological Survey on arsenic deposits in the United States available for the manufacture of white arsenic. *S. Doc.* 27. 7 pp. Submitted January 24, 1924.

Helium. A Bill authorizing the conservation, production, and exploitation of helium gas, a mineral resource pertaining to the national defense, and to the development of commercial aeronautics, and for other purposes. Introduced by Mr. Kahn, January 18, 1924. *H. R.* 5722. 4 pp.

Same. Introduced by Mr. Oddie, January 22, 1924. *S.* 2166. 3 pp.

Muscle Shoals. A Bill to authorize and direct the Secretary of War, for national defense in time of war and for the production of fertilizers and other useful products in time of peace, to lease to a corporation to be incorporated by the subscribers to a proposal relating to the manufacture of fertilizers submitted to the Secretary of War, dated January 24, 1924, Nitrate Plant Numbered 1 at Sheffield, Alabama, and certain other properties mentioned in said proposal, etc. Introduced by Mr. Hull, January 28, 1924. *H. R.* 6300. 16 pp.

Same. Introduced by Mr. Hull, February 8, 1924. *H. R.* 6781. 15 pp.

Same. A Bill to authorize and direct the Secretary of War to sell to Henry Ford Nitrate Plant Numbered 1, at Sheffield, Alabama; Nitrate Plant Numbered 2, at Muscle Shoals, Alabama, etc. Introduced by Mr. McKenzie, December 5, 1923; reported with amendments February 2 1924. *H. R.* 518. Union Calendar No. 47. 19 pp.

Same. Letter from the Secretary of War transmitting an additional offer from the Tennessee Electric Power Company, and its associates, covering the manufacture of nitrogen and fertilizers at Muscle Shoals. *H. Doc.* 173. 4 pp. Submitted January 25, 1924.

Same. Letter from the Secretary of War transmitting a proposition submitted by the Union Carbide Company, of New York, to manufacture nitrates at Muscle Shoals. *H. Doc.* 166. 6 pp. Submitted January 23, 1924.

Same. Minority views submitted by Mr. Hull from the Committee on Military Affairs. *H. R. Report* 143, Part 2. 27 pp. February 9, 1924.

Same. Report submitted by Mr. McKenzie from the Committee on Military Affairs. *H. R. Report* 143. 62 pp. February 2, 1924.

Patents. A Bill to authorize the President to constitute an Interdepartmental Patents Board. Introduced by Mr. Ernst, February 7, 1924. *S.* 2387. 3 pp.

Potash. A Bill authorizing investigation by the United States Geological Survey to determine location and extent of potash deposits in the United States. Introduced by Mr. Hudspeth, January 29, 1924. *H. R.* 6361. 1 p.

Pulp. A Bill authorizing and directing the Public Printer to provide a pulp and paper mill or mills for the manufacture of print paper for the Government, and for other purposes. Introduced by Mr. Raker, December 5, 1923. *H. R.* 114. 4 pp.

Weights and Measures. A Bill to rectify, coördinate, and decimalize the weights and measures of the United States. Introduced by Mr. Colten, January 22, 1924. *H. R.* 5942. 2 pp.

Same. Introduced by Mr. King, January 17, 1924. *S.* 2070. 2 pp.

Department of Agriculture

Field Experiments with Atmospheric-Nitrogen Fertilizers. F. E. Allison, J. M. Braham, and J. E. McMurtrey. *Department Bulletin* 1180. 44 pp. Issued January 22, 1924. Paper, 10 cents.

Hot-Water Treatment of Sugar Cane for Insect Pests—A Precaution. P. A. Yoder and J. W. Ingram. *Department Circular* 303. 4 pp. Issued December, 1923. Paper, 5 cents.

Potash from Kelp. Early Development and Growth of the Giant Kelp, Macrocystis Pyrifera. R. P. Brandt and J. W. Turrentine. *Department Bulletin* 1191. 40 pp. Issued December, 1923.

Public Health Service

Hydrogen Sulfide Literature. C. W. Mitchell and S. J. Davenport. *Public Health Reports*, 39 (January 4, 1924), 1–13.

Viscosity and Toxicity of Arsphenamine Solutions. Carl Voegtlin, J. M. Johnson, and Helen Dyer. *Public Health Reports*, 39 (February 1, 1924), 179–95.

Treasury Department

Annual Report of the Director of the Mint for the Fiscal Year Ended June 30, 1923, Including Report on the Production of Precious Metals during the Calendar Year 1922. *Document* 2928. 248 pp.

MANUFACTURERS' TECHNICAL PUBLICATIONS

Notice—*Any publications mentioned under this heading will be sent free, unless otherwise noted, to readers of* This Journal, *on request to the firm issuing the publication. When writing for any of these items kindly mention* Industrial and Engineering Chemistry.

Agitation and Mixing. *Bulletin* 10. Technical treatise on this subject, with tables and specifications. 24 pp. $7^3/_4 \times 10^3/_4$ in. The Dorr Co., 247 Park Ave., New York, N. Y.

Alcohol for Industrial Purposes. Booklet of formulas and specifications, in accordance with regulations of The U. S. Internal Revenue Bureau. 32 pp. 4×9 in. U. S. Industrial Alcohol Co., 110 East 42nd St., New York, N. Y.

Apparatus for Industrial and Laboratory Use. *Catalog C*, 1923. 112 pp. $7^3/_4 \times 10^1/_2$ in. Palo Co., 153 West 23rd St., New York, N. Y.

Ballard-Sprague Construction Service. Bulletin featuring boiler settings and chimneys in various types of plants. Some typical installations illustrated. 20 pp. $6 \times 9^1/_4$ in. Ballard-Sprague & Co., 200 Fifth Ave., New York, N. Y.

Brownell Tubular Boilers. *Bulletin* B-1, covering this equipment, with illustrations, diagrams, and technical information. 20 pp. $8^1/_2 \times 10^1/_2$ in. The Brownell Co., Dayton, Ohio.

Calorimeters and Accessories. *Catalog* D. Illustrating and describing Parr calorimeters. 38 pp. 5×7 in. Standard Calorimeter Co., East Moline, Ill.

Cambridge Instruments for the Power Plant. *List No.* 906, featuring with illustrations, descriptions, and technical data, electrical CO_2 apparatus, thermometers, gages, recorders, etc. 28 pp. $8^1/_2 \times 11$ in. The Cambridge & Paul Instrument Company of America, Inc., 3512 Grand Central Terminal, New York, N. Y.

Cast Iron Pipe for Industrial Service. Pamphlet illustrating piping installations, with history and data on pipe joints. 24 pp. 6×9 in. U. S. Cast Iron Pipe & Foundry Co., Burlington, N. J.

Chemical Stoneware. Set of bulletins in loose-leaf binder, illustrating and describing this equipment. Price lists included. $8^1/_2 \times 11$ in. General Ceramics Co., 50 Church St., New York, N. Y.

Commercial Furfural—Its Properties and Uses. Technical treatise on this subject covering developments to date. 28 pp. 6×9 in. The Miner Laboratories, 9 So. Clinton St., Chicago, Ill.

Drying Machinery for Electrical and Special Porcelain. Catalog showing applications of these dryers in the production of porcelain, with illustrations of processes. 24 pp. $8 \times 10^1/_4$ in. Proctor & Schwartz, Inc., 7th St. and Tabor Road, Philadelphia, Pa.

Endocrines, Enzymes, and Protein Compounds. Technical treatise on this subject, valuable to manufacturing chemists. Indexed. 95 pp. $3^3/_4 \times 7$ in. Digestive Ferments Co., Detroit, Mich.

Feeders, Sifters, and Mixers. *Catalog* 14, with illustrations and prices. 40 pp. 6×9 in. The Gedge-Gray Co., Lockland, Ohio.

Fitchburg Engines. Brochure giving interesting and instructive information on this equipment. Illustrations, diagrams, and tables. 40 pp. $9^1/_4 \times 7$ in. Fitchburg Steam Engine Co., Fitchburg, Mass.

Freas Apparatus. Illustrated catalog containing specifications and full description of electric constant-temperature ovens, sterilizers, water mixers, and other scientifically constructed apparatus. Price list. 28 pp. $5^1/_2 \times 8^1/_4$ in. The Thermo Electric Instrument Co., 8 Johnson St., Newark, N. J.

Judelson Evapo-Dryers. Catalog showing installations, diagrams, and tables. 16 pp. 9×12 in. Judelson Evapo-Dryer Corp., 224 West 26th St., New York, N. Y.

Ingersoll-Rand Equipment. Series of bulletins in cloth loose-leaf binder fully illustrating and describing various compressors, pumps, condensors, etc. Diagrams, tables, and other interesting and useful data. Marginal index. $6^3/_4 \times 9^1/_4$ in. Ingersoll-Rand Co., 11 Broadway, New York, N. Y.

Knight-Merco Valve Leaflet. Describing in detail a new creation in the chemical stoneware line—a valve or faucet with a lubricated plug, which cannot stick or leak. 6 pp. $8^1/_2 \times 11$ in. Maurice A. Knight, Kelly Ave., East Akron, Ohio.

Locomotives for Industrial and Contractors' Service. *Record No.* 86, fully describing and illustrating steam and internal combustion locomotives. 53 pp. 9×6 in. The Baldwin Locomotive Works, Broad and Spring Garden Sts., Philadelphia, Pa.

Louden Overhead Carrying System. *Catalog* 6, featuring, with illustrations, descriptions, diagrams, and charts, suitable systems for factories, foundries, machine shops, etc. 64 pp. $7^3/_4 \times 11$ in. The Louden Machinery Co., Fairfield, Ia.

Page Water Tube Boilers. Brochure giving interesting and instructive information on boiler installations for various purposes. Illustrations and diagrams. Of interest to those concerned with economical steam production. 38 pp. $8^1/_2 \times 11$ in. Page Boiler Co., 817 Larrabee St., Chicago, Ill.

Photomicrographic Equipment and Micro Projectors. Catalog with price list. 56 pp. $6^1/_2 \times 9^3/_4$ in. Bausch & Lomb Optical Co., Rochester, N. Y.

Platinum. A general catalog covering all forms of platinum ware and supplies. 32 pp. $8^3/_4 \times 10^1/_4$ in. Loose-leaf binder. American Platinum Works, New Jersey R. R. Ave. at Oliver St., Newark, N. J.

Polyphase Motors. *Bulletin* 30. Illustrations and descriptions of special construction. 16 pp. $6 \times 9^1/_4$ in. Century Electric Co., 1827 Pine St., St. Louis, Mo.

Power Transmission Machinery. *Catalog* 11, featuring complete line for belt, rope, and gear drive. Fully illustrated, diagrams, tables, and many technical data. 224 pp. Cloth. $6^1/_4 \times 9^1/_4$ in. The Hill Clutch Co., Cleveland, Ohio.

Pyrex Industrial Ware. Booklet giving technical information and tables in regard to the recent development of this material for industrial uses. 12 pp. 6×9 in. Corning Glass Works, Corning, N. Y.

Recording Apparatus. Series of bulletins in loose-leaf binder, covering the various types of instruments manufactured by this firm. $8^3/_4 \times 11$ in. The Foxboro Co., Inc., Foxboro, Mass.

Recording Thermometers. *Catalog* 905-A illustrates and describes the Tag Recording and Dial Indicating Thermometer. Includes specifications and prices. 20 pp. $4 \times 8^1/_2$ in. C. J. Tagliabue Mfg. Co., 18 Thirty-third St., Brooklyn, N. Y.

Redwood Construction Digest. 1923 edition. A treatise on the values and uses of Redwood and its adaption to current design and practice in buildings. 16 pp. $8^1/_2 \times 11^1/_4$ in. The Pacific Lumber Co., McCormick Bldg., Chicago, Ill.

Refining Cracked Distillates vs. Light Oils. Research bulletin on this subject, with tables. 16 pp. 6×9 in. Research Laboratories, Universal Oil Products Co., 208 So. LaSalle St., Chicago, Ill.

Resistance Machinery Equipment. *Catalog* 40, covering resistance standards, resistance boxes, and measuring instruments. 28 pp. $7^3/_4 \times 10^1/_2$ in. Leeds & Northrup Co., 4901 Stenton Ave., Philadelphia, Pa.

R-K Draft Regulation. Interesting technical treatise on this subject accompanying *Catalog* A, illustrated and descriptive of regulating apparatus for the control and air supply to the boiler furnace. 28 pp. 6×9 in. Ruggles-Klingemann Mfg. Co., Salem, Mass.

Scientific Apparatus, Refractories and Chemicals. *Catalog* 10. Illustrated with specifications and prices. 602 pp. Cloth. $8 \times 11^3/_4$ in. The Denver Fire Clay Co., 1742 Champa St., Denver, Colo.

Sharples Laboratory Super Centrifuge. General catalog with description and illustrations of this apparatus for laboratory uses. 32 pp. $8^1/_2 \times 11^1/_4$ in. Sharples Specialty Co., 23rd and Westmoreland Sts., Philadelphia, Pa.

Storing and Cataloging. Booklet illustrating and describing special equipment for storing and cataloging laboratory stock of chemicals, reagents, samples, and specimens. 16 pp. 8×11 in. Schwartz Sectional System, 312 So. New Jersey St., Indianapolis, Ind.

Swenson Evaporators. *Bulletin* E-122, containing illustrations and descriptions of standard types, their uses and applications. 16 pp. $8^1/_2 \times 11$ in. Swenson Evaporator Co., Harvey, Ill.

Strom Bearings. *Bulletin* 1, in loose-leaf binder. Technical treatise on the subject of ball bearings, giving formulas and calculations for determining loads on ball bearings resulting from various types of power-transmitting elements. Diagrams and technical data. 58 pp. $4^1/_4 \times 7^1/_2$ in. U. S. Ball Bearing Mfg. Co., 4858 Palmer St., Chicago, Ill.

Sullivan Air Compressors. *Bulletin* 77-B, covering various types of equipment with complete descriptions and illustrations. 32 pp. 6×9 in. Sullivan Machinery Co., 122 So. Michigan Ave., Chicago, Ill.

Technical and Industrial Platinum. Treatise on platinum with catalog section of illustrations, tables, and other data of value. 70 pp. $5^1/_2 \times 8^1/_2$ in. Bishop & Co. Platinum Works, Malvern, Pa.

The Thickness of Wet Paint Films. Research bulletin covering this topic, with diagrams and tables. 12 pp. 6×9 in. The New Jersey Zinc Co., 160 Front St., New York, N. Y.

York Self-Contained Refrigerating Units. *Bulletin* 70. Contains illustrations and descriptions of these units and their uses and applications in various fields. 6 pp. $8^1/_2 \times 11$ in. York Manufacturing Co., York, Pa.

MARKET REPORT—FEBRUARY, 1924

[Supplied by Drug & Chemical Markets]

THE volume of chemical business during February, except on contract shipments direct from plants, was not up to expectations. Sales from spot stocks were not only restricted to small quantities for immediate consumption, but a short month, marked by several holidays, tended further to reduce the movement of chemicals. The whole month was one series of price changes after another. The tendency was mixed, with the declines having a slight predominance. Movements in some groups showed sharp rebounds from levels below production costs, while others, especially lead and tin salts, continued an upward trend started last month. Some products, particularly where foreign competition is still a factor, eased off steadily during the period.

Bleaching powder and chlorine have recovered much strength since the first of the year and another advance of 25 cents per hundred in bleach and a half cent per pound in chlorine has been announced. Alkalies have remained steady, though new orders have not been forthcoming since the annual contract business was placed at the close of 1923. Deliveries are reported in good volume, however. Mineral acids, especially in small quantities, are slightly higher, while tank car business is passing at slightly lower levels. Manufacturers of acetone announced two reductions within about two weeks. Carbon tetrachloride is selling lower owing to keen competition. Oxalic acid is also subject to competition and prices have fallen below 11 cents a pound in some cases. Formic acid has been difficult to obtain and prices for this material have advanced. Citric and tartaric acids are easier. Formaldehyde stocks have been reduced and makers are now asking higher prices. Potassium permanganate has been selling below 14 cents a pound, owing to competition between the domestic manufacturer and importers.

Arsenic has failed to show any signs of activity during the month. The season for the manufacture of calcium arsenate is now at hand, but consumers have not yet shown enough interest in calcium arsenate to warrant manufacturers to continue producing and several have already stopped production. Arsenic has declined slightly, prices are generally quoted at $12^1/_4$ to $12^3/_4$ cents a pound, though distressed lots have sold under 12 cents. Calcium arsenate prices have been holding around $11^1/_2$ cents a pound for immediate delivery and up to 13 cents for later shipment. Copper sulfate has been in demand from agricultural sections for spring delivery. Prices are still at low levels, $4^1/_2$ to $4^3/_4$ cents a pound, but the recovery of copper prices this month may strengthen the blue stone prices. Ammonium sulfate demand has increased in the South and prices are somewhat firmer. Sodium nitrate is slightly on increased demand. Phosphate rock prices have been reduced.

Metal prices have been advancing during the month, tin showing the most important increase with 7 cents a pound. All tin products, oxide, crystals, and salts have advanced with the rise in metal prices. After a long dormant period, copper advanced sharply from $12^3/_4$ cents a pound to $13^1/_2$ cents a pound. Lead and zinc advanced $5.00 a ton followed by advances in lead acetate, carbonate, and oxide. Mercury declined, but recovered quickly to its former prices of $60.00 a flask. Sodium bichromate has strengthened and makers are quoting higher prices at $7^1/_2$ cents a pound. Potassium bichromate is also higher. Sodium cyanide is lower. Sodium acetate is firmer. Sodium prussiate is unchanged but firmer. Domestic material is now competing strongly with the lower priced imported prussiate. Potassium prussiate is lower at $19^1/_2$ cents a pound. Domestic caustic potash is lower while imported is fairly steady. Sal ammoniac is scarce, but prices are unchanged owing to lessened demand. Sodium hyposulfite is stronger. Salt cake supplies are more plentiful and prices are much easier.

Following the recent advances in gasoline, in competition with which it is sold, benzene has again advanced. Toluene, solvent naphtha, and xylenes are all higher. Demand has been excellent and producers have been hard pushed in some cases to make deliveries. Phenol scarcity has become more pronounced, and consumers are having considerable difficulty in obtaining their requirements. Producers are sold well ahead and the only materials available are odd lots in the open market. Prices have not responded appreciably owing to cautious buying on the part of consumers. Sales have been reported generally at $36^1/_2$ and 37 cents a pound. Naphthalene demand for spring delivery has been good, while prices are remaining steady at low levels. Supplies appear plentiful this year and the 9-cent price of last year is unlikely. Cresylic acid is more plentiful and prices are generally lower around 70 cents a gallon. Intermediates have been more or less routine, with here and there a gradual decline to lower levels owing to the dull demand. Gamma and H acids are lower. Dimethylaniline is easier. Diethylaniline is higher owing to a temporary scarcity. Anthraquinone is higher. *P*-nitraniline is lower. Resale salicylic acid is cheaper at 35 cents a pound.

Cottonseed oil has been weak owing to a lack of demand and liquidation of stocks. Linseed oil has been advancing steadily owing to the scarcity of seed in the eastern market. Raw oil in carlots is named at 94 cents a gallon.

INDUSTRIAL CHEMICAL PRICES
Average Price Per Hundred Pounds of
Twenty Representative Heavy Chemicals

Courtesy of Drug & Chemical Markets
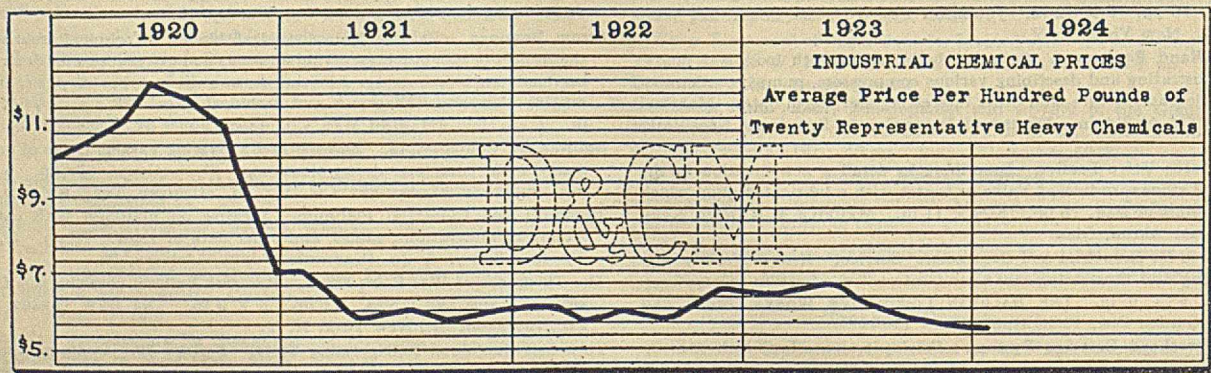
FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

INORGANIC CHEMICALS

	Feb. 1	Feb. 15	Jan. 1924
Acid, Boric, cryst. bbls......lb.	.11	.11	.11
Hydrochloric,comm'l. 20° lb.	.01¼	.01¼	.01¼
Hydrofluoric, 30% bbls...lb.	.07	.07	.07
Hydriodic, 10% U. S. P...lb.	.73	.73	.73
Nitric, 42°, cbys. c/1 wks.lb.	.06½	.06½	.06½
Phosphoric, 50% tech....lb.	.08	.08	.08
Sulfuric, C. P.............lb.	.09	.09	.09
66° tks. wks.......ton	15.00	15.00	15.00
Oleum, 20%........ton	18.00	8.00	18.00
Alum, Ammonia, lump......lb.	.03½	.03½	.03½
Potash, lump..........lb.	*.02⅞	*.02⅞	*.03
Chrome..........lb.	.05½	.05½	.05½
Soda, ground........lb.	.04	.04	.04
Aluminum Sulfate (iron-free).lb.	.02½	.02½	.02½
Ammonium Carbonate, pwd..lb.	.10½	.10½	.10½
Chloride, white gran....lb.	.07½	.07½	.07½
Ammonia, anhydrous......lb.	.30	.30	.30
Ammonia Water, drums, 26°.lb.	.06¾	.06¾	.07½
Arsenic, white.............lb.	.12¾	.12½	.13¼
Barium Choride.........ton	*82.50	*82.50	*85.00
Nitrate..............lb.	*.08½	*.08½	*.08½
Barytes, white.........ton	33.50	33.50	33.50
Bleaching Powd., 35%, works			
..............100 lbs.	1.50	1.75	1.25
Borax, cryst., bbls..........lb.	.05¾	.05¾	.05¾
Bromine, pure, wks........lb.	.29	.29	.29
Calcium Chloride, fused, f.o.b.			
N. Y................ton	24.30	24.30	24.30
Chlorine, liquid............lb.	.04½	.04½	.04½
Copper Sulfate........100 lbs.	4.55	4.55	4.65
Iodine, resublimed..........lb.	4.55	4.55	4.55
Lead Acetate, white crystals..lb.	.14¼	.14¼	.14
Nitrate...............lb.	.12	.12	.12
Red............100 lbs.	11.65	11.65	11.40
White (Carb.).........lb.	.10	.10	.09¾
Lime, live and hydrated, bbl..lb.	.01½	.01½	.01½
Oyster shell...........lb.	.03½	.03½	.03½
Lime Acetate.........100 lbs.	4.00	4.00	4.00
Magnesium Carbonate, tech..lb.	.08	.08	.08
Magnesite, calcined........ton	55.00	55.00	55.00
Phosphorus, yellow........lb.	.35	.35	.35
Red..............lb.	.75	.75	*.75
Plaster of Paris, tech ....bbl.	3.30	3.30	3.30
Potassium Bichromate......lb.	.09⅝	.09⅝	.09½
Bromide, imported......lb.	.17	*.17	.17
Carbonate, calc.,80–85%.lb.	*.05¼	*.05¼	*.06
Chlorate, cryst.........lb.	*.07½	*.07½	*.07½
Hydroxide, 88–92%....lb.	*.06½	*.06½	*.06¾
Iodide, bulk, U. S. P....lb.	3.75	3.75	3.75
Nitrate.............lb.	.06½	.06½	.06½
Permanganate, U. S. P...lb.	*.13¾	*.13¾	*.14
Prussiate, red..........lb.	*.40	*.40	*.42
Yellow.............lb.	*.20	*.19½	*.22
Salt Cake, bulk.........ton	22.00	22.00	24.00
Silver Nitrate.............oz.	.44	.44	.44
Soda Ash, 58%, bags....100 lbs.	*1.94	*1.94	*1.94
Caustic, 76%, N. Y. 100 lbs.	3.66	3.66	3.66

	Feb. 1	Feb. 15	Jan. 1924
Sodium Acetate............lb.	.05	.05	.05
Bicarbonate....... 100 lbs.	2.25	2.25	2.25
Bichromate........lb.	.07¼	.07½	.07⅜
Bisulfite, powd.......lb.	.04½	.04½	.04½
Chlorate..............lb.	.06½	.06½	.06½
Cyanide, 96–98%......lb.	.22	.22	.23
Fluoride, tech........lb.	.09	.09	.09
Hyposulfite, bbls... 100 lbs.	2.75	2.75	2.75
Nitrate, 95%..... 100 lbs.	2.50	2.50	2.52
Nitrite..............lb.	.08¼	.08¼	.08½
Prussiate, yellow........lb.	.11½	.11½	.11½
Phosphate (di-sod.), tech.lb.	.03½	.03½	.03½
Silicate, 40°.......100 lbs.	.80	.80	.80
Sulfide, 60%, fused....lb.	.04	.04	.04
Strontium Nitrate...........lb.	*.12	*.12	*.12
Sulfur, flowers.........100 lbs.	3.00	3.00	3.00
Crude, mines......long ton	14.00	14.00	14.00
Tin Bichloride, 50% sol'n....lb.	.14	.14	.13½
Oxide.................lb.	.53	.53	.51
Zinc Chloride, U. S. P.......lb.	.20	.20	.25
Oxide, bbls............lb.	.08⅛	.08⅛	.08⅛

ORGANIC CHEMICALS

	Feb. 1	Feb. 15	Jan. 1924
Acetanilide, U. S. P., bbls....lb.	.32	.32	.32
Acid, Acetic, 28 p. c.... 100 lbs.	3.38	3.38	3.38
Glacial ....100 lbs.	12.78	12.78	12.78
Benzoic, U. S. P.........lb.	.72	.72	.72
Carbolic, cryst., U. S. P.,			
drums............lb.	.30	.30	.30
50- to 110-lb. tins...lb.	.32	.32	.32
Citric, crystals, kegs.....lb.	*.48	*.48	*.48
Oxalic, cryst., bbls., wks.lb.	.11½	.11	.12
Pyrogallic, resublimed...lb.	1.50	1.50	1.55
Salicylic, U. S. P........lb.	.35	.35	.35
Tannic, U. S. P., bbls....lb.	.83	.83	.83
Tartaric, cryst., U. S. P...lb.	*.28	*.28	*.31
Acetone, drums.............lb.	.21	.19	.25
Alcohol,denatured, complete. gal.	.48	.48	.48
Ethyl, 190 proof, bbls...gal.	4.83	4.83	4.83
Amyl Acetate.............gal.	4.65	4.65	4.65
Camphor, Jap, refined, cases .lb.	.79	.79	.87
Carbon Bisulfide, c/1........lb.	.06	.06	.06
Tetrachloride........lb.	.08½	.08½	.10½
Chloroform, U. S. P., drums..lb.	.35	.35	.35
Creosote, U. S. P...........lb.	.45	.45	.40
Cresol, U. S. P.............lb.	.23	.23	.25
Dextrin, corn..........100 lbs.	3.59	3.59	3.64
Imported Potato........lb.	.07½	.07½	.07½
Ether, U. S. P., 100 lbs.......lb.	.13	.13	.13
Formaldehyde, bbls.........lb.	.11	.11	.10¾
Glycerol, dynamite, drums...lb.	.15	.15	.16½
Methanol, pure, drums......gal.	.92	.92	.92
Methylene Blue, med........lb.	2.25	2.25	2.25
Petrolatum, light amber......lb.	.04½	.04½	.04½
Pyridine ....gal.	3.25	3.25	3.75
Starch, corn, pow'd.....100 lbs.	3.17	3.17	3.22
Potato, Jap.............lb.	.06	.06	.06
Sago.................lb.	.05	.05	.05

* Resale or Imported (not an American maker's price).

MEDICINAL CHEMICAL PRICES
Average Price of Twenty representative Fine Chemicals
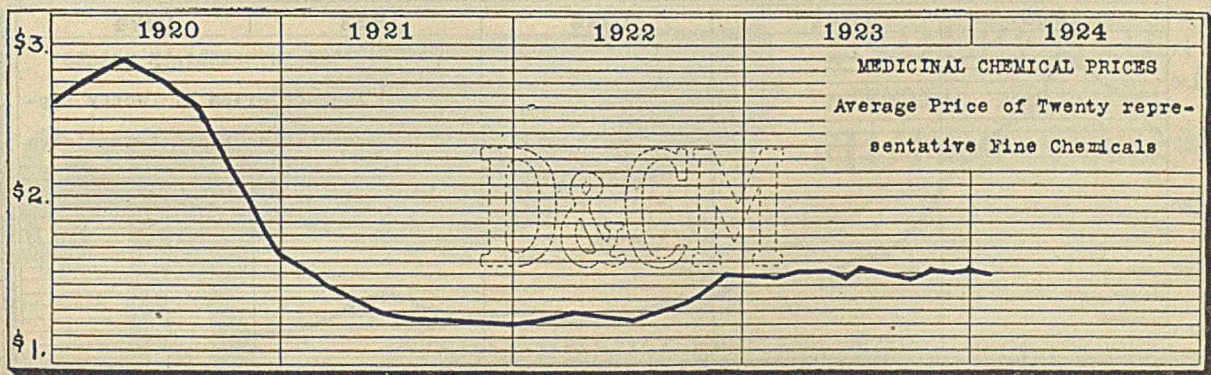
OILS, WAXES, ETC.

	Feb. 1	Feb. 15	Jan. 1924
Beeswax, pure, white.........lb.	.36	.36	.36
Castor Oil, No. 3.............lb.	.15	.15½	.14
Ceresin, yellow..............lb.	.08	.08	.08
Corn Oil, crude, tanks, mills...lb.	.09¾	.09⅝	.10
Cottonseed Oil, crude, f. o. b. mill.....................lb.	.09	.08½	.09½
Linseed Oil, raw, lc/l........gal.	.92	.94	.90
Menhaden Oil, crude, mills...gal.	—	—	.50
Neat's-foot Oil, 20°..........lb.	.17¼	.17	.17½
Paraffin, 128–130 m. p., ref....lb.	.04	.04	.04
Rosin, "F" grade, 280 lbs....bbl.	5.75	5.85	5.80
Rosin Oil, first run..........lb.	.43	.43	.43
Shellac, T. N................lb.	.60	.60	.63
Sperm Oil, bleached winter, 38°....................gal.	.84	.84	.84
Stearic Acid, double pressed...lb.	.12¼	.12¼	.12
Tallow Oil, acidless..........lb.	.10	.10	.10
Turpentine, spirits of........gal.	.94	1.00	.94

METALS

Aluminium, No. 1, ingots.....lb.	.28	.28	.28
Antimony, ordinary......100 lbs.	10.25	10.75	10.00
Bismuth....................lb.	2.75	2.75	2.75
Copper, electrolytic..........lb.	.12¾	.13½	.13
Lake..............lb.	.12¾	.13½	.13
Lead, N. Y............100 lbs.	8.30	8.50	8.00
Nickel, electrolytic..........lb.	.29	.29	.29
Platinum, refined, soft.......oz.	122.00	122.00	122.00
Quicksilver, flask......75 lbs. ea.	60.00	60.00	60.00
Silver, foreign...............oz.	.64¼	.64⅝	.64¾
Tin.......................lb.	.50	.51½	.47
Tungsten Wolframite....per unit	8.50	8.50	8.50
Zinc, N. Y.............100 lbs.	7.00	7.30	6.70

FERTILIZER MATERIALS

Ammonium Sulfate, expt.100 lbs.	2.90	2.90	2.75
Blood, dried, f. o. b. N. Y...unit	4.15	4.15	4.30
Bone, 3 and 50, ground, raw..ton	25.00	25.00	25.00
Calcium Cyanamide, unit of ammonia..................	2.25	2.25	2.25
Fish Scrap, dried, wks.......unit	4.90	5.00	4.75 & .10
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68%.....ton	3.25	2.25	3.25
Florida, 70%........ton	3.55	2.50	3.55
Florida, 74–75%........ton	4.50	3.75	4.50
Tennessee, 72%........ton	5.50	5.50	5.50
Potassium Muriate, 80%....unit	.68	.68	.68
Tankage, high-grade, f. o. b. Chicago..............unit	3.70 & .10	3.65 & .10	3.65 & .10

COAL-TAR CHEMICALS

Crudes

Anthracene, 80–85%.........lb.	.75	.75	.75
Benzene, pure, tanks.......gal.	.23	.25	.20
Naphthalene, flake..........lb.	.06½	.06½	.06½
Phenol, drums..............lb.	.36	.37	.30

	Feb. 1	Feb. 15	Jan. 1924
Crudes *(concluded)*			
Toluene, pure, tanks........gal.	.24	.26	.22
Xylene, 2 deg. dist. range, drums................gal.	.45	.50	.50
Intermediates			
Acids:			
Anthranilic..............lb.	.96	.96	.96
Benzoic, tech...........lb.	.70	.70	.70
Cleve's...............lb.	1.00	1.00	1.00
Gamma...............lb.	1.65	1.50	1.65
H...................lb.	.75	.72	.75
Metanilic.............lb.	.60	.60	.60
Monosulfonic F.........lb.	2.30	2.30	2.30
Naphthionic, crude......lb.	.62	.62	.62
Nevile & Winther's......lb.	1.10	1.15	1.10
Picric...............lb.	.25	.25	.25
Sulfanilic.............lb.	.20	.20	.20
Tobias'..............lb.	1.00	1.00	1.00
Aminoazobenzene..........lb.	1.15	1.15	1.15
Aniline Oil................lb.	.16½	.16½	.16½
Aniline Salt...............lb.	.24	.24	.24
Anthraquinone (sublimed).....lb.	1.00	1.15	1.00
Benzaldehyde, tech..........lb.	.75	.75	.75
U. S. P.............lb.	1.50	1.50	1.50
Benzidine Base............lb.	.82	.82	.82
Benzidine Sulfate..........lb.	.70	.70	.70
Diaminophenol............lb.	3.80	3.80	3.80
Dianisidine...............lb.	4.60	4.60	4.60
p-Dichlorobenzene..........lb.	.17	.17	.17
Diethylaniline.............lb.	.55	.55	.50
Dimethylaniline............lb.	.39	.37	.39
Dinitrobenzene............lb.	.19	.19	.19
Dinitrotoluene............lb.	.19	.19	.19
Diphenylamine............lb.	.48	.48	.48
G Salt...................lb.	.55	.55	.55
Hydroquinol..............lb.	1.40	1.40	1.40
Monochlorobenzene.........lb.	.10	.10	.10
Monoethylaniline..........lb.	1.00	1.00	1.00
b-Naphthol, dist...........lb.	.26	.26	.26
a-Naphthylamine..........lb.	.35	.35	.35
b-Naphthylamine..........lb.	.76	.76	.76
m-Nitroaniline.............lb.	.78	.78	.78
p-Nitroaniline.............lb.	.72	.70	.74
Nitrobenzene (Oil Mirbane)...lb.	.10	.10	.10
p-Nitrophenol.............lb.	.75	.75	.75
o-Nitrotoluene............lb.	.10	.10	.10
p-Nitrotoluene............lb.	.55	.55	.55
m-Phenylenediamine.........lb.	.96	.96	.96
p-Phenylenediamine.........lb.	1.45	1.45	1.45
Phthalic Anhydride.........lb.	.25	.30	.25
R Salt..................lb.	.55	.55	.55
Resorcinol, tech...........lb.	1.40	1.40	1.40
U. S. P.............lb.	2.25	2.25	2.25
Schaeffer's Salt............lb.	.60	.60	.60
Sodium Naphthionate........lb.	.62	.62	.62
Thiocarbanilide............lb.	.30	.30	.30
Tolidine (base)............lb.	.95	.95	.95
Toluidine, mixed...........lb.	.31	.31	.31
o-Toluidine..............lb.	.14	.14	.14
p-Toluidine..............lb.	.85	.85	.85
m-Toluylenediamine.........lb.	.90	.90	.88
Xylidine.................lb.	.50	.50	.50

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