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EDITORIALS

Pull Together

The JOURNAL now enters a new era of opportunities and responsibilities. For a time at least, while chemical and general industry remains stationary, there is likely to be less development of facilities for industrial research than can be considered desirable or perhaps necessary in view of all the facts. With the compelling force of war removed it will be more necessary than ever to keep in view the future of chemical industry in America and to use all the great influence of our SOCIETY and JOURNAL to the end that necessary research and cordial governmental coöperation with chemical industries essential to both peace and defense be not relinquished. That Mr. Howe, our new editor, with the aid and backing of the SOCIETY, can and will carry out to its completion the program of work already so ably begun is assured. In accomplishing his task he has the cordial good wishes of all of us. W. D. RICHARDSON

What of Chemical Industry?

The tide of the great war was turned the day that necessity drove the Allies to coördinated effort, and forced upon them a policy of coöperation under a single commander with full power. A machine without coördination of moving parts is junk; a business enterprise not well coördinated is advancing to meet the sheriff, and a regiment of men not trained in coördination of action is simply a mob; yet it took the allied nations three years' time and a near-defeat to see that national and world problems are governed by simple home-known rules.

American Chemical Industry is being hard pressed these days. Foreign competition, tariff delay, governmental regulation, labor, freight and fuel costs, foreign exchange, all seem to be wonderfully organized and perfectly coördinated under the unified command of General Business Depression, with headquarters somewhere in the U. S. A. American Chemical Industry has lost much ground in the fight against the General and the divisions he has marshaled with such uncanny skill, largely because they have not seen the light of full and complete coördination of effort even as the Allies did.

Is it not about time for American Chemical Industry to lay aside localisms, party politics, commercial smoke screens or whatever it is that stands in the way, and come out in the open, as the Allies finally had to do, consolidate the whole interest into a common battle line, unify the command, appoint a Commander-in-Chief with power, and settle the question here and now in 1922, as to whether or not we are going to have a real American Chemical Industry? M. C. WHITAKER

Stand behind the Editor

With this issue, a new hand guides the policies of THIS JOURNAL. Upon the shoulders of the Editor falls the responsibility for reflecting the sentiment of the more than 15,000 members of the AMERICAN CHEMICAL SOCIETY. His is the voice which speaks the opinion of the chemists of this country, whether it pertain to matters of professional interest, to the country's economic and industrial welfare, or to patriotic response to the Nation's need. There is no way by which the Editor can better feel the pulse of the SOCIETY than by direct communication with its members, individually or through the collective groups in the Local Sections. Write to the Editor with every constructive suggestion you can offer for the improvement of THIS JOURNAL. Such letters have come to the Editor's desk all too seldom. Again, the readers make the atmosphere which leads firms to seek the advertising pages. Mention THIS JOURNAL when corresponding with advertisers, present or prospective.

It is a physical impossibility for the Editor personally to cover all fields necessary to keep the pages alive and up-to-date. Individual members can be of great assistance to the Editor in locating hidden mines of information. It is to be hoped the day will soon arrive when the SOCIETY's financial condition will justify the addition to the editorial staff of an adequate field force.

Speaking out of the abundance of five years' experience, I would urge that the members of the SOCIETY, individually and collectively, stand dynamically behind the incoming Editor. Energetic coöperation will make THIS JOURNAL hum. CHAS. H. HERTY

Howdy

Fellow chemist, please meet the new Editor! And before you read further turn back to page 2 of THIS JOURNAL for 1917 and look again at Dr. Herty's "By Way of Introduction." He has come near his mark. May we come as near ours.

We conceive our work to be that of helping to advance technical chemistry, to aid chemical industry and all industry by espousing the cause of scientific and industrial research (if there is a difference), and to create a proper appreciation and understanding of chemistry among our nonchemical people. We must keep in mind the average man, whether it be in the articles we accept or any work performed. We must never forget that progress depends upon fundamental research and that it is from industry that we derive support vital for such research. To coöperation we must add correlation and coördination.

While we have been reminded that we have more than 15,000 bosses who cannot be pleased simultaneously, we prefer to count on more than 15,000 helpers. We are stockholders together in this enterprise. This is *Your* journal. The Editor wants your frank opinion, suggestive or unfavorable, as it may be. We hope to hear policies and needs discussed in various Local Sections as was so successfully done by the New York Section December 9.

We chemists still have a deal of work to do. We can do it together. Let's go.

The Staff

The Directors have been able to appropriate a modest sum for an Associate Editor who is to be appointed. His headquarters will be in New York City, and he will devote himself to plant and field in an effort to build up the technological side of the JOURNAL. This addition to the staff has long been desired and is sure to add strength. The Assistant to the Editor, Miss N. A. Parkinson, is thoroughly experienced, and comes to us from the *Journal of the Association of Official Agricultural Chemists*, where she has been Associate Editor. Miss Thomas, Miss Reynolds, and Miss Gordon will continue their valuable work.

The new headquarters will be 810 Eighteenth Street, N. W., Washington, D. C. Here we shall be easily accessible by whatever route you travel in the city.

"Come in, rain or shine."

Appreciation and a Wish

It is really remarkable how our Society has grown and how it has become a potent factor in everyday life.

In quietly going over its several publications evidence appears that it is interested not only in pure science, but in the application of the principles of the science to all industries dependent upon such principles.

One must feel proud of the splendid contributions which fill the pages of the *Journal of the American Chemical Society*, and one must also recognize the worth-while things appearing in the *Journal of Industrial and Engineering Chemistry*. The contributions to the latter Journal are most helpful to the great rank and file of American chemists, who are giving, in a very unselfish way, their best efforts to the establishment of industries in the home land, a goal to which American chemists have aspired since the founding of the Republic.

> *This people of Washington and Lincoln are conquering the difficult problems of to-day, no less worthily, and with the faith and confidence which they bequeathed to us. We are sure to find the ways to restored prosperity and our meed of happiness.*—Warren G. Harding.
>
> ◆
>
> The above message is the first ever signed by a President of the United States for billboard purposes. It is being used in a prosperity campaign by the International Association of Rotary Clubs.

Again, *Chemical Abstracts* must appeal to every member of the Society. It has meant very much to me in my own work. It has directed me to hundreds of papers which, perhaps, would have escaped my attention, or which I would have discovered only after long, tedious search.

One of the happiest moments I have had during the past year was when it was determined to institute a section on Chemical Education. Our teachers deserve the very best that can be provided. Most of them are also investigators, heroically devoting themselves to instilling the principles of chemistry into the minds of vast student bodies destined for future industrial activity. Much of this noble work is being done under most unsatisfactory conditions. The first meeting of teachers of chemistry, in New York last September, showed clearly how eager they were to be of service in this fundamental preparation and to make sacrifice for the best interests of chemistry throughout the land.

I can't refrain from expressing the wish that as all the many interests, represented in the great membership of the Society, are working for the upbuilding of American chemical industries, sight will not be lost of the fact that reciprocity is only fair; and that the industries as they arise, develop, and succeed, shall see to it that ample means are provided for research in pure science, for the erection of laboratories, for the maintenance of a well qualified group of experimenters, and last but not least, for the payment of adequate salaries to our self-sacrificing teachers, that they may be easy in mind and able to throw themselves wholeheartedly into their particular occupation.

There is no reason at all why such should not be the case; and it ought to be our purpose to acquaint our neighbors of the great laity as to what chemical science is, how closely it comes to every man, woman and child of our country, how its pursuit is, in the end, their happiness and comfort, and that they should be supporters and benefactors of a profession of which it is an honor to be a part.

The achievements in publication and in other directions have been due largely to the loyal support given the Society. Continued support may be counted upon to accomplish our future tasks.

Edgar F. Smith

Distinguished Service

Five years ago, on January the first, 1917, Dr. Chas. H. Herty entered upon his duties as editor of This Journal. They have been years of great events in the world at large and years of extraordinary activity in the field of our profession. During all this period of development and stress the *Journal of Industrial and Engineering Chemistry* under Dr. Herty's guidance has faithfully reflected the advances in the applications of chemistry, to industry and warfare, which have so profoundly influenced both. But it has done much more. It has voiced in aggressive and convincing editorials the sound Americanism of the chemists of the country. It has consolidated opinion. It has made clear to all who would read the close relationship between the chemical industries and national prosperity and defense.

To reach a wider audience and extend the influence of the Society Dr. Herty established the News Service, through which, with the cordial coöperation of the press, the notable advances in chemistry have been placed before the public and their bearing upon the affairs of the community made manifest. To this Service the present general recognition of the vital significance of chemical science is largely due.

In pursuance of his clearly defined policy of establishing American chemistry in its true relation to practical affairs, Dr. Herty developed a singular aptitude for the presentation of its claims before Congressional Committees and public bodies. He convinced by the cogency of his facts, persuaded by the charm of his personality, and inspired by the splendid courage of his convictions.

The influence of Dr. Herty as an educator, his efficiency as an administrator when president of the Society, and his distinguished success an an editor were due not only to his chemical scholarship, but in large measure to his exceptional personal quality. He combines the courtesy of the Southern gentleman with the aggressiveness of the crusader. His remarkably wide acquaintance is a working asset of the utmost value, for he has a habit of converting acquaintances to friends.

For many years Dr. Herty has been an outstanding figure in the American Chemical Society. Few, if any, have served it more variously and effectively. He has earned and carries with him to his new environment the gratitude and good wishes of the chemists of America.

A. D. Little

Do You Remember?

It seems only a few days ago that we were being urged to make America independent in essentials and the then Secretary of the Interior was urging men to "rediscover America." Among other things we wanted a potash industry. We wanted it so badly that every source was sought and tried. The Government experimented with kelp, we heard much of feldspar, of greensands, of alunite, of natural lakes, and of California deposits. Progress was made, millions were spent, and some research and chemical engineering of a high order performed. Chemists and investors knew something of the competition to be met when normal times returned, but they counted on Americans meaning what they said when they clamored for a potash industry.

So research was recognized as the key to the situation—purer product at lower cost. In one large plant, if we take the cost per unit of K_2O during the first four months of 1919 as 100 per cent, it was 58.3 per cent for the same period of 1920 and in 1921, 32.6 per cent. Quality was assured. Production ran into thousands of tons although the inspired daily press articles would have you believe there can be no American potash industry. To have a potash industry there must be a market for potash.

Before us is a copy of the contract between "The American Agricultural Chemical Company and others with Deutsches Kalisyndikat, G. m. b. H.," dated September 28, 1921. The full list of buyers who are parties of the second part follows:

The American Agricultural Chemical Company
Virginia-Carolina Chemical Company
International Agricultural Corporation
Armour Fertilizer Works
Swift & Company
F. S. Royster Guano Company
Arkansas Fertilizer Company
Baugh & Sons Company
Berkshire Fertilizer Company
Caraleigh Phosphate & Fertilizer Company
Darling & Company
E. Rauh & Sons Company
Federal Chemical Company
F. W. Tunnell & Company
Georgia Fertilizer & Oil Company
G. Ober & Sons Company
Griffith & Boyd Company
Gulf Fertilizer Company
I. P. Thomas & Son Company
Miller Fertilizer Company
Mutual Fertilizer Company
Olds & Whipple
Piedmont-Mt. Airy Guano Company
Read Phosphate Company
Reliance Fertilizer Company
Richmond Guano Company
Robertson Fertilizer Company, Inc.
Rogers & Hubbard Company
Smith Agricultural Chemical Company
Southern Fertilizer & Chemical Company
W. B. Tilghman Company, Inc.
Wuichet Fertilizer Company
Wilson & Toomer Fertilizer Company
York Chemical Works

These firms agree to purchase at least 75 per cent of their requirements on this contract, this amount, 35,680 tons, being lumped together to obtain extra quantity discounts. The contract is too long to reprint. We quote:

> 1—Such participant shall state in its price lists that Potash can now be had in all required quantities, and that it is advisable to buy mixed goods containing as high a percentage of Potash as is suitable to the respective crops; and
>
> 2—Such participant shall instruct its selling organization and salesmen to sell and recommend mixed goods containing as high a percentage of Potash as is suitable to the respective crops.

Such coöperation is rewarded by an extra discount!

And as for anti-dumping:

> Seller hereby also assumes and agrees to pay any tax or duty affecting deliveries under this contract which may be imposed or assessed by the United States Government under the Anti-Dumping Act of 1921 or any amendment thereto which may be hereafter enacted provided however in case of such amendment Seller shall not be required to pay any tax or duty in excess of amount of tax payable under existing provisions.

Now what of the remaining 25 per cent, an amount which our industry *can* supply? Bids were asked November 14 to be made within a week. November 16, American potash was offered to meet any foreign quotation, even though that meant a loss to the producers. The reply came that if the bid had been made a few days before things might have been different but contracts had already been made with French interests. Do we want an American industry? We would like to know more about the factors at work and whatever other side there may be to this transaction.

Meanwhile research goes forward even though the warehouses are full of American potash which Americans refuse to purchase. Do we want the industry?

Creating Good Will

In the *Journal of Commerce*, New York, issue of December 2, there appears the following paragraph under the caption "A. C. S. Not a Mendicant:"

> It is refreshing to find one organization which can hold its convention and practically pay its own way and which at the same time is willing to do so. The usual thing in conventions is for the committee on arrangements to solicit as much money from the business men of the community as is humanly possible, spend whatever part of it is necessary and talk of refunding the balance pro rata. Somehow these refunds are never made. The recent convention of the American Chemical Society furnished the refreshing contrast to this attitude on the part of societies and organizations in general. Plans were early matured by the committee in charge calling for the payment of as great a proportion of the expenses of the meeting by the members themselves as possible. It was, of course, necessary to do some soliciting of funds. So successful were the efforts of the committee, however, that the society was able to pay approximately 80 per cent of its own expenses. The really remarkable thing, however, was the handling of the surplus. Pro rata return of all funds remaining after the payment of expenses was made to the firms who contributed. About 40 per cent of the solicited funds were returned in this way. Is it any wonder that many cities compete for the honor of the American Chemical Society meeting?

Of course the *Journal* did not appreciate that on several occasions Local Sections of the SOCIETY have been equally successful in managing national conventions. People generally are finding that many chemists are good managers and that when a Section of the SOCIETY undertakes a project of this sort it is put through on a sound business basis.

Who Will Be Next?

In these days when an honest effort is being made to bring about an era of brotherly love, we would like to believe that after all our bitter lessons we have reached a point where there can be straightforward dealing and fair, stimulating competition for such business as the world affords. But we are rudely shaken by the following official report and made to realize anew that "eternal vigilance is the price of safety."

We reproduce the document in its entirety from *Idea Nazionale* of August 28, 1921.

> No. 1784. General Private GERMAN EMBASSY AT ROME
>
> Rome, 25th May 1921
>
> TO THE MINISTER FOR
> FOREIGN AFFAIRS,
> BERLIN.
>
> I reply to the invitation contained in Circular of 13th May to all commercial attachés, to report to your Ministry as to the situation, and our activity and our commercial development abroad, and I have the honor to report as follows:
>
> The figures of German commerce in Italy show that after the Armistice our traders were not inactive in reconquering the Italian market compared with France, England and the United States and maintaining our supremacy, but that does not mean that we have reached the state of your circulars of 20.8.1920 and 29.8.1920.
>
> In order that we may create for ourselves a favorable political situation, taking advantage of the malcontent of the Italian people, and especially of the Nationalist and Nittian parties against the Powers of the Entente, a political situation which might in due course be favorable to us when Germany should be faced by fresh complications, it is necessary to strengthen this discontent in order to consolidate our situation through economic action.
>
> To this end, the point at which we have arrived is only a quarter of the way. We must create such economic interests and bonds with Italy that whatever happens, Italy will have to follow our political lead.
>
> First of all, it is necessary that a systematic supply of German goods be sent here, even below cost price to a considerable extent. Inundating the Italian market with German goods we will not only have a place sympathetic to Germany, because,

as many of our agents and commercial representatives have verified, Italian consumers gladly accept cheap articles, but we will also create a situation for Italian industry which will render any continuation of activity impossible. This without doubt will cause such a crisis that, besides keeping Italy in constant agitation, will enable us to become the sole masters of the Peninsular trade, the more so as, from our information as to French activity in Italy, it appears that the French fear the outbreak of a revolution here which might cause them similar losses to those suffered in Russia.

The enclosed copy of a report by Sir Capel Cure, British Commercial Attaché, proves that the British too fear the unstable nature of the social situation in Italy.

Further, such situation would enable us to purchase the Italian industries at a very low rate, which would be the key of the situation, since it would also allow us to control trade between Italy and the Balkans in such a way that Italy would not compete with us for those markets (see circular 30th October 1920 regarding Italo-Jugo Slav treaty). This, of course, will happen as soon as Italy is forced to close down.

We have before us a varied field of development in Italian industry, *viz.*, trade in rubber, Fiat, Spa, besides all the tire factories and motor car engine factories which are already in a state of acute crisis on account of the huge German stocks of these lines sent to Italy.

The Siemens Schuckert already approached the Turin companies last September when the factories were occupied by the workmen, but without result. On my advice, the Siemens has already arranged for the absorption of the Fiat through a combination Stinnes-Fiat in the Alpinen and through the purchase by the Deutsche Bank, which has an interest in the Siemens, of the shares which are in the hands of the Banca Commerciale Italiana, amounting to 90,000 Alpinen shares and 100,000 Fiat shares, owned by said Bank. The transaction is on the way to completion, and Messrs. Cavallini, Brunicardi, Trombetti, and Dante are backing it, to whom the Siemens will pay a percentage of $4^{1}/_{2}$% as was decided at the meeting held in this Embassy in September last. *Then we have the dyeing trade in Italy*, which, though in a precarious state of development, holds the promise of an assured future. It is, however, necessary that, in order to follow out in this branch too the method of peaceful destruction advised by me, the Italian government should not take precautions to prevent the import of coloring matters from abroad, as otherwise it is certain that the Italian industry which, it appears to me, are seeking American capital to support them, might assume a more solid position in the Peninsula, a position which it would be more difficult to destroy.

I have had a promise from the Italian cotton-spinners of the possibility of action on their part against possible provisions of the Italian government. As authorized by you, for my part I have promised that any such action will be compensated by the despatch of textile machines from Germany at very low prices.

It must not be forgotten, however, that the Italian textile industry too offers a field for economic development for Germany in Italy, whether because they are at present going through a period of crisis, or because they obstruct our path towards the East. I understand that in the economic treaties which Italy is on the point of concluding with Jugo Slavia, she demands that the Jugo Slavs shall acquire 200,000 quintales (2000 tons) of textiles per annum in Italy; and it seems that this proposal has been received with pleasure by the Jugo Slavs, since as a matter of fact the Italian cotton-spinners have known how to penetrate that market. Therefore, if we succeed in absorbing part of the Italian cotton industry (I have already made tentative proposals for the Rossi Cotton Mill and for the Prato factory, but up to the present I have had no result, and the negotiations have been passed on to the Schimmelpfeng Agency and to the office of Consul Oster), we could reduce Italian competition in the Balkans, where we could present our product as being Italian.

Then we have the metallurgical industry in Italy, and this is the most important of all since the development which took place during the war is such, that the matter must be taken into serious consideration.

In this connection I will refer to the matter again, pointing out that our participation in the Piombino establishments is assured. Messrs. Cavallini and Brunicardi are taking charge of the question of the Alti Forni (Smelting furnaces) of Porte Ferraio in the interests of the firm of Krupp. They say that at the present moment the owners could ask 210 million lire, but that if the present crisis continues, even half that sum might be sufficient.

Then we have made an offer for the Electric Railway Workshops of Milan, a combination between the Pirelli and Eradania and with the Cotton Transport Corsorzio which could be absorbed, and offers regarding the fleet of Deutsche-Levant Linie, which could become an Italian Navigation Company.

The most important question is in fact that of the control of Italian fuel, which constitutes the integral part of Italian economic life.

The infiltration of the products of the A. E. G. into Italy has destroyed the industry in electrical materials which it will be easy to absorb, the more so as several members of that industry, indicated in my telegram No. 10878, assured me that in view of the business crisis, those Companies seek to obtain foreign capital.

If we assure a supply of electric material on the Italian market, we could obtain contracts for furnishing electric material for several hydro-electric works in construction, and for the State Railways. But it is necessary for the German Companies to understand the necessity of their branches in Italy remaining under the Italian name.

I have entered into agreement for the conclusion of contracts between the A. E. G. Siemens, and the Societa Adriatica of electricity of the group Velpi-Negri for furnishing of the necessary material into the Veneto, that is to say turbo-alternators, turbines, pipes for the waterfall, and all the material, and the furnishing of the material as capital participation of said company, since these supplies are calculated at a value of over eight million lire.

This regarding white fuel.

Then we have at our disposal the Italian wealth of lignite. The Italians do not know how to get the most out of this, and almost treat it as a thing of little value. On the contrary, it is a matter of 300 million tons of which—as I have already reported sub. n. 178 ND—only 3 million tons per annum are used, whilst 115 million tons per year could be got, as the deposits are estimated to be more than 35 meters deep.

Add that by distillation, a thousand tons of mineral oil could be obtained, since lignite has a percentage of 25% of the components of such oil. The deposits of bituminous schist, valued at 115 million tons with 12 and up to 18 per cent of naphtha are worthy of notice, and these two are in a very slightly developed state, which may be attributed to lack of means on the part of the owners.

The Consortium of Chemical Products of Berlin, the Deutsche Bank, and the Discount Gesellschaft are already in treaty with various Italian groups.

As will be seen from this explanation, there is much to do in Italy, but action must be guided by the following rules in order to avoid clashing with Italian susceptibility.

(1) The Deutsche Italienische Vereinig should be able to continue to bring its influence to bear.

Instructions must be given to the Deutsche Italienische Vereinig so that its bulletins shall be inspired to draw attention to the lack of Italian products in Italy, the damage resulting from such lack, and the attempts at economic penetration on the part of foreign countries. Such criterion must also inspire the newspaper campaign of said organization.

(2) The setting up in Milan too of an information office at the Consulate General for Germany with the aim of following the labor movements in North Italy, and to report to Germany in relation to these movements, the necessity to send German material and products in order to increase the crisis.

(3) As to fuel, it is necessary that after the refusal of the Italians of our offer to collaborate in the development of the lignite mines, and for the supply of the market with fuel against facilities of German property which has been so sequestrated, our action shall be turned towards private individuals.

With respectful regards,

The Commercial Councillor
STROHEKER

Now read it again. Note the plan to prevent the development of a chemical industry, first, by making importation of chemicals easy and, second, by purchasing support for this measure with low priced textile machinery. But those who would thus sell themselves are insecure, for there follows a plan for their own "peaceful destruction." Note also that the report is dated May 25, 1921, and not 1914. With such a spirit abroad in the world can we afford to deprive American industry—chemical and otherwise—of any means for defense? Italy, France, and England have adopted strong measures for their industrial defense. We must guard our own.

ORIGINAL PAPERS

A Chemically Controlled Automobile[1]

By George Granger Brown

Department of Chemical Engineering, University of Michigan, Ann Arbor, Michigan

The impending shortage of motor fuel and petroleum has been brought forcibly to our attention by a large number of writers within the last few months. Careful estimates indicate that we are probably at the peak of petroleum production and that the production of gasoline in the United States will be unable to exceed the demand for more than five or ten years. At the present time gasoline is selling for nearly $2.00 per American gallon on the continent of Europe, and we may expect an early permanent rise in price in this country.

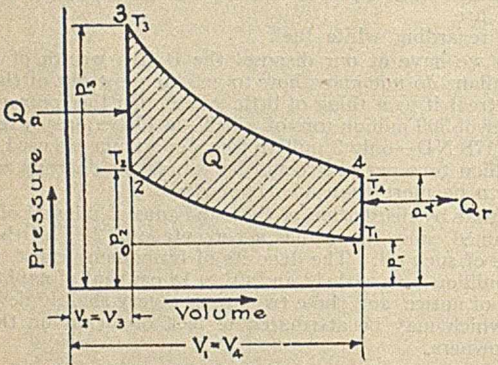

Fig. 1—Ideal Otto Cycle on Pressure-Volume Diagram

It is possible that this shortage may be postponed or temporarily relieved by the development of new sources of raw material, by increasing the yield of oil wells and by more efficient production and handling of gasoline. All these considerations are receiving the attention of chemists and engineers. It is the purpose of this paper to indicate the saving of fuel that may be made by the application of chemical engineering principles to the utilization of gasoline in the automobile engine.

The internal combustion engine, when properly controlled, is a very efficient machine as compared with other prime movers. Its over-all thermal efficiency is then 30 to 35 per cent, but the thermal efficiency of the average automobile is not over 15 per cent. As the Bureau of Mines found that "the combustible gas in the average automobile exhaust from one gallon of gasoline amounts to 30 per cent of the total heat in a gallon of gasoline,"[2] it is evident that the average automobile is wasting in unburned gas alone twice as much energy as it is converting to work.

This loss, entirely preventable by proper control of the mixture, is not only an expensive practice, but a criminal waste of our natural resources. Twenty-five years ago, there were four automobiles in the United States; now there are nine million. Throughout this period fuel has been cheap, and profits large, and the need for carefully controlled combustion has not been felt until very recently. Moreover, the development of the automobile has been essentially mechanical, and naturally the manufacturer has depended almost entirely upon mechanical principles for increased efficiency, overlooking the fact that the combustion of gasoline in an automobile engine is a rather complicated chemical reaction.

Thermal Efficiency

The automobile engine operates on the Otto cycle, shown ideally on the pressure-volume diagram in Fig. 1.[3] The explosive mixture is drawn into the cylinder along the path 0–1. The intake valve closes at 1, and the charge is compressed adiabatically along the path 1–2. It is exploded or burned at constant volume 2–3, giving up the heat of combustion, Q_a, to the products of combustion, which then compose the working mixture instead of the vapor-air mixture. The power stroke (adiabatic expansion) is represented by the path 3–4. The exhaust valve then opens and the gases pass out along 4–1 at constant volume carrying the rejected heat, Q_r, out through the exhaust to the atmosphere. The remaining burned gases are pushed out by the piston along the path 1–0. This completes the cycle, and the heat $Q = Q_a - Q_r$ has been transformed into work represented by the area 1–2–3–4–1. As the efficiency is the ratio of the output over the input:

$$\text{Efficiency} = \frac{Q}{Q_a} = \frac{Q_a - Q_r}{Q_a} = 1 - \frac{Q_r}{Q_a} \qquad (1)$$

$$Q_a = WC_v\ (T_3 - T_2)\ \text{heat added} \qquad (2)$$

$$Q_r = WC_v\ (T_4 - T_1)\ \text{heat rejected} \qquad (3)$$

where W is the weight of charge and C_v the specific heat at constant volume

$$\frac{T_2}{T_3} = \frac{T_1}{T_4} \qquad (4)$$

$$\text{and for adiabatic curves}\ \frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{K-1} \qquad (5)$$

$$\text{Efficiency} = 1 - \left(\frac{V_2}{V_1}\right)^{K-1} \qquad (1a)$$

$$\text{Efficiency} = 1 - \left(\frac{1}{r}\right)^{K-1} \qquad (1b)$$

From thermodynamic reasoning then, the thermal efficiency of the Otto cycle increases with the compression ratio r and with the ratio of specific heats k or $\frac{C_p}{C_v}$. The compression ratio, a mechanical consideration, is fixed by the engine design, and k, the chemical factor, is entirely dependent upon the mixture ratio. From the following list it is evident that high efficiency demands lean or diluted mixtures, *i. e.*, mixtures with an excess of air.

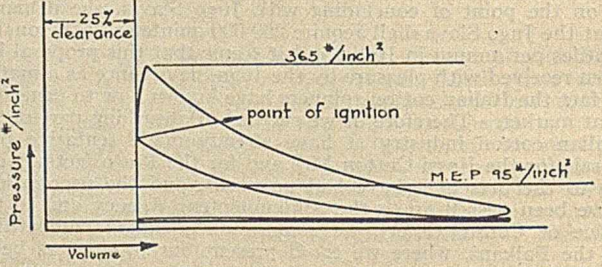

Fig. 2—Average Pressure-Volume Diagram of Otto Engine at Full Load

Gas	K
Oxygen	1.408
Nitrogen	1.408
Carbon dioxide	1.31
Water vapor	1.2
Gasoline vapor	1.1 (approx.)

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[1] Presented before the Division of Industrial and Engineering Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] A. C. Fieldner, This Journal, 13 (1921), 57.

[3] A. F. Greiner, *Michigan Technic*, 32 (March 1919).

When the value of k in Equation 1b is taken as 1.408, we obtain the efficiency of the air standard cycle which is used generally as a means of comparison. The measured efficiency of a properly controlled engine is of the order of 62 to 65 per cent of the theoretical air standard. If the measured efficiency be compared with that for an engine working, not upon air, but with the actual gasoline-air mixture employed, as represented in Fig. 2,[3] and if allowance be made for the fact that the specific heat of the gases increases with temperature, a better basis of comparison will be obtained. Compared with this "corrected ideal efficiency" the measured efficiency is of the order of 80 per cent of the theoretical maximum.

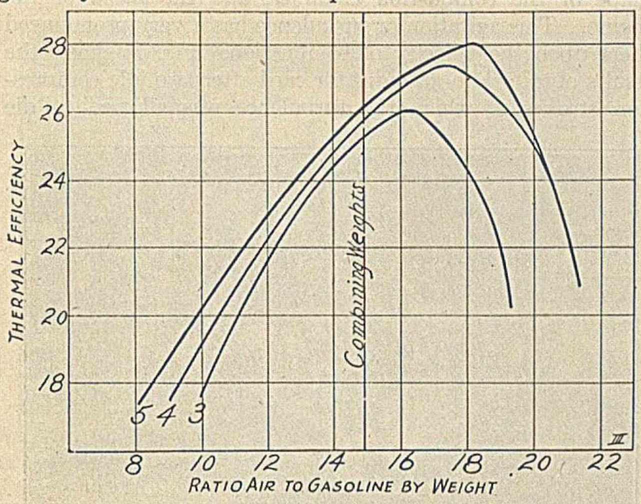

FIG. 3—EFFECT OF MIXTURE CONCENTRATION AND COMPRESSION RATIO (FIGURES AT END OF CURVES) UPON THERMAL EFFICIENCY WITH THROTTLE WIDE OPEN AND ENGINE RUNNING AT CONSTANT SPEED

Even if it were possible to eliminate entirely all heat losses in the exhaust and to cooling the water by further mechanical refinements, the increase in efficiency could not exceed 20 per cent. But the efficiency, or miles per gallon, of the average automobile can be practically doubled by proper control of the mixture, or K in the above formula.

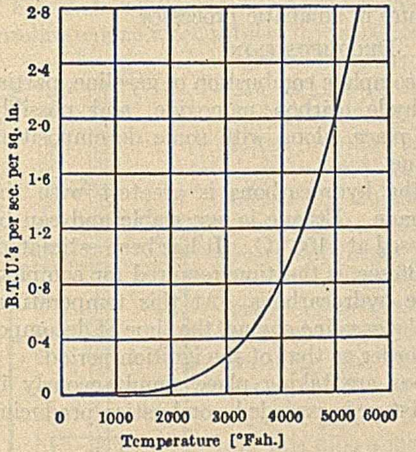

FIG. 4—RADIATION LOSSES

The relative importance of compression ratio and mixture proportion is brought out more strikingly in Fig. 3,[4] which shows the influence of these two factors upon the thermal efficiency. The increase in efficiency obtained by higher compression is due to two factors. It gives a relatively longer working stroke, and the increased compression makes for a higher mixture temperature and more rapid explosion.

The high efficiency obtained with dilute or lean mixtures is due to various factors. The lower specific heats make possible the same temperature and pressure increase with a less amount of heat energy. The radiation losses are less from diluted or lean mixtures containing an excess of air because of two factors; the radiation from the diatomic gases is less than that from carbon dioxide and water vapor, and mixtures containing an excess of air develop a lower temperature upon combustion than those containing combining proportions of gasoline and air. This latter statement is made clear by Fig. 4,[5] which shows the amount of heat radiated as dependent upon temperature alone.

REACTION VELOCITY

In order to complete the reaction or in fact to have an explosion at all, the speed of reaction must be at least equal to the rate of heat dissipation; otherwise the heat energy of the spark or of the adjacent gases ignited by the spark will be dissipated before the main body of the charge is raised to the ignition point.

Essentially there are three factors determining the speed of combustion: concentration, temperature, and agitation or turbulence making for more intimate contact. Catalysis is a fourth factor, as is noticed when moisture or steam is present in considerable amount in the explosive mixture. The influence of concentration is best determined by application of the law of mass action. If we write the equation for the combustion of gasoline as follows:

$$C_6H_{14} + 9.5O_2 \longrightarrow 6CO_2 + 7H_2O$$

the velocity of reaction will vary as

$$C_{C_6H_{14}} \times C_{O_2}^{9.5}.$$

If the atmosphere contains a per cent of O_2, and the mixture of maximum velocity contains x per cent by volume of gasoline,

$$C_{C_6H_{14}} \times C_{O_2}^{9.5} = x\left[(100-x)\frac{a}{100}\right]^{9.5} = x\left[(100-x)\right]^{9.5}\left(\frac{a}{100}\right)^{9.5}.$$

Since a is a constant, this expression is a maximum when $x(100-x)^{9.5}$ is a maximum.

In other words, so long as the composition of the atmosphere remains constant, its oxygen content has no influence on the gasoline content giving maximum velocity of reaction so far as the law of mass action is concerned. Then, other conditions being constant, the mixture of maximum reaction velocity will contain exactly the same percentage of gasoline as if the air were pure oxygen, regardless of the per cent of oxygen in the atmosphere.

But the rate of chemical action increases very rapidly with a rise in temperature. Except with certain highly unsaturated hydrocarbons having a negative heat of formation, such as acetylene, the maximum temperature is produced by the mixture containing vapor and oxygen in combining proportions. This factor of maximum temperature will act therefore in opposition to mass action and tend to decrease the

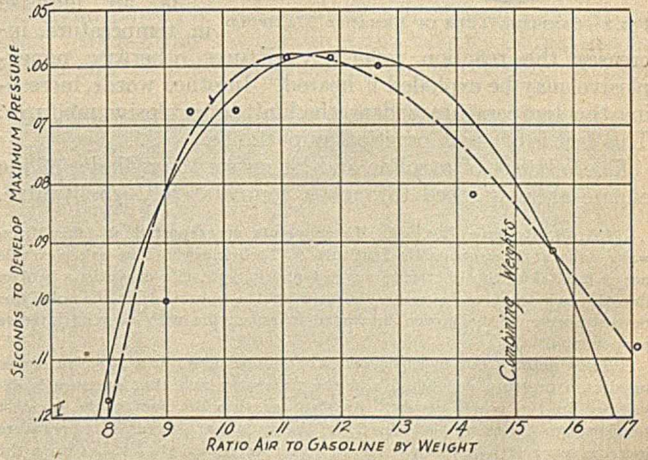

FIG. 5—VELOCITY OF COMBUSTION OF GASOLINE-AIR MIXTURES

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[4] A. W. Judge, "High Speed Internal Combustion Engines," Pitman & Sons, 1918

[5] A. B. Browne, "Handbook of Carburetion," J. Wiley & Sons, Inc., 1916.

excess of gasoline in the mixture of maximum reaction velocity demanded by mass action, to an extent depending upon the cooling effect, or the specific heat of the excess gasoline.

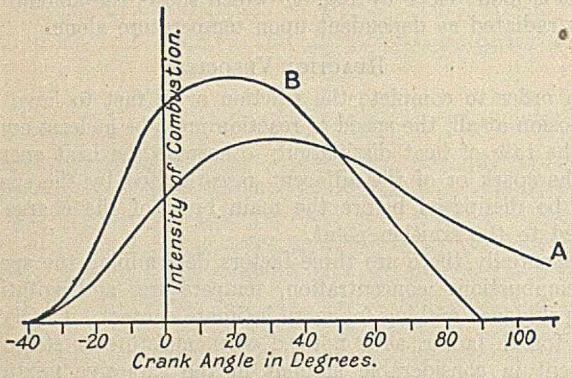

Fig. 6—Intensity and Velocity of Combustion of 12 : 1 and 16 : 1 Air-Gasoline Mixtures

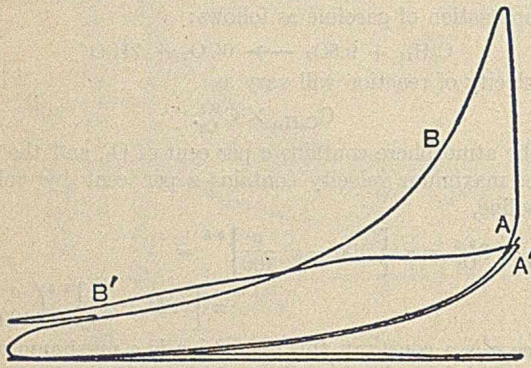

Fig. 7—Indicator Diagram of Turbulent and Quiet Mixtures

But the mixture of maximum reaction velocity of any combustible gas and air has always an excess of the combustible constituent over the combining proportion, due to the influence of mass action, as seen in Fig. 5.[6] Fig. 6[4] shows the more intense and more rapid combustion of a mixture of twelve parts of air (Curve B) over that of a lean mixture of sixteen parts of air (Curve A) as occurs in an engine cylinder, all other conditions being constant.

As an increase in temperature increases the reaction velocity, mixtures otherwise nonexplosive may be exploded if heated. In other words, increasing the temperature widens the limits of explosive mixtures. This fact is of great practical importance.

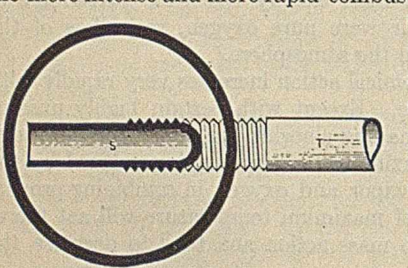

Fig. 8—Sampling Tube in Exhaust Manifold

The mixture of gasoline and air enters the cylinder of the engine at high speed through a comparatively small valve. This velocity of the entering charge agitates the mixture in the cylinder to a greater or less degree, depending upon the shape of the combustion chamber, and the speed of the engine. This agitation or turbulence has a very pronounced effect upon the velocity of combustion. Fig. 7[7] shows the results obtained on an indicator card after two idle compression strokes in which the turbulence was allowed to die down. The curve AB corresponds with normal firing and the expansion line A′B′ corresponds with the second case mentioned, in which all conditions were the same, except decreased turbulence. The ignition periods were 0.037 and 0.092 sec., respectively, or in a ratio of 1 : 2.5.

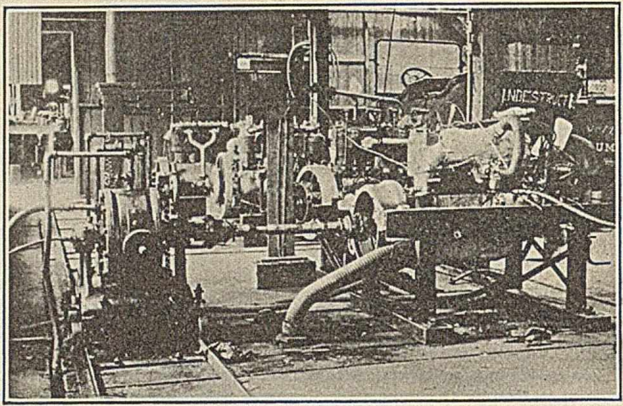

Fig. 9—Engine Set-up in Automobile Laboratory, University of Michigan

Pressure has been found to have practically no influence upon the speed of reaction so long as the temperature remains constant. But increased compression in an engine means increased temperature, for the absolute temperature varies as the absolute pressure in adiabatic processes.

Decomposition

In addition to the complete combustion of gasoline, partial combustion to aldehyde, carbon monoxide, and possibly hydrogen also takes place, along with some decomposition of the hydrocarbon fuel.

The stability of the hydrocarbons is greatest with the lowest paraffin, methane. Ethane is less stable and can be very rapidly decomposed at 1100° C. It has been estimated[8] that at 1500° C., 0.036 sec. is the time required for complete decomposition of the hydrocarbons. At this temperature, which is attained in the gasoline engine, the time of decomposition is of the same order as that of the ignition period.

These two reactions are taking place simultaneously in the cylinder as the mixture is exploded, combustion producing

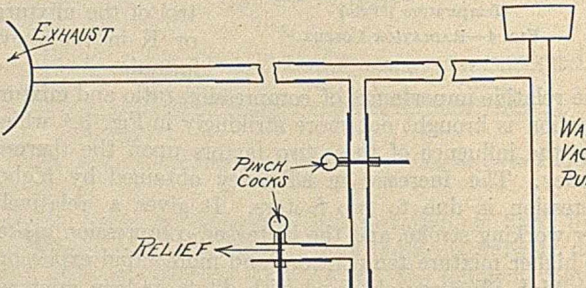

Fig. 10—Connections for Sampling and Analyzing Exhaust Gases

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[6] A. B. Browne, *Loc. cit.* These points are reported as taken from work done at Massachusetts Institute of Technology. The writer of this paper has taken the liberty to suggest another possible curve in a broken line through these same points, as he is of the opinion that the solid line better represents the power developed in an engine with varying mixture proportions.

As is pointed out in this paper, the engine power is a function of the maximum pressure developed and the time at which that pressure is developed in the power stroke. As that mixture developing the greatest temperature increase also develops the greatest pressure, temperature increase has a greater influence upon power developed than it has upon the reaction velocity. Then we should expect to find the maximum power with a mixture containing more nearly combining proportions than the mixture giving maximum reaction velocity.

Compare the curves in Fig. 5 with the curve for 80° in Fig. 16.

[7] Dugald Clerk, Gaseous Expt. Com. Reports, **1912**, 23, 24.

[8] Katz, U. S. Bureau of Mines, *Technical Paper* **183**.

heat and work, and decomposition of the gasoline generally absorbing heat and depositing carbon residue. As decomposition of the fuel takes place much more rapidly at higher temperatures, the lower temperature developed by the combustion of lean mixtures is of advantage in decreasing and eliminating the fuel knock and the deposition of carbon in the cylinders. Dugald Clerk has accomplished the same result by introducing cold exhaust gas into the cylinder charge. This method is more effective in reducing the temperature, but probably not so efficient, owing to the higher specific heat and radiation loss of carbon dioxide over air. Also, it would introduce complications to the design and operation of the engine.

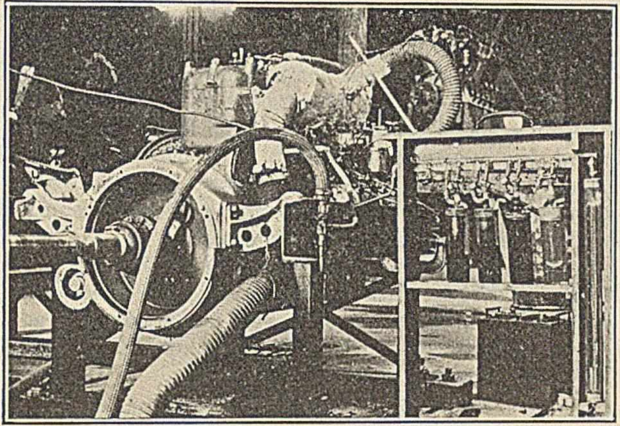

FIG. 11—SET-UP FOR SAMPLING AND ANALYZING EXHAUST GASES

EXPERIMENTAL WORK

Fig. 9 shows the set-up used to determine the action of a gasoline engine when subject to various conditions of temperature and concentration of mixture. The engine is shown connected to a hydraulic dynamometer. Speed was taken by an indicating revolution counter, and the torque was determined by balancing the arm of the dynamometer on the platform of a Fairbank's scale. A mercury manometer was connected to the intake manifold so that the pressure in the manifold might be recorded. A quarter-inch pipe threaded and cut as shown in Fig. 8 was inserted in the exhaust pipe in the manner indicated. To this pipe a modified form of Orsat apparatus and vacuum pump used as an aspirator were connected as shown in Figs. 10 and 11. Using the vacuum pump in this manner kept the tubing clear of dead gas.

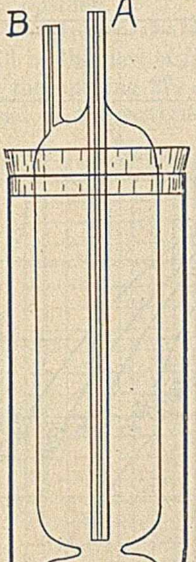

FIG. 12—ABSORPTION PIPET

Fig. 12 shows the construction of the pipets used in the Orsat apparatus. The caustic and pyrogallate pipets were filled with glass tubes and the two cuprous chloride pipets were filled with twisted copper strips. The pipets were connected to the capillary manifold by rubber tubing provided with pinchcocks. The gas, admitted through tube A, bubbled through the solution, which was displaced and forced into the outer vessel. The gas was removed from the pipet through tube B. Five passages of the gas through the absorbing solution were found ample for all gases encountered in this work.

Fig. 13 is a chart used to determine the mixture proportion from exhaust gas analysis. It was prepared for use with the Standard gasoline obtained in Michigan in the fall of 1920 but is practically correct for the present market gasoline. The ordinate represents percentage composition of exhaust gas and the abscissa pounds of air to one pound of gasoline.

The large hot air stove over the exhaust manifold can be plainly noticed in Fig. 14, which also shows the carburetor and the thermometer in the air intake.

RESULTS—Fig. 16 shows graphically the data taken in determining the horsepower developed by the engine at wide open throttle and constant speed, but with varying mixture proportions and temperature of the air supply. By keeping the speed and throttle constant, the turbulence or agitation of the mixture is constant and its effect may be neglected. Then any change in power must be due to mixture proportion or temperature.

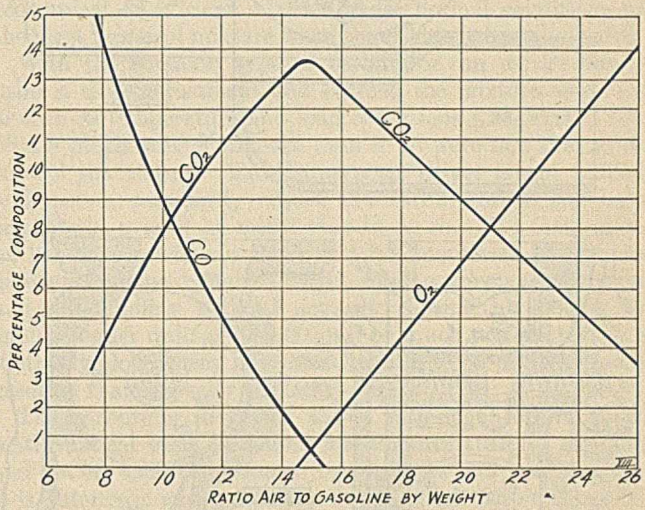

FIG. 13—RATIO AIR TO GASOLINE FROM EXHAUST GAS ANALYSIS

The power and torque developed by an engine are directly proportional to the mean effective pressure of the working substance on the piston. For maximum power, it is desired to develop the maximum pressure as early as possible in the power stroke, or to explode the maximum quantity of gasoline as rapidly as possible. Maximum power is developed, particularly with cold mixtures, when the proportion of air to gasoline is slightly more than that giving maximum velocity of combustion. Increasing the temperature decreases the density of the mixture and similarly diminishes the weight of charge taken into the cylinder. Then for maximum power, a comparatively cold rich mixture is desired. With higher temperatures the velocity of reaction is greater and the power curve flattens out as the effect of mass

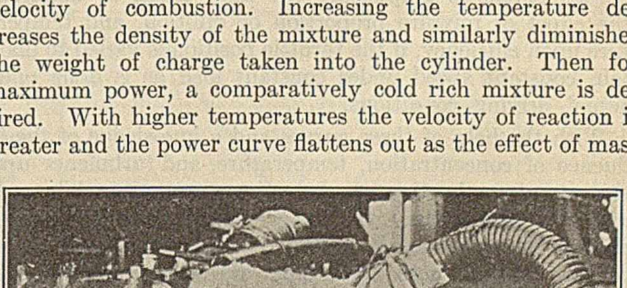

FIG. 14—CARBURETOR CONNECTIONS SHOWING LARGE HOT AIR STOVE AND MANOMETER CONNECTION IN INTAKE MANIFOLD

action becomes less noticeable as the influence of temperature becomes more pronounced.

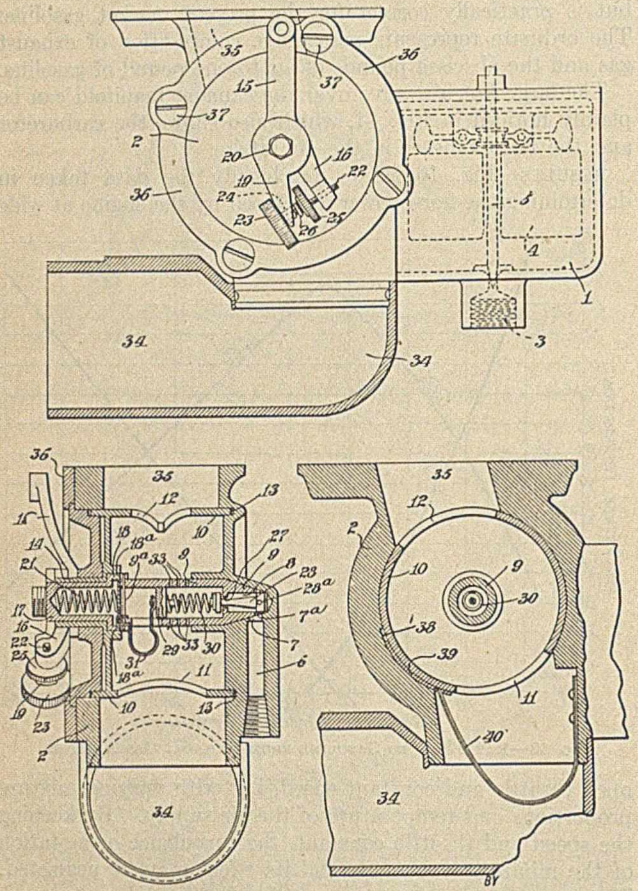

FIG. 15—CONSTRUCTION OF CARBURETOR GIVING AUTOMATIC CONTROL

In all industrial combustion problems, increased efficiency can be obtained by returning as much heat as possible from the waste gases to the combustion zone by preheating the air. This is doubly true in the gasoline engine, for hot air not only helps to vaporize the gasoline but also increases the rate of combustion so that a leaner mixture can be burned with increased efficiency.

Fig. 17 shows graphically the data taken to determine the effect of mixture proportion or dilution, and temperature upon efficiency, if the throttle position is varied to maintain constant speed under constant load as is done under actual driving conditions.

With the help of these curves and a knowledge of the influence of concentration, temperature, and turbulence upon the rate of combustion, the behavior of an automobile under road conditions may be easily explained. The greatest mileage per gallon can be obtained with a hot dilute mixture, because under these conditions the engine develops its greatest efficiency. If the engine is cold, a more concentrated mixture is required to maintain the velocity of reaction above the critical point necessary for explosion. If a car being driven at constant speed along a smooth level highway, using the leanest possible mixture that can be completely burned, encounters a grade or other resistance, the engine slows down. The diminished velocity of mixture into the cylinder decreases the turbulence and velocity of combustion to such an extent that the engine backfires, misses, and may even stop, unless some measure is employed to increase the velocity of combustion. This can best be done by supplying a richer mixture until conditions have returned to the former state of normal load.

In starting a cold engine, the air has a definite weight per unit volume, which steadily decreases with increasing temperature, as shown in Fig. 19. Also the gasoline has a certain viscosity which steadily decreases with increasing temperature, so that the weight of gasoline flowing through a constant orifice increases with rising temperature as indicated in Fig. 18.[5] Then, as increasing temperature gives a greater weight of gasoline and a lesser weight of air when the reverse is desired for maximum efficiency, it is necessary that the carburetor compensate for temperature changes by automatically partly closing the gasoline orifice or opening the air port as the temperature of the air rises.

If we define normal load as the load on the engine when driving the car at a constant speed along a level highway, the suction in the manifold of an engine under normal load for different throttle openings varies as shown in Fig. 20, the average of a number of tests.

AUTOMATIC CHEMICAL CONTROL

A carburetor was built as shown in Fig. 15. The gasoline enters the float chamber 1 at 3 and passes through duct 6 up to the gasoline valve made by part 7 in the casing and part 7*a* in the stem valve 9, which is in the axis of the drum throttle 10 containing the air inlet 11 and the mixture outlet 12. The gasoline valve can be adjusted in relation to the throttle by the thumb screw 23 and locked in place by the nut 20 so that when the throttle lever 15 is moved the gasoline valve moves in unison with the throttle. The mixture outlet and air inlet are so calibrated that the suction in the mixing chamber is constant so long as the engine is running under "normal load." If the engine is running under any load greater than that "normal" for that particular throttle position, the suction in the manifold and in the mixing chamber will be less.

This variation in the manifold suction is utilized to vary the mixture proportions in the following manner: Within the valve stem 9 is an opening, 27, in which the governor 28 is free to reciprocate endwise of the valve stem 9. This gover-

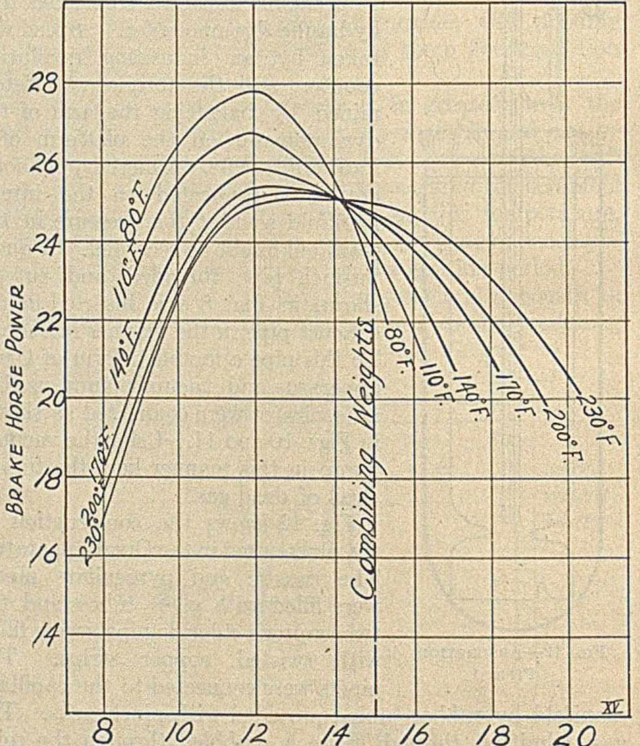

FIG. 16—BRAKE HORSEPOWER DEVELOPED WITH VARYING TEMPERATURE OF AIR (FIGURES AT THE END OF CURVES) AND MIXTURE CONCENTRATION, WITH CONSTANT SPEED AND WIDE OPEN THROTTLE

nor 28 has a taper shank which restricts the effective area of the opening 27 by an amount corresponding to the section of the taper shank of the governor which happens to be within the opening.

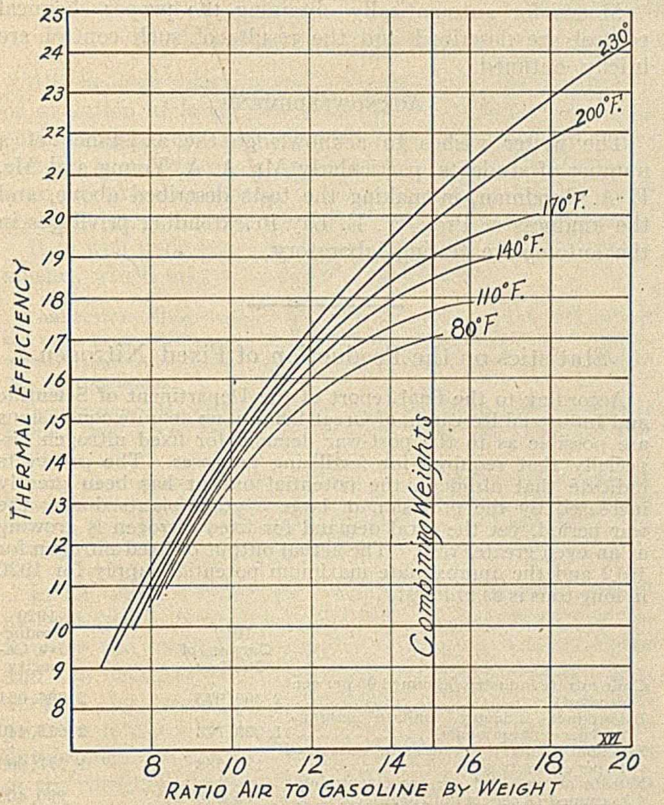

Fig. 17—Effect of Mixture Concentration and Temperatures of Air (Figures at End of Curves) upon Thermal Efficiency with Speed and Load Constant

The stronger the suction in the mixing chamber, the stronger will be the flow of fuel and the greater will be the restriction of the opening 27, as the pressure of the fuel flow upon the head of the governor compresses the spring 30, making the larger part of the taper effective and to that extent closing the fuel opening 27.

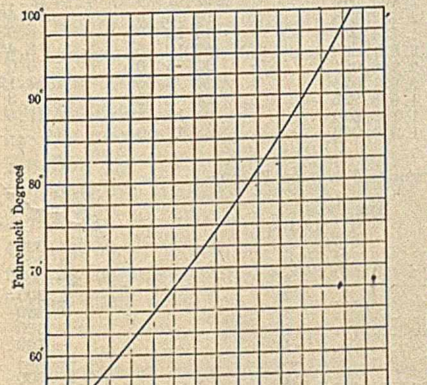

Fig. 18—Relative Flow of Gasoline through a Constant Orifice under Different Temperature Conditions

The position of the governor is also controlled by the position of the sliding block 29. The position of this block 29 is determined by the bimetal thermal regulator 31, which is fastened to the valve stem at one end and at its other end rests in a socket in block 29. Upon an increase in temperature the thermal regulator 31 curls up in a direction to move block 29 to the left and permit the governor 28 to move a like distance toward the left, thereby restricting the opening 27 an amount proportional to the movement of the thermal regulator. Upon a decrease in temperature the thermal regulator uncurls, causing the governor 28 to move a like distance toward the right, exposing a greater effective area of the opening 27.

It has been found possible to calibrate this governor and thermal regulator to obtain automatically any desired change in mixture proportion upon change in engine load or change in temperature. It is possible simply to compensate for the decreased density of air and decreased viscosity of fuel with increasing temperature, or further to restrict the flow of gasoline so as to obtain always the leanest possible or most efficient mixture. Likewise the change in mixture proportion with changing engine load may be simply sufficient to compensate for decreased turbulence to prevent missing and backfiring; or may be sufficient to change from the most economical or efficient mixture under normal conditions to the most powerful mixture when the engine is heavily loaded.

With the common type of carburetor, an expert driver using a dash adjustment and keeping the mixture as dilute or lean as temperature and load conditions will permit, can obtain much greater mileage than if he were not able so to control the mixture. But the average driver is not skilled and cannot constantly adjust the carburetor to the best advantage, even if he might care to do so. "In fact, when he has once made a carburetor adjustment rich enough to give good engine operation with a cold engine on acceleration and hill-climbing without actually causing his engine to 'gallop' under ordinary conditions, he much prefers to leave it strictly alone, using anywhere from 10 to 50 per cent more gasoline than is really necessary."[9]

The carburetor described above is designed on an exact mathematical basis to deliver a definite mixture of gasoline and air for each condition of temperature and load, and as it is automatic and positive in action much better chemical control can be obtained by its use than with a dash adjustment even in the hands of a skilled operator.

RESULTS OF CHEMICAL CONTROL—By application of the principles of chemical control developed above, and the means for positively and automatically obtaining that control as described, the miles per gallon have been invariably increased from 25 to over 100 per cent over that previously obtained.

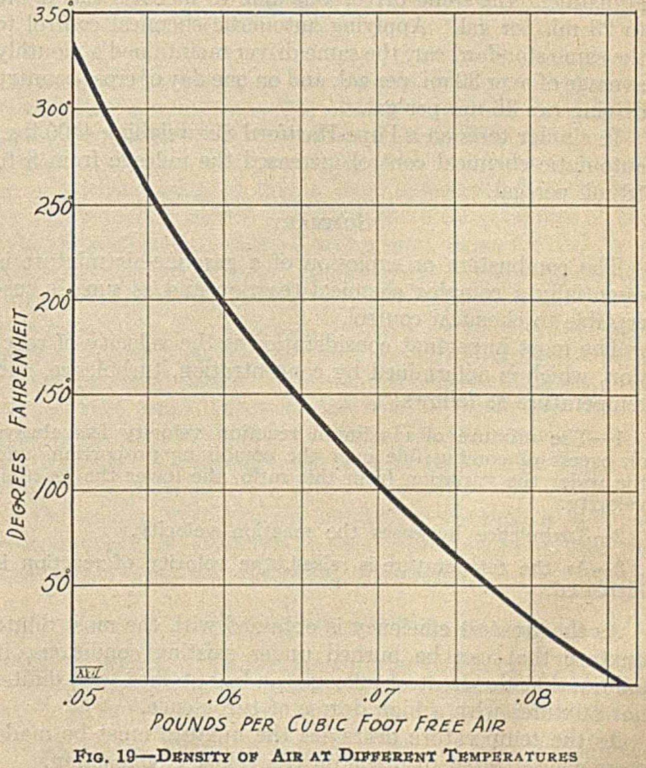

Fig. 19—Density of Air at Different Temperatures

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[9] W. E. Lay, "Saving Fuel with the Carburetor," *J. Soc. Automotive Eng.*, 7 (1920), 188.

A standard Ford touring car being driven without dash adjustment averaged 19 mi. per gal. By utilizing the dash adjustment the same driver was able to increase this figure to 23 mi. per gal. Applying automatic chemical control to the same standard car, the same driver maintained a monthly average of over 30 mi. per gal. and on one day of cross-country driving ran 36 mi. per gal.

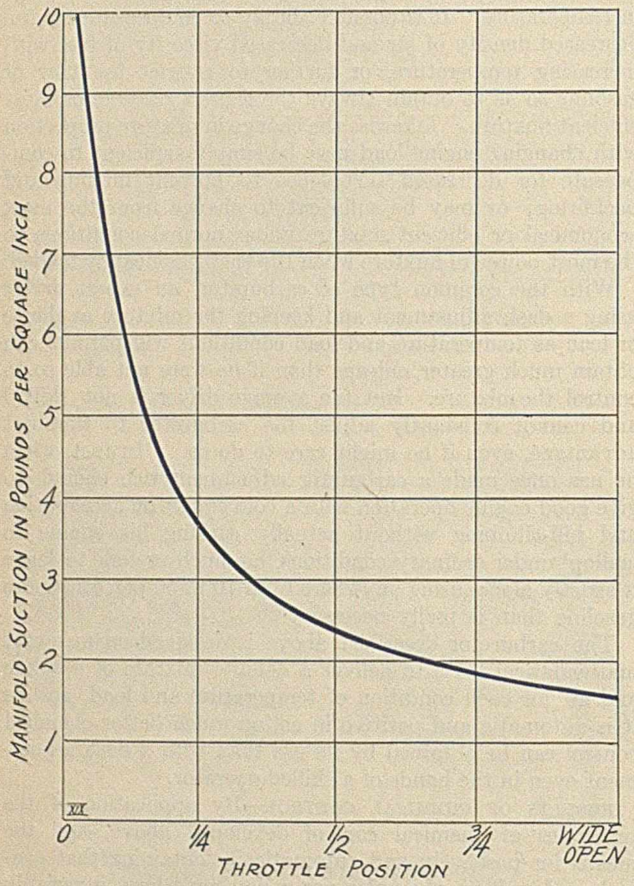

Fig. 20—Manifold Suction for Different Throttle Positions with Engine under "Normal Load"

In similar tests on a Pope-Hartford Six weighing 4400 lbs., automatic chemical control increased the mileage from 8 to 18 mi. per gal.

Summary

The combustion or explosion of a gasoline-air mixture is essentially a complex chemical reaction and as such is susceptible to chemical control.

The most important consideration is the velocity of reaction, which is determined by concentration, turbulence, and temperature as follows:

1—The mixture of maximum reaction velocity has always an excess of combustible over the combining proportions and the wider the variation from this ratio, the lower the reaction velocity.

2—Turbulence increases the reaction velocity.

3—As the temperature is raised, the velocity of reaction is increased.

As the greatest efficiency is obtained with the most dilute mixture that can be burned under existing conditions, it follows that the greatest mileage can be obtained with dilute, hot mixtures with a high degree of turbulence.

As the temperature decreases the mixture must be made more concentrated to maintain the velocity of reaction.

Since the turbulence decreases as the engine speed decreases, the reaction velocity must be maintained by increasing the concentration of the mixture as greater load is put on the engine.

Means for automatically obtaining the proper chemical control are described and the results of such control are briefly outlined.

Acknowledgment

The writer wishes to acknowledge the assistance of a number of students, particularly Mr. A. A. Young and Mr. E. A. Goodman, in making the tests described above, and the kindness of Prof. W. E. Lay in extending privileges in the automotive testing laboratory.

Statistics on the Production of Fixed Nitrogen

According to the final report of the Department of Scientific and Industrial Research, of Great Britain, no definite conclusions are possible as to the post-war demand for fixed nitrogen, especially that required for fertilizing purposes. The prospects indicate that although the potential output has been greatly increased by the provision of large fixation plants during the war period, yet the total demand for fixed nitrogen is growing at an even greater rate. The actual output of fixed nitrogen for 1912 and the approximate maximum potential supply for 1920 in long tons is as follows:

	1912 Output of Product	1920 Productive Capacity
Chile nitrate industry (assumed 95 per cent product)	2, 586, 975	2, 966, 061
By-product industry (sulfate assumed 24.5 per cent ammonia)	1, 229, 773	2, 015, 440
Fixation industry—cyanamide (assumed 16 per cent nitrogen)	126, 538	1, 777, 000
Nitrate of lime and arc process products (assumed 13 per cent nitrogen)	75, 000	290, 400
Synthetic ammonia	......	1, 503, 000
Total of fixation industry	201, 538	3, 570, 400
Grand Total	4, 018, 286	8, 551, 901

Since the price of Chile nitrate may be said still to dominate that of fixed nitrogen generally, the statistics relating to it are of great importance and are presented in fairly complete form.

Production and Prices of Chilean Nitrate

	Production long tons	Price long ton ex ship Liverpool	Price long ton f. o. b. Chile
1913	2, 464, 540	£11 1 8	.....
1914	2, 432, 328	10 8 9	£8.56
1915	1, 734, 932	12 13 0	6.99
1916	2, 877, 899	17 12 5	8.45
1917	2, 966, 061	25 5 0	10.0
1918	2, 831, 026	26 6 6	13.12
1919	1, 658, 826	21 2 9	13.3
1920 (first half)	1, 182, 000	24 18 8	17.5
(second half)	1, 310, 000	23 17 0	.....

Nitrogen Fixation Plants

	Plants	Capacity Metric Tons
Arc Process		
Germany	2	4, 000
France	2	1, 300
Norway and Sweden	3	30, 000
Italy	2	1, 200
Canada	1	800
United States	1	300
Switzerland	1	700
Total	12	38, 300
Cyanamide Process		
Germany	7	120, 000
Austria	2	22, 000
France	9	58, 000
Norway and Sweden	3	28, 000
Italy	5	18, 000
Switzerland	3	7, 000
Canada	1	12, 000
Japan	4	20, 000
United States	1	40, 000
Total	35	325, 000
Synthetic Ammonia Process		
Germany	2	300, 000
United States	1	8, 000
Total	3	308, 000
Grand Total	50	671, 300

Heat Transfer[1,2,3]

By W. H. McAdams and T. H. Frost

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

All chemical reactions are accompanied by the absorption or evolution of heat; hence in every problem in chemical engineering design, provision must be made for the satisfactory transference of the heat quantities. Furthermore, even in processes which involve practically no chemical changes, one or more problems of heat transfer usually arise.

It is well understood that heat may flow by three mechanisms, which may be defined[1,*] as follows:

> Conduction—Heat passing from one part of a body to another part of the same body, or from one body to another in physical contact with it, without appreciable displacement of the particles of the body, is said to flow by conduction.
>
> Convection—Convection is the transfer of heat from one place to another within a fluid (gas or liquid) by the mixing of one portion of the fluid with another.
>
> Radiation—A hot body gives off heat in the form of radiant energy. When this energy strikes another body, part is reflected. If this second body is transparent or translucent, another part is transmitted. The remainder is absorbed, and quantitatively transformed into heat.[†]

In all cases of commercial importance the heat flows by at least two of these mechanisms. The laws governing the flow by the various mechanisms have long been available and the mathematical statements of these laws have been verified by numerous experiments. The all-important problem is not a further elucidation of these laws, but the development of equations from which the numerical values of the *coefficients* of heat transfer may be calculated. Such equations may be used both in designing new apparatus and, for apparatus already built, in predicting the change in capacity caused by changing operating conditions.

Object of Present Articles

It is the purpose of this series of articles to review the reliable data for these coefficients, to present new data for certain important cases for which sufficient data are not available, and, where possible, to correlate these data by developing general formulas for certain cases.

Where heat flows by radiation, it usually flows also by the mechanisms of conduction and convection acting simultaneously. Since the law governing the flow by radiation is quite different from that governing the flow by conduction and convection, the rate of flow by radiation is calculated by the proper equation and added to that calculated for the flow by the other two processes. The cases in which the flow by conduction and convection is the controlling factor will be discussed first, but before taking up definite cases it is desirable to discuss in detail the mechanism of flow by conduction and convection, and the method of analyzing such data.

Potential Concept

The flow of heat by conduction and convection is determined by Newton's law in the following form,[2] which is analogous to Ohm's law for the flow of electricity:

$$\frac{Q}{\theta} = \frac{\Delta T}{r_1 + r_2 + r_3} = \frac{\Delta t_1}{r_1} = \frac{\Delta t_2}{r_2} = \frac{\Delta t_3}{r_3} \qquad (1)$$

where $\frac{Q}{\theta}$ = B. t. u. transferred per hr.
ΔT = Average *over-all* difference in temperature between the hot and cold fluids.
Δt = Average difference in temperature between two boundaries of any definite part of the path.
r = Thermal resistance of any definite part of the path.

Since three resistances are met in the cases which are to be discussed later, these are indicated by the subscripts 1, 2 and 3.

Film Concept[1]

When a liquid or gas is in contact with a solid there is strong evidence to show the presence of an adhering relatively stationary film[3] of fluid on the surface of the solid, a film which becomes thinner as the velocity of the fluid parallel to the surface increases, but which breaks away from the solid only at very high velocities, if at all. Through such a film, heat can be transmitted by conduction only, although once the heat has penetrated through the film the hot molecules are picked up and carried away mechanically by the swirling motion of the main body of the fluid, *i. e.*, the transfer is mainly a matter of convection, and in the latter case the resistance to flow will be negligible. Since most liquids and gases are exceedingly poor conductors of heat, it is not surprising to find a large resistance to heat flow at the boundary surface of a fluid and solid (and also at the boundary between a liquid and a gas), accompanied by a large drop in temperature at this point. The temperature change in the neighborhood of a solid-fluid boundary is indicated in Fig. 1. Through the solid there is a fall, t_2–t_3, which is usually small compared to the temperature drop in the boundary itself. Through the surface film the drop t_3–t_4 is very great, but once the zone of stationary fluid is passed the temperature soon reaches that of the main portion of the fluid. No attempt has been made to draw Fig. 1 to scale.

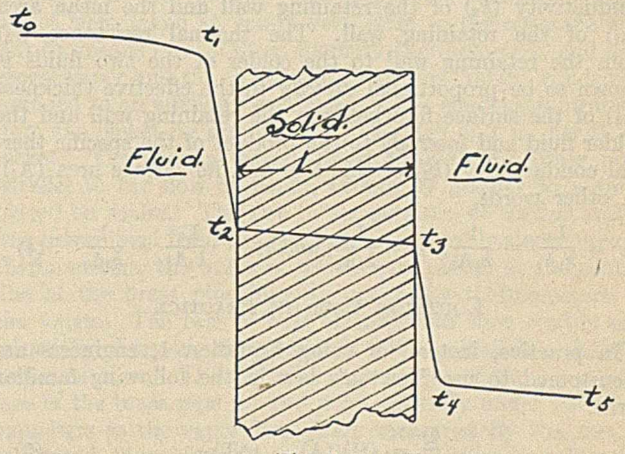

Fig. 1

The rate of heat loss by conduction through a layer of any material of thickness L and conductivity k may be calculated from the following equation:

$$\frac{Q}{\theta} = \frac{k}{L}\,(A)\ (t_3 - t_4) \qquad (2)$$

where t_3 and t_4 = temperatures of the two faces of the layer.
k (or K) = thermal conductivity of the material, expressed as B. t. u. per hr. per sq. ft. per °F. per ft. thickness.

This equation may be applied to flow of heat through the stationary film of fluid on the surface of solid, provided the term h be used to designate the ratio k/L, where L is a defi-

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[1] Received November 5, 1921.

[2] Published as Contribution No. 4 from the Department of Chemical Engineering, Massachusetts Institute of Technology.

[3] Part I of series of articles on this subject.

[*] Numbers in the text refer to Bibliography, page 18.

[†] Except in those relatively rare cases where photochemical reactions are induced, or energy is consumed in other special ways.

nite (though unknown) effective thickness of the surface film; *i. e.*, Equation 2 becomes:

$$\frac{Q}{\theta} = hA\,(t_3 - t_4) \qquad (3)$$

This coefficient h is often called the "film coefficient" or "surface coefficient." In English units, h is expressed as B. t. u. per hr. per sq. ft. per ° F. temperature difference. In contradistinction to k, the "coefficient of conductivity" previously discussed, *the "surface coefficient" (h) contains no element of thickness.*

Thus it is seen that in the many important cases where heat is flowing from one fluid through a retaining wall to another fluid, three resistances are met. The resistance (r_1) met by the heat in flowing from the hotter of the two fluids to the retaining wall is known to be proportional *directly* to the effective thickness (L_1) of the surface film of fluid at this boundary and *inversely* as the product of the specific thermal conductivity (k_1) of the first fluid film and the surface area (A_1) of that boundary. The thermal resistance (r_2) of the retaining wall is known to be proportional *directly* to the actual thickness (L_2) of the retaining wall and *inversely* as the product of the specific thermal conductivity (k_2) of the retaining wall and the mean area (A_2) of the retaining wall. The thermal resistance (r_3) from the retaining wall to the colder of the two fluids is known to be proportional *directly* to the effective thickness (L_3) of the surface film between the retaining wall and the colder fluid and *inversely* to the product of the specific thermal conductivity (k_3) of this film and its surface area (A_3). In other words,

$$r_1 = \frac{L_1}{k_1A_1} = \frac{1}{h_1A_1};\; r_2 = \frac{L_2}{k_2A_2};\text{ and } r_3 = \frac{L_3}{k_3A_3} = \frac{1}{h_3A_3} \qquad (4)$$

EQUATION USED IN PRACTICE

In practice, instead of using Equation 1, engineers are accustomed to use Newton's law in the following familiar form:

$$\frac{Q}{\theta} = (H)\,(A)_{av.}\,(\Delta T)_{av.} \qquad (5)$$

where H = an *over-all* coefficient of heat transfer from the hotter to the colder fluid, based on a suitable area ($A_{av.}$) of heat transfer surface. (Units: H = B. t. u. per hr. per ° F. average over-all temp. diff. per sq. ft. of suitable heat transfer area.)

The use of this equation is standard practice, and no objection is raised to this procedure, *provided* the value of H is correctly determined. The problem confronting the designer is the estimation of the numerical value of this over-all coefficient, and it will be shown that it is to be determined by a large number of factors.

A comparison of the preceding equation shows:

$$HA_{av.} = \frac{1}{r_1 + r_2 + r_3} = \frac{1}{\frac{L_1}{k_1A_1} + \frac{L_2}{k_2A_2} + \frac{L_3}{k_3A_3}} = \frac{1}{\frac{1}{h_1A_1} + \frac{L_2}{k_2A_2} + \frac{1}{h_3A_3}} \qquad (6)$$

Consider the case where steam is condensing at constant pressure on the outer surface of a pipe and cooling water is flowing throughout the pipe at a definite velocity. Each of the three resistances will have a definite value under these conditions, thus fixing the value of the over-all coefficient H. Now if the water velocity be doubled, the thickness of the film of water on the tube wall will be decreased. Experimentally, it is found that this thickness is not quite halved, and hence h_3 is not quite doubled; in general, the coefficient h_3 between the pipe and the cooling water varies directly as some power, n, of velocity. Now the other two resistances will remain practically unchanged, so if an attempt is made to express H as a function of the water velocity, it will result in the introduction of this variable to a power other than the true value of n. The literature furnishes numerous examples of such cases, and while the formulas proposed by such writers would give the correct result if *all* the experimental conditions were reproduced, they furnish little information to one interested in the numerical value of H for a case in which the mechanism is identical, and yet where a different combination of fluids and kinds of retaining wall is involved. Furthermore, it is true that such writers have neglected to include one or more very important variables in their equations (such as viscosity), with the result that variables shown in their equations for H must also take care of fluctuations in the variables omitted. Since viscosity varies quite rapidly with temperature, this last situation makes it practically impossible to duplicate the results of such experimenters even when working with the same fluids and retaining walls, unless one is within the same range of temperature that prevailed in the experimental work. The logical and by far the simplest method is the development and tabulation of equations for the various *film* coefficients. With reliable data of this sort available, the designer can calculate the film coefficients for the case of interest to him and combine them by means of Equation 6, using the resulting value of $HA_{av.}$ in Equation 5. When it is realized that nine or more variables affect the over-all coefficient H in the important case of the transfer of heat in condensers, it is seen that it is practically hopeless to get an accurate expression for H, unless one adopts the simplification of calculating the special value of H for the particular case in hand from equations involving h_1 and h_3, each of which is determined by a number of variables fewer than those which determine H. The truth of this statement will be illustrated by the use of equations given below. It is felt that the lack of progress in the development of equations for the prediction of heat transfer coefficients is due primarily to the prevailing custom of submitting the data in the form of *over-all* coefficients (H), and the failure to utilize suitable "mental pictures" concerning the various resistances involved.

CASES TO BE CONSIDERED

The study of the film coefficients of heat transfer, h, by the joint mechanism of conduction and convection will include the following:

I—Condensing vapor to solid (h_v).
II—Liquid (not boiling) to solid, or vice versa (h_L).
III—Gas to solid, or vice versa (h_g).
IV—Solid to boiling liquid (h_b).

I—CONDENSING VAPOR TO SOLID

PREVIOUS WORK AND SCOPE OF PRESENT INVESTIGATION

In spite of the numerous tests of heat transfer apparatus heated by condensing vapors, the only reference found concerning direct measurements of the film coefficient (h_v) are those by Clement and Garland[4] who investigated the film coefficient from condensing steam to the outer surface of a 1-in. steel tube. The direct measurement of this coefficient was made possible by the use of thermocouples flush with the outer tube surface. The values of h_v observed by these investigators ranged from 1470 to 2410 B. t. u. per hr. per ° F. difference in temperature between steam and pipe surface per sq. ft. film area. These observers seem to have made no attempt to explain these variations or to suggest values for vapors other than steam.

Because of the lack of data in this important field, the writers have undertaken an investigation to obtain data for a number of condensing vapors, for the ultimate purpose of developing a general formula from which the coefficent from any condensing vapor to a pipe could be predicted.

VARIABLES INVOLVED

Remembering that the film coefficient of heat transfer, h_v, in question is determined by the ratio of the thermal conductivity, k, of the condensate to the effective thickness, L, of the condensate on the tube, the authors predicted that h_v would be affected directly by the thermal conductivity[5] of the condensate, and inversely by the viscosity[6] of condensate, because the more viscous the condensate, the greater would be the thickness of the layer of condensate adhering to the tube. If the surface of the tube is coated with rust or other foreign material to produce an appreciable temperature drop a "cleanliness"[7] correction must be made, which also takes care of the surface condition or roughness of the tube. Possibly some function of velocity (either parallel or at right angles to the tube, or both) will affect the coefficient, and if this is the case a correction for hydraulic radius, m, will also have to be made, for the reason developed under Case III of this series. An additional variable of great importance is the proportion of noncondensable gas[7] present in the vapor.

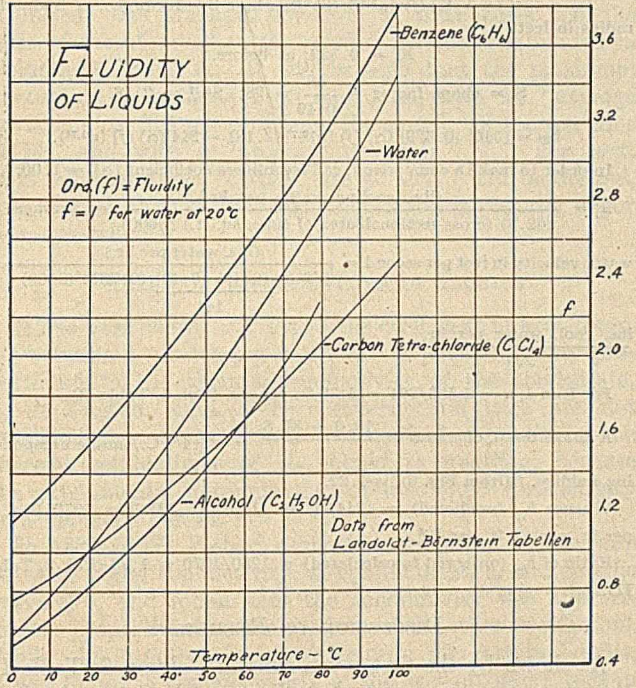

FIG. 2

Since viscosity is approximately a hyperbolic function of temperature, and fluidity (the reciprocal of viscosity) is nearly a straight line function of temperature, it was decided to introduce fluidity in the numerator of the equation for h_v instead of viscosity in the denominator.[*] The variation of fluidity f of several liquids with temperature is shown in Fig. 2.

Hence it was expected that the general formula for a vapor containing a small but uniform proportion of noncondensable gas would take the form:

$$h_v = (b)\,(c_1)\,(k)\,(f)\,(v)^n/(m)^p \qquad (7)$$

where h_v = predicted value of the film coefficient of heat transfer between a condensing vapor and a pipe, expressed as B. t. u. per hr. per sq. ft. per °F.
b = Experimentally determined coefficient of proportionality.
c_1 = Cleanliness factor, as previously defined.
k = Thermal conductivity of condensate on the wall of the tube, B. t. u. per hr. per °F. per sq. ft. per ft. thickness.
f = Fluidity of condensate at average film temperature in relative[†] units. See Fig. 2 for values.
v = Average velocity of vapor, parallel to the tube or at right angles to the tube, in convenient units.
n = Exponent of velocity to be experimentally determined.
m = Hydraulic radius of vapor passage, in feet.
p = Exponent of hydraulic radius, to be experimentally determined.

APPARATUS AND METHOD USED IN PRELIMINARY EXPERIMENTS

The saturated vapor being investigated was passed through the annular space between standard 1.5-in. steel pipe and a 0.675-in. o. d. and 0.49-in. i. d. brass pipe placed concentrically with the jacket. The vapor temperatures in the jacket were taken at points very close to the entrance and exit by means of calibrated mercury thermometers, and any excess vapor and the condensate from this "main" condenser were led to an auxiliary condenser. The condensate drained from the jacket by gravity due to a pitch of 1 in. per ft. of jacket. The cooling water flowed through the brass pipe parallel to the flow of vapor, thence by gravity to a tank placed on scales. The rise in temperature of cooling water was determined from the readings of two calibrated mercury thermometers, the bulbs of which were placed at the center line of the brass pipe directly under the thermometers in the vapor. The rate of heat transfer was then readily obtained by observing the weight of water passed in a definite period of time. The "skin" temperatures of the outer surface of the brass pipe (at two points directly under the thermometers in the vapor line) were measured by the use of calibrated "base-metal" thermocouples, using a millivoltmeter and a "cold junction" in the standard manner. The actual distance between each pair of couples and thermometers was 47.75 in.

TABLE I (CORRECTED DATA)

RUN No.	Temp. °C. (Outer) Surface Brass Pipe		Temp. °C. of Vapor		Temp. °C. Cooling Water		Cooling Water Lbs./Hr.
	Entrance (1)	Exit (2)	Entrance (3)	Exit (4)	Entrance (5)	Exit (6)	(7)
1	78.5	81.5	100.6	98.0	19.0	37.8	1585
2	78.7	79.5	101.0	98.5	19.1	34.2	2030
3	81.5	81.2	106.4	104.0	19.1	35.4	2105
4	79.2	77.6	102.0	99.0	19.5	34.7	2195
5	101.5	106.5	117.0	115.0	17.0	48.6	900
6	88.0	84.5	100.3	99.0	17.3	39.8	973
7	88.5	85.1	99.5	98.8	17.0	40.0	942
8	54.5	64.0	77.2	73.0	19.5	38.5	156
9	56.5	67.0	80.4	76.4	19.5	42.2	147
10	61.0	69.5	80.8	77.0	19.3	42.2	141

The rate of water flow was adjusted to give a sufficient rise in temperature of cooling water, and the rate of flow of vapor was adjusted to suit the capacity of the condenser. In some cases, excess vapor was used in order to determine the effect of varying the velocity of the vapor.

RESULTS

Table I shows the data[8] obtained, with all corrections for thermometer calibrations and conversions of thermo-

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[*] Under certain conditions of operation the temperature of the condensate will be sufficiently different at entrance and exit of the apparatus to raise the question of the proper average viscosity of the condensate. Inasmuch as viscosity is not a linear function of temperature it will be difficult to work out a correct formula for obtaining the average viscosity. On the other hand, since fluidity is a straight line function of temperature it matters little whether one averages temperatures and reads off the corresponding fluidity or whether the fluidity corresponding to each temperature is determined and then averaged. By dealing with fluidities one obtains the correct average regardless of which method of averaging is used, whereas in working with viscosities different results would be obtained, neither of which would be correct.

[†] Viscosity data in c. g. s. units (poises, or second dynes per sq. cm.) were taken from the literature, and since the viscosity of water at the standard temperature chosen (20° C.) is 0.0100 in these units, f (the fluidity of the liquid at the temperature in question relative to water at 20° C.) = the reciprocal of the viscosity in centipoises. For example, the c. g. s. viscosity of liquid benzene at 70° C. is 0.00355, and the corresponding value of f is 1/(0.00355)(100) = 2.82 for benzene at 70° C.

couple reading to temperatures made. The rate of flow of cooling water has been reduced to an hourly basis and all temperature readings are the average of four sets of readings taken during each run, the variation in no case exceeding 1° C.

Table II shows results of calculations from the observed data.

TABLE II

RUN No.	B.t.u./Hr. Transferred	Average Temp. Diff. Steam to Pipe (° C.)	h_v	f (Cond.)	K (Cond.)	h_v/fk	Vel. Cooling Water Ft. per Sec.	h_w (Obs.)	Ratio $\frac{h_w\text{ (Obs.)}}{h_w\text{(Calc.)}}$
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
					STEAM				
1	53,600	19.3	2190	3.05	0.329	2180	5.39	1280	1.20
2	55,200	20.6	2110	3.05	0.329	2100	6.90	1300	1.06
3	61,700	23.7	2060	3.12	0.329	2010	7.16	1420	1.10
4	60,000	22.1	2150	3.04	0.329	2150	7.45	1460	1.10
5	51,200	12.0	3360	3.86	0.329	2650	3.06	851	1.12
6	39,400	13.4	2310	3.16	0.329	2220	3.31	805	1.09
7	39,000	12.4	2475	3.16	0.329	2380	3.20	789	1.10
					CARBON TETRACHLORIDE VAPOR				
8	5,340	14.8	283	1.85	0.0610	2510	0.533	196	1.05
					BENZENE VAPOR				
9	6,010	15.5	306	2.81	0.0806	1350	0.50	217	1.18
10	5,820	12.6	366	2.87	0.0806	1580	0.48	187	1.06
								Av.	1.11

SAMPLE CALCULATIONS (DATA FOR RUN 1, STEAM)

(*a*) *Calculation of* h_v

$$\frac{Q}{\theta} = (1585)\ (1.8)\ (37.8 - 19.0) = 53{,}600 \text{ B. t. u. per hr. (Col. 1, Table II).}$$

Temperature diff. (° C.) initial = 100.6 − 78.5 = 22.1
Final = 98.0 − 81.5 = 16.5

$$\text{Mean} = \frac{22.1 + 16.5}{2} = 19.3 \text{ (Col. 2, Table II).}$$

$$\text{Condensing surface} = \frac{(47.75)\ (0.675)\ (3.14)}{144} = 0.703 \text{ sq. ft.}$$

Observed film coefficient on vapor side (h_v) =

$$\frac{53{,}600}{(19.3)\ (1.8)\ (0.703)} = 2190 \text{ B. t. u. per hr. per ° F. per sq. ft. (Col. 3, Table II).}$$

$$\text{Temp. condensate} = \frac{100.6 + 98.0 - 19.3}{2} = 89.6\ (\text{°C.}).$$

Corresponding fluidity (see Fig. 2) = 3.05 (Col. 4, Table II).

Thermal conductivity (K) of condensate = value in Landolt-Börnstein's "Tabellen" at room temperature converted into English units (B. t. u. per hr. per sq. ft. per ° F. per ft.) by multiplying by 242 (Col. 5, Table II).

$$\frac{h_v}{fK} = \frac{2190}{(3.05)\ (0.329)} = 2180 \text{ (Col. 6, Table II).}$$

(*b*) *Calculation of* hw *(observed)*

To calculate the film coefficient on the water side, it is necessary to know the drop in temperature from the inner wall of the brass tube to the main body of the water in the tube. This equals the drop from the outer wall of the brass tube to the water, less the drop through the brass tube. The latter is readily calculated, since the thermal conductivity and thickness of the brass tube is known, namely, k = 63.0 B. t. u. per hr. per sq. ft. per ° F. per ft., and L = (0.675 − 0.49)/(2) (12) or 0.00771 ft.

The average area of the tube (based on the mean diameter of 0.583 in.) is (47.75) (0.583) (3.14)/144 = 0.607 sq. ft., and the resistance (L/KA) is (0.00771)/(63.0) (0.607) = 0.000202.

The ° C. drop through the brass tube is:

$$\frac{Q\ (0.000202)}{\theta\ (1.8)} = \frac{Q/\theta}{8910}$$

The drop for Run 1 is, then, 53,600/8910 = 6.0° C.

From outer wall to water (° C.) =

Initial = 78.5 − 19.0 = 59.5
Final = 81.5 − 37.8 = 43.7

$$\text{Mean} = \frac{59.5 + 43.7}{2} = 51.6.$$

From inner wall to water = 51.6 − 6.0 = 45.6° C.

$$\text{Inside cooling surface} = \frac{(47.75)\ (0.49)\ (3.14)}{144} = 0.510 \text{ sq. ft.}$$

$$\text{Observed coefficient, pipe to water, } hw = \frac{53{,}600}{(0.510)\ (1.8)\ (45.6)} = 1280$$

B. t. u. per hr. per ° F. per sq. ft. (Col. 8, Table II).

(*c*) *Predicted value film coefficient* (hw)

As shown under Case II of this series,

$hw = (340)\ (c_1)\ (\text{K})\ (f)\ (u^{0.76})\ (\text{S}^{0.17})$, where S = reciprocal of hydraulic radius in feet.

$$\text{K} = 0.329, \text{ as before.}$$

$$\text{S} = \text{shape factor} \doteq \frac{48}{0.49} = 98;\ \text{S}^{0.17} = 2.18.$$

$$hw = (340)\ (0.329)\ (c_1)\ (f)\ (u)^{0.76}\ (2.18) = 244\ (c_1)\ (f)\ (u^{0.76}).$$

In order to make a comparison, call cleanliness coefficient (c_1) = 1.00.

$$u = \frac{\text{(lbs. cooling water per hr.)}}{(62.3)\ \text{(cross-sectional area of tube, sq. ft.)}\ (3600)} = \text{average}$$

$$\text{water velocity in feet per second} = \frac{\text{(lbs. water per hr.)}}{(62.3)\ \frac{(0.49)\ (0.49)}{144}\ (0.785)\ (3600)} = \frac{\text{lbs. cool. water per hr.}}{294}.$$

For Run 1, u = 1,585/294 = 5.39 ft. per sec. (Col. 7, Table II).

$$\text{Average temp. of water} = \frac{19.0 + 37.8}{2} = 28.4\text{° C., and correspond-}$$

ing fluidity, f (from Fig. 2), is 1.22.

Whence h_w (predicted) = (244) (1.0) (1.22) $(5.39)^{0.76}$ = 1070 B. t. u. per hr. per sq. ft. per ° F.

Ratio of h_w (observed to calculated) = 1280/1070 = 1.20 (Col. 9, Table II).

DISCUSSION OF RESULTS

As shown by the first seven runs in Column 3, Table II, the average of the observed coefficient of heat transfer from condensing steam to pipe is about 2400 B. t. u. per hr. per ° F. per sq. ft., which checks fairly well with Clement and Garland's range of 1470 to 2410. Of course there is no reason to believe that the percentage of air in the steam was exactly the same in the two series. The observed coefficient from condensing vapor to pipe in the case of carbon tetrachloride and benzene (see Runs 8, 9, and 10, Col. 3, Table II) are approximately 280 and 340, respectively. Thus it is seen that the coefficient (h_v) in the case of steam is approximately eight times that observed for these two organic vapors.

If each individual value for the vapor film coefficient is divided by the conductivity and fluidity of the condensate, the average is 2240 for the steam runs, 2500 for the carbon tetrachloride, and about 1500 for the benzene (see Col. 6, Table II). Thus by correcting for fluidity and conductivity of the condensate, the eight-fold ratio between organic vapor and steam is reduced to less than two-fold. It will be noted that no allowance was made for variation of thermal conductivity of condensate with temperature, as no reliable data were available for this purpose. The values used for K in English units were obtained by multiplying those quoted for room temperature in the 1912 Landolt-Börnstein Tables by the conversion factor of 242, which converts thermal conductivity from c. g. s. (French) to English units.

It must be remembered that the ratio of h to fk should be further corrected for variations in concentration of noncondensable gas in the vapor and vapor velocity. No attempt was made in these preliminary experiments to control the percentage of noncondensable gas, which may have been present to the extent of the solubility of air in the liquids vaporized. In some of the runs excess vapor was used, and it appears that h/fk varies somewhat with vapor velocity. However, the few points available at present do not warrant the introduction of a velocity correction at this time. This work is being continued and it is hoped to publish additional data at an early date.

The experimental method used also made it possible to determine directly the film coefficient of heat transfer between the brass pipe and the cooling water, and the observed coefficients on the water side, h_w, are tabulated in Column 8, Table II. By means of an equation to be quoted in the next paper of this series, the value of this water film coefficient was predicted for each of these cases and the ratio of the observed to the predicted value is tabulated in Column 9, Table II. It will be seen that the maximum fluctuation is between 1.05 and 1.20, with an "average deviation" of 3.4 per cent from the average of the ten runs (1.11), and with a "probable deviation" of 1 per cent. It is felt that these "checks" are all that could be desired, and that they show that the coefficients, h_v, on the vapor side are reliable.

THERMAL CONDUCTIVITIES OF LIQUIDS

It has been shown above that the coefficient of heat transfer between a condensing vapor and a pipe is directly proportional to the thermal conductivity of the condensate, k, in English units. Where experimental data are not available, it is desirable to have a method of predicting the thermal conductivity of the liquid in question, because the experimental determination of the liquid conductivity is a difficult matter.

In 1885 H. F. Weber[9] derived an empirical relationship between liquid conductivity, k, specific heat, c, and specific gravity, s, and found that the conductivity was approximately proportional to the product of the other two factors. While this rule worked satisfactorily for certain liquids, it was found to deviate widely in the case of others, and in 1893 Weber[10] introduced an additional correction term which satisfactorily correlated the experimental values of thermal conductivities, as shown by Table III.

TABLE III—THERMAL CONDUCTIVITY OF LIQUID[1]

SUBSTANCE	Observer	Thermal Conductivity Eng. Units K	Sp. Gr. s	Sp. Ht. c	Mol. Wt. M	$\sqrt[3]{\frac{M}{s}}$	$\frac{K}{sc}=a_1$	$\frac{K}{sc}x\sqrt[3]{\frac{M}{s}} = a_2$
Methanol	Weber	0.12	0.81	0.586	32	3.41	0.263	0.895
Ethyl alcohol	Weber	0.1025	0.804	0.579	46	3.86	0.221	0.853
Propyl alcohol	Weber	0.0902	0.819	0.518	60	4.18	0.213	0.891
Chlorobenzene	Weber	0.0731	1.111	0.352	112.5	4.65	0.187	0.871
Carbon tetrachloride	Weber	0.0610	1.63	0.205	153.8	4.56	0.182	0.840
Benzene	Weber	0.0806	0.873	0.460	78.0	4.48	0.201	0.900
Aniline	Weber	0.0990	1.039	0.497	93	4.47	0.192	0.857
Toluene	Weber	0.0742	0.884	0.440	92	4.71	0.191	0.896
Carbon disulfide	Graetz	0.0647	1.263	0.240	76.1	3.93	0.215	0.840
Chloroform	Weber	0.0697	1.503	0.234	119.4	4.31	0.198	0.855
Water	Weber	0.329	1.000	1.006	18	2.62	0.329	0.861
Glycerol	Weber	0.155	1.26	0.576	92	4.18	0.214	0.893
Acetic acid	Weber	0.1141	1.069	0.487	60	3.83	0.220	0.842
					Av.		0.217	0.868

[1] All data are for room temperature; source Landolt-Börnstein "Tabellen," 1912 Ed.

Column 7, Table III, shows k divided by (s) (c), and it is seen that the proportionality constant a_1 in the expression

$$k = a_1cs \tag{9}$$

varies from 0.18 to 0.33. When the values in this column are multiplied by the cube root of the ratio of the molecular weight of liquid to the specific gravity of liquid, $\sqrt[3]{\frac{M}{s}}$, the variations in the revised constant, a_2, are much less, being only from 0.84 to 0.90. Hence, Weber's revised equation states that

$$k = 0.868\ (c)\ (s)\ \sqrt[3]{\frac{s}{M}}. \tag{10}$$

Thus by Equation 10 the predicted value of k for water (in English units) is (0.868) (1) (1)/$\sqrt[3]{18}$, or 0.332, which checks well with the experimental value for water of 0.329 B. t. u. per hr. per sq. ft. per °F. per ft. of thickness. Equation 10 indicates a variation of k with temperature. If the specific heat, c, rises more rapidly with increasing temperature than the specific gravity, s, decreases, the thermal conductivity, K, of the liquid will increase, while if the reverse is true, k will decrease. Now the effect of temperature on k has not been checked experimentally, but it is seen that the variations of c and s with temperature are in opposite directions, and hence the effect of temperature on K will not be great.

NOMENCLATURE TABLE

A = Area of heat transfer surface in sq. ft.
a_1 = "Constant" in Equation 9.
a_2 = Proportionality constant in Equation 10.
b = Experimentally determined coefficient of proportionality in Equation 7.
c = Specific heat of the condensate, B. t. u. per lb. per °F.
ι = Cleanliness factor in Equation 7.
= Fluidity of condensate at temperature in question relative to that of water at 20° C. (68° F.) as unity. See Fig. 2 for values.
H = *Over-all* coefficient of heat transfer from hot fluid to colder fluid expressed as B. t. u. per hr. per sq. ft. per °F. *over-all* temperature difference. See Equation 5.
h = *Film* coefficient of heat transfer in B. t. u. per hr. per sq. ft. film area per °F. temperature drop through the *film*.
h_v = Value of h from condensing vapor to pipe.
h_w = Value of h from pipe to cooling water.
k (or K) = thermal conductivity of substance as B. t. u. per hr. per sq. ft. per °F. drop in temperature through the substance per ft. of thickness. See Table III or Equation 10 for values of k for condensate.
L = Effective thickness of film in ft., or thickness of retaining wall in ft.
M = Molecular weight of condensate (see Equation 10).
m = Hydraulic radius in ft. = cross-sectional area (sq. ft.) of path of fluid divided by wetted perimeter in ft. For a circular pipe, m equals one-fourth the inside pipe diameter in ft.
n = Exponent of velocity, to be experimentally determined.
p = Exponent of hydraulic radius, to be experimentally determined.
Q/Θ = B. t. u. transferred per hr.
r = Thermal resistance of any definite part of the path = L/kA. See Equation 4.
s = Sp. gr. of condensate.
(ΔT) = Average *over-all* difference in temperature between hot and cold fluids (see Equation 5).
(Δt) = Average drop in temperature through any definite part of the path.
u = Average linear velocity of cooling water in ft. per sec.
v = Velocity of vapor in convenient units.

SUMMARY

1—The nature of the problems arising in the field of heat transfer has been outlined, together with a rational method for studying these problems.

2—A discussion is given of the nature of the variables likely to affect the coefficient of heat transfer in the important case of the flow of heat from condensing vapors to a pipe, and it is shown that the main variables are fluidity and thermal conductivity of the condensate and concentration of noncondensable gas in the vapors.

3—The results of preliminary experiments made to determine the numerical value of the coefficient of heat transfer between certain condensing vapors and a pipe show that the coefficient in the case of steam averages about 2400 B. t. u. per hr. per sq. ft. per °F. and 310 B. t. u. per hr. per sq. ft. per °F. in the case of benzene or carbon tetrachloride. It is seen that the coefficient for steam is approximately eight times that found in the case of benzene or carbon tetrachloride.

4—If this coefficient is divided in each case by the product of the thermal conductivity of the condensate and

the fluidity, the resulting values for these three vapors vary less than two-fold.

5—Inasmuch as thermal conductivity plays such an important part in determining the coefficient for any given vapor, H. F. Weber's equation for predicting the thermal conductivity is quoted and its application is illustrated by a table of values.

6—These experiments are being continued for the purpose of determining the effect of other variables which may affect the coefficient of heat transfer between condensing vapor and pipe.

7—From the results of these preliminary experiments the numerical value of the coefficient of heat transfer between (0.49 in. inside diameter) pipe and cooling water is found to vary from 200 to 1500 B. t. u. per hr. per sq. ft. per °F., while the water velocity varies from 0.5 to 7.5 ft. per sec. It is shown that these results check within 10 per cent of the values figured from an equation to be published in the next article of this series.

Acknowledgment

The writers wish to express their appreciation of suggestions offered by various friends, and of the work of Mr. A. Wishnew, who performed the greater part of the experimental work herein described.

Bibliography

1—Walker, Lewis and McAdams, "Chemical Engineering Notes."

2—(*a*) Carl Hering, *Chem. Met. Eng.*, **9** (1911), 652; (*b*) J. W. Richards, "Metallurgical Calculations," McGraw-Hill Book Co., Inc., **1918**; (*c*) See Note 1; (*d*) Marks' "Mechanical Engineering Handbook," McGraw-Hill Book Co., Inc., **1916**.

3—The existence of a stationary liquid or gas film at the point of contact with solid surfaces and its low heat conductivity has long been appreciated. The first mention of a water film was made by Peclet in 1844 ("Traite de la Chaleur-Liege," Chapter 8, p. 131) and since that date many investigators have checked this idea and demonstrated the existence of the film. The most tangible conception of the gas film is represented by Langmuir (*Phys. Rev.*, **34** (1912), 421) although the film concept was not his originally. The explanation in terms of the film concept of the effect of velocity upon heat transfer is definitely stated and the part played by velocity in tearing down this film noted.

4—Clement and Garland, Univ. of Ill., Engineering Experiment Station, *Bulletin* **40** (1909).

5—Nusselt (*Z. Ver. deut. Ing.*, **1908**, 1750) introduced the thermal conductivity of air in his formula for the film coefficient between a gas and a tube.

6—Bell (*Proc. Eng. Soc. W. Pa.*, **32** (1916–17), 797) points out that the *over-all* coefficient of heat transfer in a condenser would be a function of the fluidity of the condensate.

7—Orrok (*Trans. Am. Soc. Mech. Eng.*, **32**) introduces a cleanliness coefficient in connection with the *over-all* coefficient in a condenser, and a correction for the percentage of noncondensable gas in the steam.

8—The greater part of these data was taken from the undergraduate thesis of Wishnew (Mass. Inst. Tech. Chemical Engineering Thesis, **1921**).

9—H. F. Weber, *Berl. akad. Ber.*, **1885**, 809, and Exners Reppert, **22** (1886), 116.

10—H. F. Weber, *Wied. Ann.*, **48** (1893), 173.

The Decolorizing Action of Bone-Black[1]

By Claude H. Hall, Jr.

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This investigation was suggested by Bancroft[2] in his list of problems in colloid chemistry. There are only three important references bearing on the phase of the subject under discussion: Bancroft[3] gives a synoptical account of charcoal before the war, chiefly from an industrial point of view; Knecht[4] agrees with Patterson, but introduces no new evidence; and Patterson,[5] who describes at considerable length the extraction from bone-black, and the examination of a nitrogenous material to which is due the decolorizing action of the bone-black. The object of this investigation was to repeat the work of Patterson, which has never been confirmed, and to carry his researches a step further.

Experimental

The procedure finally adopted as most satisfactory is to digest about 15 g. of bone-black with 90 cc. of 15 per cent hydrochloric acid for 20 min., filter through an alundum crucible, and dry residue at about 120° C. The loss is approximately 30 per cent, chiefly mineral matter. Suspend the crucible containing the residue in a small beaker of concentrated sulfuric acid and allow it to remain on a water bath for 2 hrs. Filter through the same crucible and wash with 80 per cent sulfuric acid. The sulfuric acid extract is poured into 0.5 l. of water and the whole put aside for several hours. At the end of that time a brown precipitate will be found to have collected on the bottom of the beaker and may be filtered off through a fine filter. It is almost impossible to wash this precipitate, because it becomes colloidal as soon as the sulfuric acid is removed.

This extracted material is the active decolorizing agent of the bone-black, for a few drops of its concentrated suspension in water are equal in decolorizing action to several grams of good bone-black.

The next and most important step was to determine whether by the precipitation of this substance on wood charcoal, or other porous material, an active charcoal could be produced. The precipitation was carried out by mixing wood charcoal in the sulfuric acid suspension of the extract, adding water, and filtering. The material thus prepared was found to be about twice as active as the original bone-black, but this is easily explained by the fact that the extract from about 15 g. of bone-black was suspended on about 6 g. of wood charcoal.

Discussion

It may be concluded that the decolorizing action of bone-black is entirely due to a mixture of nitrogenous decomposition products of bone cartilage, etc., which are carried by the charcoal proper. These compounds are described by Patterson, and his results have been confirmed by the author. The compounds are insoluble in ethyl alcohol, ether, benzine, and chloroform, soluble in ammonium hydroxide, concentrated sulfuric acid, and concentrated hydrochloric acid, from the latter two of which they are precipitated by water. They have the empirical formula $C_{25}H_{20}N_4O_6$.

The real nature of these bodies and the mechanism of the reaction, however, still remain a mystery.

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[1] Presented before the Division of Physical and Inorganic Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] This Journal, **13** (1921), 155.

[3] *J. Phys. Chem.*, **24** (1920), 201.

[4] *J. Soc. Chem. Ind.*, **28** (1909), 700.

[5] *Ibid.*, **22** (1903), 608.

School for Water Plant Operators

During the week of January 16, 1922, a course on "Wholesome Water Production" is to be given in Dallas, Texas, under the auspices of the city Health Department, with the coöperation of the Texas State Board of Health and the Texas Water Works Association. This is the fourth short course offered free of charge to water plant operators. The work is not highly technical, but will cover comprehensive and practical points in the purification of water.

Potash from Kelp. V—The Applicability of Kelpchar as a Bleaching and Purifying Agent[1,2,3]

By J. W. Turrentine and H. G. Tanner

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During the past few years there has been an awakened industrial interest in the unique adsorptive quality of charcoal. In many instances, products that are ordinarily purified by recrystallization, distillation, or chemical precipitation of the foreign substances can now be brought to an even higher degree of purity by a simple treatment with activated charcoal. The utilization of activated charcoal, or decolorizing carbon, as it is frequently termed, by the industries in large quantities awaits only the advent of a carbon of high activity that can meet the requirements of the trade. The possibilities along this line have been observed by many, as is witnessed by the large volume of patents and articles on decolorizing carbon recently published, and the many researches and tests conducted by industrial concerns. Carbonaceous matter of various sorts has been treated in many different ways in the hope of finding a carbon that would surpass all others in its purifying powers.

Carbons, both of vegetable and animal origin, have been used for sugar purification for over a century, and during this time favoritism has been constantly shifting among bone-black, vegetable carbons, and purely chemical methods of bleaching the sugar sirups. Recent improvements in vegetable charcoal have inclined sugar manufacturers again in this direction.

Through the work of Zerban[4] it was established that a good decolorizing carbon could be made from the Pacific Coast kelp, *Macrocystis pyrifera*, which is the kelp that has been made the basis of the kelp products industry of Southern California. Zerban found that a carbon could be prepared that was equal to the best vegetable charcoals on the market, and some of these carbons, according to Coates,[5] possess from fifty to seventy-five times the decolorizing value of good bone-black.

Subsequent to Zerban's tests, the manufacture of bleaching carbon as a by-product in the extraction of potash from kelp was incorporated in the plans for this experimental plant, and researches looking to its large-scale production were immediately inaugurated. Success attended these studies. Bleaching carbon is being manufactured from kelp in quantities of one thousand pounds per day at a fair cost, and has been successfully introduced under the trade name "kelpchar." Its manufacture will be described in a subsequent paper.

The Testing of Carbons

At the outset it was necessary to develop a reliable and quick method of determining the activity of the carbon in order that the various processes of manufacture could be controlled. No universal method seemingly exists whereby the decolorizing value of carbon on solutions of different types may be expressed, since the decolorization of a complex solution is influenced by a great many factors. Carbons are specific in their action. For these reasons, it is desirable to test a carbon in a manner as nearly parallel as possible to the way in which it will be applied on a large scale.

Wickenden and Hassler[6] advocated testing carbons designed for the purification of oils by causing the carbon to remove a dye dissolved in oil. The weight of carbon producing the same degree of decolorization as a unit quantity of another carbon selected as a standard gave the necessary data for judging the value of the carbon under test. The method is open to the objection that the carbon in the laboratory is made to remove an impurity different from those which it is expected to remove in the plant. The carbon may be specific to the dye and not to the coloring matter occurring in the oil. Of course, any method of control analysis which is empirical depends for its accuracy upon the closeness wherewith the method parallels the procedure to be observed in actual practice.

Zerban and Freeland suggested a method of determining the decolorizing value of a carbon as applied to cane-sugar sirups. Their original method prescribed boiling a quantity of dilute cane molasses with a unit amount of carbon under examination and comparing the filtrate colorimetrically with another filtrate prepared from the same amount of a second carbon chosen as a standard. Unless the two carbons were of equal quality, the filtrates produced would not agree either as to tint or intensity of color. This made comparison difficult, and to overcome this Zerban[7] and his collaborators recommended the use of a Hess-Ives tint photometer. Carbons were compared on the basis of the amount of color left in solution. If one carbon removed all but 20 per cent of the color and another all but 5 per cent, the latter was four times as efficient as the former.

In this laboratory a method of evaluating carbon has been devised for plant control which possesses simplicity and has given satisfaction.

PROCEDURE—A stock solution of molasses is prepared by dissolving 50 g. of cane molasses in about a liter of water. After bringing the solution to neutrality with sodium hydroxide or acetic acid as required, 3 cc. of glacial acetic acid, 15 g. of sodium acetate, and 2 cc. of formaldehyde are added.

Of this solution 80 cc. are brought to boiling with 2 g. of the carbon to be tested. The mixture is filtered while still hot, and the filtrate is matched with a set of filtrates prepared in the same manner but with different quantities of a standard carbon. The weights of the unknown and the standard carbon samples producing the same degree of decolorization are taken as representing the relative efficiencies of these carbons. For convenience, the ratio of these weights is calculated to the percentage basis, figuring the standard carbon as 100 per cent.

The standard carbon may be any carbon arbitrarily selected for the comparison. The set of standard filtrates deteriorates on standing, and should be prepared fresh daily.

DISCUSSION—This method combines reliability with speed. The presence of sodium acetate does not appreciably affect the action of the carbon on the natural impurities in the sugar solution, and serves to maintain a constant H-ion concentration throughout a series of tests. This is very important since the amount of color adsorbed by a carbon is very sensitive to changes in acidity (or alkalinity), especially near the neutral point. It frequently happens, when testing carbons from widely different sources, that some of them will contain a small amount of acid and others, alkali. If the sugar solution be neutral or be not fortified against changes in concentration of either H or OH ion, one carbon may be

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[1] Received August 26, 1921.

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

[3] Parts I to IV, This Journal, 11 (1919), 864; 12 (1920), 682, 786; 13 (1921), 605.

[4] This Journal, 10 (1918), 812.

[5] *Ibid.*, 13 (1921), 150.

[6] *Ibid.*, 8 (1916), 519.

[7] Louisiana State Agricultural Experiment Station, *Bulletin* 167 (1919), 12.

tested in an alkaline medium and the other in acid. The results will not be comparable in the least degree.

With adjustments in concentration to suit the individual requirements, beet molasses or malt sirup may be used instead of cane molasses.

No buffer salt is required if carbons are to be tested on solutions that are strongly acid, such as concentrated citric or lactic acid.

The Applications of Kelpchar

CANE SUGAR—The sugar manufacturer is fortunate in having a choice of methods for refining his product. He may resort to either purely chemical or purely adsorptive processes, or a combination of the two. Zerban[8] has made extensive experiments with the physical methods of refining sugar, and concludes that cane juice clarification may be brought about without the use of any chemicals whatever, but simply by the use of efficient adsorbents. It was found by laboratory and factory tests that in comparison with the sulfitation process, at least the same quantity of first sugar of greatly superior quality can be made by clarification with 0.5 per cent kieselguhr, followed by treatment with 1 per cent of an active vegetable carbon, and filtering the juice in both cases, which is easily and rapidly done. The first molasses, he states, is so very light in color that the recovery of high-grade sugar can probably be materially increased, still leaving a molasses of higher market value than that made by the usual plantation methods. Essentially the same result was obtained with kelpchar.

More recent tests of this nonchemical method of preparing white sugar direct were conducted by Mr. J. F. Brewster of the Bureau of Chemistry, U. S. Department of Agriculture, and others at the Louisiana State University Experiment Station at New Orleans. Cane juice from the mill was filtered hot, first through kieselguhr to remove coarse suspended matter, then was treated with 1 per cent of carbon (ash- and moisture-free basis) calculated on the original weight of juice. These treatments were made at the Station sugar house, and may be regarded as being on a factory scale as far as the filtration is concerned. An ordinary plate and frame filter press was used. Parallel runs were made with four carbons; carbon A, an imported carbon; B and C, American carbons; and kelpchar.

Table I shows the total color remaining in the juice after treatment with kieselguhr and then with carbon. These color units were determined by means of the Hess-Ives tint photometer. Table II shows colloids remaining in the juices after treatment with kieselguhr and carbon, respectively. The results were obtained by dialyzing the juices until free from crystalloids, then evaporating to dryness, and weighing the solid residue. Results are expressed in g. per 100 cc. of juice.

TABLE I—TOTAL COLOR REMAINING IN JUICES AFTER TREATMENT

RUN No.		TOTAL COLOR	CARBON	TOTAL COLOR
1	Kieselguhr	83.17	A	13.40
2	Kieselguhr	84.56	Kelpchar	13.36
3	Kieselguhr	86.03	B	3.20
4	Kieselguhr	81.56	C	16.90

The color remaining in the juice and not that removed is regarded as determining the usefulness of the decolorizing agent, since the color remaining will appear in the sugar and molasses.

TABLE II—COLLOIDS IN JUICES AFTER TREATMENT

RUN No.		Colloids G. in 100 Cc.	CARBON	Colloids G. in 100 Cc.
1	Kieselguhr	0.0226	A	0.0111
2	Kieselguhr	0.0318	Kelpchar	0.0114
3	Kieselguhr	0.0371	B	0.0113
4	Kieselguhr	0.0333	C	0.0234

Thus, the sugar manufacturer may make white sugar direct from cane juice, or he may make brown sugar and sell to the refineries, there to be redissolved, bleached, and recrystallized. Refinery practice prescribes most commonly the use of bone-black as the bleaching agent. Kelpchar would appear to be a desirable substitute. The foregoing results, from a long list, would seem to establish beyond a peradventure the ability of kelpchar to decolorize sugar solutions. Its activity has been shown to be about twenty-five times that of bone-black. The significance of this fact will be discussed subsequently. Its use necessarily following that prescribed for active carbons, it cannot be used in percolators but must be added to the solutions and filtered out—a simple and easily standardized process.

Sugar refiners desire a charcoal that will remove inorganic substances, such as lime and iron, as well as the colored organic compounds. It is unquestionable that charcoals do adsorb inorganic material, even of low molecular weight, although in absolute units the quantity is seldom more than a few milligrams per gram of charcoal.[9] But since there is only a small percentage of inorganic material in sugar sirup, it may be that most of it likewise can be eliminated by kelpchar. No data are available for proof, but it is only reasonable to suppose that the greater the adsorptive ability of charcoal, the greater would be its tendency to remove the inorganic impurities by adsorption. The impression prevails that bone-black removes a large portion of the inorganic salts present in sugar solutions purified therewith, but records of the actual tests on which this belief is founded seem to be lacking. If these cannot be removed sufficiently by direct adsorption, they might possibly be converted into insoluble compounds which could be removed by filtration.

CARAMEL—A test solution of sugar was employed which had been colored to read 50. The percentage color removed was read as the percentage of decolorization. Comparison was made between kelpchar and two of the best known imported carbons. These are designated as "A" and "B." The former is the same carbon as that designated by the same letter in the tests on cane sugar recorded above; and, likewise, in tests on glucose given below.[01]

TABLE III—DECOLORIZATION OF CARAMEL SOLUTION

Weight of Sample Gram	KELPCHAR		CARBON A		CARBON B	
	Reading	Per cent Color Removed	Reading	Per cent Color Removed	Reading	Per cent Color Removed
0.25	11.0	78	16.5	67	19.0	62
0.50	7.5	85	10.5	79	11.0	78
0.75	5.5	89	8.0	84	8.0	84
1.00	4.5	91	7.0	86	7.0	86

GLUCOSE—The effects of various amounts of kelpchar, carbons A and B, and kieselguhr were determined on light glucose liquor as it came from the press. The decolorizing agents were added and the mixture heated for one-half hour on the steam bath, then filtered, and the colors read in a four-inch cell with yellow and red Lovibond glasses. The filtered samples were placed on ice over night and the brilliancy or haziness noted. The original liquor tested 4 yellow and 1 red. It became hazy very quickly. All solutions treated with kieselguhr became hazy.

TABLE IV—DECOLORIZATION OF LIGHT GLUCOSE LIQUORS

Per cent Material	KELPCHAR			CARBON A			CARBON B		
	Yellow	Red	Condition	Yellow	Red	Condition	Yellow	Red	Condition
0.1	3.2	1.0	Hazy						
0.2	1.2	0.3	Brilliant	0.27	0.7	(Slightly hazy)	2.0	0.2	Brilliant
0.4	0.7	0.1	Brilliant				0.9	0.1	Brilliant
0.6	0.4	0.1	Brilliant	0.8	0.2	Brilliant	0.7	0.1	Brilliant
0.8	0.2	0.1	Brilliant				0.5	0.1	Brilliant
1.0	0.2	0	Brilliant	0.7	0.1	Brilliant	0.4	0	Brilliant

With kelpchar and carbon B very brilliant liquors were obtained where 0.2 per cent or more decolorizing material was used. Below 0.2 per cent the liquor became hazy on

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[8] Louisiana State Agricultural Experiment Station, *Bulletin* **173** (1920).

[9] Osaka, *Mem. Coll. Sci. Kyoto*, **1** (1915), 257.

[10] This test and the following one on glucose were made in the Edgewater plant of the Corn Products Refining Co., and the results were submitted through the courtesy of Dr. C. E. G. Porst.

chilling. Although in this case the only experiment performed was with 0.1 per cent kelpchar, hazy liquors were also formerly obtained when 0.1 per cent carbon B was used, whereas with 0.2 per cent carbon B the light liquor from the presses remained brilliant for several days. These experiments confirm the conclusion that 0.2 per cent activated carbons produce permanently brilliant glucose liquor. Below this amount, liquors do not remain brilliant. Kieselguhr, even up to 1 per cent, gave hazy liquors, and had but little effect on clarifying the liquors.

MALT SIRUP—The high prices obtainable for sugar and sugar substitutes which coincided with the inauguration of national prohibition had as a result the stimulation of interest in the manufacture of malt sirup as a product to which breweries and distilleries could be applied. Malt sirup is naturally yellow or brown in color, due to the presence of such substances as chlorophyll, polyphenols, iron and caramel, and it finds a more ready acceptance and a less restricted use if decolorized. Its bleaching proved a more difficult matter than that of cane sugar. Quantities of kelpchar sufficient to bleach to absolute colorlessness a solution of cane molasses of an equal intensity of color still left perceptible yellows in the solutions of malt sirup. In addition, colloidal materials, some of them of the nature of peptones and albumens, which slowly precipitated and caused a reversion to haziness, were likewise removable by kelpchar.

In testing the activity of kelpchar as a bleaching agent for malt sirup, the following method has been recommended:

To 1 kg. of sirup add 2200 cc. water. After thorough mixing the Brix reading should be 25° (sp. gr. 1.106 at 17.5° C.), a variation of 1° either way being allowable. To a liter of this solution 20 g. of the carbon to be tested are added, and the whole placed on a water bath where it is brought to a temperature of 90° C. and permitted to remain thereat for 20 min. It is filtered through double filter papers, the filtrate being returned if not clear. The filtrate is then compared colorimetrically with the original solution, with a Schreiner or other colorimeter. The color should be reduced to 95 per cent of its original intensity. The volumes may be varied to suit the convenience of the operator.

For malt sirup a certain latitude in characteristics of the carbon is allowable. Thus water-soluble sulfates and chlorides of the alkalies and alkaline earths are permissible to the extent of 1 per cent, and free hydrochloric or sulfuric acid to the extent of 0.2 per cent. The carbon must be acid or neutral.

CITRIC ACID—In the manufacture of citric acid from lemons, the product is colored even after the acid has been precipitated as calcium citrate from the original juice and filtered, and the acid liberated again with sulfuric acid. Sufficient coloring matter is carried through the process to leave the solution dark brown and to require bleaching. The coloring matter here present is for the most part of the sort that can be adsorbed with carbons. However, in most cases enough iron salts are taken up during the process of manufacture to impart a distinct coloration on its own account. The ferric ion is not readily adsorbed from such solutions and it is, therefore, precipitated as the ferrocyanide. For the removal of the other coloring matter kelpchar is ideal, its efficacy having been established by laboratory and plant tests, and likewise by its application over a considerable period of time as the adopted plant reagent of a large citric acid manufactory.

The requirements of a carbon for the decolorization of citric acid are rigorous. Since an acid is sought of the purity prescribed by the U. S. P., it is essential that no impurity be taken up from the carbon. Therefore, the carbon must contain no alkalies, magnesium salts, or other soluble ash constituents. It must be free from hydrochloric acid and must not contain more than a trace of sulfuric acid. A small amount of calcium sulfate is allowable, but traces of iron or other things which will impart color are prohibited. There are few applications of carbons where more strict requirements are to be met.

OILS—Glick[11] has studied the action of different charcoals on a number of vegetable oils and finds that, with the exception of coconut oil, a mixture of fuller's earth and charcoal is more effective than fuller's earth alone. Charcoal alone is better on coconut oil.

The application of kelpchar to the purification of oils is a field in which but little work has been done, but the results obtained already indicate a potentially wide usefulness for this reagent in the oil industries. The mobility of the liquid to which the carbon is applied being a factor in the rate of reaction, the more viscous oils are the more difficult to bleach. Thus, the results obtained with oils are apt to be disappointing when compared with those obtained with aqueous solutions. It is only when the various decolorizing agents for oils are compared that the value of kelpchar is shown. However, it has been shown to effect a marked improvement in some classes of mineral oils where it both lightens the color and increases the brilliancy, and a moderate application to specimens of yellow gasoline and distillate rendered them entirely colorless.

DYE INTERMEDIATES—Starting with the purest of chemicals and with elaborate control of the reactions in preparing an intermediate, it is seldom possible to prevent entirely the formation of tars. Consequently the intermediates must be purified. The final purification is usually by distillation or recrystallization, but these methods are not always as effective as desired. Adsorbents such as bone charcoal and fuller's earth have been used to some extent to remove the tars, but their low activity has prevented their wide application. On the other hand, kelpchar because of its great activity has been found to be highly efficacious in this respect.

A quantity of impure aniline, for example, which showed a pronounced orange-red color was heated to the boiling point with 2 per cent by weight of kelpchar and immediately filtered. This eliminated the orange tint. The purified aniline was diazotized and coupled with β-naphthol, and the product filtered and dried. It was decidedly more brilliant and of a purer shade of red than the same pigment made from the unpurified aniline. A further improvement was obtained when the β-naphthol solution (in sodium carbonate) was likewise purified by treating with kelpchar. Also, crude o-toluidine, xylidine, and p-nitroaniline[12] were purified, the former two by the method applied to aniline. In the purification of p-nitroaniline, 100 g. of the material were dissolved in hot 30 per cent H_2SO_4, 2 g. of kelpchar added, and the mixture filtered. The filtrate was added to a large volume of water, and the precipitated p-nitroaniline filtered off and dried. The appearance of the product was greatly improved, and when coupled with β-naphthol it gave a product that was far more brilliant than that produced by a similar process of purification without the use of kelpchar.

PRECIPITATION OF METALS—That charcoal precipitates gold from solutions of its haloid salts has long been known,[13] and commercial application was made of this principle at some plants formerly using the chlorine process for extracting gold from its ores.[14] Since 1888 chlorination has been gradually displaced by the cyanide process, in which gold is dissolved from ore as potassium or sodium aurocyanide $KAu(CN)_2$.

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[11] *Cotton Oil Press*, **4** (1921), No. 10, 41.

[12] Contributed through the courtesy of E. I. du Pont de Nemours & Co.

[13] Wm. Henry, "An Epitome of Chemistry," London, **1801**, 95; Weffen, *Ann.*, **55** (1845), 241; **59** (1846), 354.

[14] Sir T. K. Rose, "Metallurgy of Gold," 6th Ed., **1919**, 319.

On the large scale this gold is usually recovered from the highly dilute solution (commonly from one to ten parts gold per million) by metallic zinc in the form of shavings or dust, but charcoal has been employed to some extent as a precipitant in Australia and New Zealand.[15]

The comparison of kelpchar with other charcoals and with zinc dust as a precipitant of gold from cyanide solutions was made by Dr. W. J. Sharwood of the Homestake Mining Co., Lead, S. D., through whose courtesy the following statement of results has been made possible.[16]

Table V—Precipitation of Gold from Cyanide Solution by Charcoals and Zinc Dust

Grams to 300 Cc.	Precipitant	Percentage Pptd. of Original Gold
0.5	Graphite, powdered	None
0.5	Old pine charcoal, 100-mesh	None
0.5	Reheated pine charcoal, 100-mesh	95.0
0.5	Peach-pit charcoal, 100-mesh	90.7
0.5	Kelp charcoal sifted through 100-mesh, coarse rejected	70.0
0.3	Old pine charcoal, 100-mesh	None
0.3	Reheated pine charcoal, 100-mesh	85.8
0.3	Peach-pit charcoal, 100-mesh	80.3
0.3	Kelp charcoal, unsifted, only 5-min. contact, preliminary test	40.3
0.3	Kelp charcoal, 100-mesh	53.7
0.3	Kelp charcoal, 100-mesh	55.2
0.3	Kelp charcoal, reheated, 100-mesh	84.9
0.3	Special zinc dust, 300-mesh	73.0
0.1	Special zinc dust, 300-mesh	38.1
0.03	Special zinc dust, 300-mesh	5.0

It may be of interest to note here that similar zinc dust, when used on a very large scale in still smaller proportions than in the last test, 0.004 to 0.005 per cent of the weight of solution carrying $4.00 to $6.00 gold per ton (7 to 10 parts gold per million), the zinc being added at the moment of pumping to a filter press, regularly precipitates 99.8 per cent of the gold contents. Comparing this with the above results makes it seem probable that kelpchar, if applied under favorable conditions, might show a greater efficiency as a gold precipitant than these small-scale tests indicate.

These tests were made on a cyanide mill solution whose gold value was about $4.20 per ton. Agitation was effected by shaking for exactly 10 min. in a mechanical shaker with a horizontal throw of 2 in. and at a speed of 240 r. p. m. The solution was contained in bottles of 360-cc. capacity. After shaking, it was filtered only once.

Qualitatively, kelpchar likewise precipitates gold rapidly from haloid solutions.

Seemingly, what is being dealt with in these experiments is not activity of decolorizing carbons as that term is understood in the other parts of this paper. Since charcoals of no recognized ability as decolorizing carbons are more efficient precipitants for gold than kelpchar, it is obvious that the function here recorded is of a different order from that to which kelpchar owes its value.

OTHER APPLICATIONS—The efficacy of kelpchar has been demonstrated in the bleaching of lactic acid; vinegar; molasses for the growing of white yeast; glycerol; grape, and other fruit juices, and fruit sirups and concentrates; honey; potassium tartrate and tartaric acid; phosphoric acid; photographic chemicals; alkaloids; and pharmaceuticals.

The proposed applications for kelpchar are numerous and are promising of usefulness. The stability of explosives could probably be enhanced through the removal by kelpchar of those impurities, such as the highly nitrated phenolic compounds in TNT[17] which contribute to instability. The relationship between adsorption and surface phenomena suggests the use of kelpchar as a contact or catalytic agent to induce desired reactions.[18] The catalytic action of active carbons in reactions between gases is illustrated by their use in the formation of carbon tetrachloride from chlorine and natural gas. It should prove of value in promoting reactions in both gaseous and liquid media. The adsorption of bacteria from solutions with active carbons should be a simple matter and more nearly quantitative with a carbon of the activity of kelpchar. Likewise the results obtained from the internal application of charcoal to correct digestive disorders should be much more pronounced where active carbons of the order of kelpchar are used. Its application in the field of gas-absorbing charcoals is now under investigation.

Reactivation of Kelpchar

The restoration of the decolorizing power of kelpchar has been effected satisfactorily by the established methods of reactivating carbons, and, in addition, new and original processes of accomplishing that purpose have been developed.

Numerous processes have been described and patents granted for reactivating spent carbons, but the principles involved are few. What is desired essentially is the removal of the coloring matter and other impurities which have saturated the adsorptive capacity of the carbons. Their removal is accomplished by heating the carbon to a temperature which effects their volatilization, or, more commonly, their destructive distillation and possibly the simultaneous activation of any residual carbon remaining after their distillation. Or, where the chemical nature of the adsorbed impurities is understood, the carbon may be treated with some reagent which will enter into combination with the impurities to form compounds more soluble, so that they can be washed out without a change of medium. Or, they may be oxidized by the application of an oxidizing agent of the nature of chromate or permanganate. This likewise presupposes an understanding of the nature of the compounds to be removed.

The reactivation of vegetable carbons by heating naturally suggests itself, since that is the conventional method of reactivating bone-black. The bone-black is washed, dried, and fed by gravity through vertical retorts. The granular nature of the material and its relatively high density makes this possible. The high percentage of ash, also, reduces the tendency to oxidation and consequent loss. Vertical retorts have not been found to be wholly applicable to the reactivation of vegetable carbons, however, since they are pulverulent and of low density and do not readily flow through a vertical retort of the diameter required for efficient heating. Horizontal retorts and mechanical conveying, accordingly, have been adopted.

The disadvantages of this method of reactivation are pronounced. The carbon must be dried, and to transport the carbon from the filter, where separated, and prepare it for re-burning requires considerable manipulation and time. The retorts are expensive to construct and to operate. Being made of cast iron and being maintained at the temperature required for reactivation (a red heat), they are easily damaged and readily deteriorate. It is difficult to prevent the escape of dust and the consequent disfigurement of the plant. The method has little more than precedent to recommend it. However, the cost involved where active carbons are being used, while per unit weight no greater, per unit of activity is vastly less. If such an expense for reactivation is allowable where bone-black is the reagent used, it is relatively insignificant where active carbons are employed.

The following method has been applied to the reactivation of kelpchar with entire success: First, on the laboratory scale, kelpchar was saturated with the impurities contained in cane molasses, and was then washed, dried, and retorted

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[15] W. D. Johnston, U. S. Patent 522,260 (1894); W. H. Gaze, "Practical Cyanide Operations," London, 1898, 13 and 121; *Chem. Eng. Min. Rev.*, 10 (1917), 48; *Chem. Met. Eng.*, 18 (1918), 642.

[16] See also Clark & Sharwood, *J. Chem. Met. Soc. S. Africa*, 10 (1910), 234.

[17] Weiss, This Journal, 10 (1918), 1028.

[18] This Journal, 11 (1919), 639.

at 800° C. It was then cooled, washed with dilute hydrochloric acid and then with water, and dried. Its activity had been completely restored. Subsequently, users of kelpchar reported that they had repeatedly reactivated it by this method in an entirely satisfactory manner.

WET METHODS—The better known of the wet methods of reactivation is the one prescribing the use of a caustic wash. Lime, caustic soda, and soda ash are the alkalies recommended. Where these unite with the coloring matter adsorbed on the carbon to form compounds much more soluble than the coloring matter uncombined, their use is efficacious. Thus, in the bleaching of sugar, the coloring matter is made up principally of phenolic compounds, which form highly soluble salts with caustic soda, and these salts are easily washed off with water. Similarly, basic pigments are removable with an acid wash. The principle is applicable where the chemical nature of the pigment is known. While this method is applied commercially to only a limited extent, it offers some distinct advantages in the saving of the cost, maintenance and operation of retorts, loss of carbon through combustion, and the elimination of dust. In the proposed automatic and countercurrent application of kelpchar,[19] the apparatus for the reactivation of the carbon would be similar in principle and possibly in design to that used in its application as a bleaching agent, and could easily be a continuation of it. The costs involved for caustic, acid, and water, and for operating the apparatus, would not be excessive. It has much to recommend its further study and application.

Kelpchar has been reactivated as follows: A portion of the material which had been saturated with the coloring matter adsorbed from cane molasses was washed with a dilute solution of caustic soda. After washing to remove the excess of caustic, and treating with hydrochloric acid and then with water to restore neutrality, the carbon was dried. It was found to have regained entirely its original activity.

CHEMICAL METHODS—The strictly chemical methods of reactivation offer a wide field for research. It remains only to determine the chemical identity of the compounds saturating the spent carbon, whereupon reagents which will oxidize or reduce or otherwise alter or destroy them or render them soluble can be discovered and applied. They can be applied countercurrentwise so as to insure their efficient use, and their application can be made entirely automatic.

The electrolysis of an acid, alkaline, or neutral salt solution either in anode or cathode compartment, or without diaphragm, carrying a suspension of the kelpchar would result in the liberation of electrolytic products of a nature to oxidize or reduce the materials to be removed from the carbon. In addition, there would be the tendency of the coloring matter to migrate under the influence of the electric current away from the carbon.

Little work, also, has been reported on methods involving a change in medium. Compounds of sufficiently low solubility to admit of their being adsorbed from water solution might be so soluble in some other medium, such as alcohol, solvent naphtha, or benzene, as to make possible their removal by washing with such a liquid. The destruction and removal of the organic matter on the carbon by fermentation has been suggested and shown to be applicable,[20] but is restricted to those compounds that are fermentable.

In short, while the best known method of reactivating kelpchar in particular and decolorizing carbons in general, the retort method, is efficacious and economical and answers the requirements of the moment, it would appear to be destined to yield to more exact and efficient methods. The potential advantages of the wet methods are such as to warrant their prompt and elaborate study.

IMPORTANT CHARACTERISTICS OF A GOOD DECOLORIZING CARBON

ACTIVITY OR ADSORPTIVE CAPACITY—By the activity of a carbon is meant its ability to remove coloring matter or other impurity from a liquid. The greater the activity, the smaller the amount required for a given result. The greater the activity, other things being equal, the greater the intrinsic value. A reduction in the quantity of carbon reduces the floor space and size of filters required, affording a saving in the initial cost of buildings and apparatus, decreases the operating costs for filter cloths, labor and repairs, and increases output. With a very slight increase in the amount of carbon used, greater decolorization of the solution may be had which, in the case of a crystalline product, means less washing of the crystals on the centrifugals. A smaller quantity of carbon means a smaller loss of product in the filter cake, and a smaller consumption of wash water. Only a small amount of carbon has to be handled in the reactivation apparatus, there being an attendant saving in both installation and operation. This cost being so much per pound, it should be inversely proportional to the activity. This is of especial importance, as the cost of reactivating bone-black, for example, represents a heavy expense in the aggregate.

Since adsorptive capacity is certainly the most important characteristic of a decolorizing carbon, it is inevitable that such carbons will be purchased in terms of their activity, at so much per unit of activity. The procedure in use in the buying of potash salts, coal, and numberless other commodities purchased on the basis of analysis and intrinsic value has not been established in the purchase of carbons. In arriving at a price which he is willing to pay, the purchaser is inclined to take bone-black as the standard, but considers the unit of weight rather than the unit of activity. At present no unit of activity has been established, but this only awaits the prosecution of some greatly needed researches to that end. When it is established, kelpchar, which on analysis shows an activity twenty-five times that of bone-black, will bring a price twenty-five times that of bone-black. Furthermore, processes of manufacture developed for kelpchar which make it possible to produce grades of greatly increased activity over that now produced will be put into practice, where now in the absence of a fair appreciation of higher degrees of activity only the lower grades can with profit be manufactured.

SIZE OF PARTICLES—The higher degrees of activity are obtainable only with certain degrees of fineness. The ideal of a carbon coarse enough to admit of percolation and possessing the activity of kelpchar does not seem to be attainable. Adsorption being a surface phenomenon, either a fine state of division or extreme porosity is a prerequisite.

Assuming the same degree of effective activity, the coarser a carbon is, the better, since it is more readily filtered from a solution. Filtration is more rapid and a heavier filter cake is allowable on the filters, and a coarser filter medium can be used. Conversely, the finer a carbon is, assuming the same shape of carbon particle, the sooner will a filter become clogged and the more often must the filtering operation be interrupted. As an aid to filtration, coarser materials, such as kieselguhr, are sometimes added with the carbon. But the logical way to overcome the difficulty is to use filters which make automatic or at least easy the frequent breaking and removal of the filter cake. The rotary vacuum and the centrifugal filters in many applications are ideal for this purpose.

The degree of fineness of kelpchar is determined largely by the method of manufacture. While fine, it is remarkably free-filtering. A typical specimen on analysis showed a physical composition such that 9 per cent was retained on a

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[19] THIS JOURNAL, 13 (1921), 605.

[20] *J. Soc. Chem. Ind.*, 16 (1903), 565

20-mesh sieve; 17.8 per cent on a 40-mesh; 19 per cent on a 60-mesh; 5.5 per cent on an 80-mesh; 5.4 per cent on a 100-mesh; 44 per cent passing the last named.

With the development of the art it might prove advantageous to screen to uniform sizes. On the other hand, the presence of coarse particles assists in the removal of the finer.

SHAPE OF PARTICLE—Size of particle is not the sole factor determining filterability. Much depends on the shape, since the rate of filtration depends on the maintenance of open interstices between the particles, yet wide differences in filterability are noted where it is not possible to observe under the microscope a difference in shape of particle to account for them.

HARDNESS OF PARTICLES—While it is hoped that a carbon will be offered the trade which is both highly active and at the same time cheap enough to warrant its being thrown away after one usage, the probabilities are that the cost of reactivating will always be less than that of manufacturing. If carbons are to be used repeatedly, unless their particles are hard they will break down under repeated handling and eventually be objectionably fine. On the other hand, the harder the particle, the more abrasive the carbon is and the shorter will be the life of the apparatus used in handling it. The latter is the more serious objection. It is easier to design apparatus which will handle the carbon without unduly breaking down the particles than it is to find materials of construction which will withstand abrasive action. Here is an excellent field for engineering research.

ABSENCE OF SOLUBLE IMPURITIES—Carbons of vegetable origin contain residues of the inorganic constituents of vegetable matter. Thus, there may be expected small amounts of calcium, magnesium, and iron, the amount depending on the process of manufacture. The calcium may be expected in the form of sulfate since in this form it is the more difficult to remove. The presence of sulfates leads to the formation of sulfides and free sulfur through their reduction. Since the preparation of carbon from activated charcoal consists essentially in the removal of these impurities with both acid and water, the amount in which they are present depends on the thoroughness with which it has been refined. Small amounts of free acid may likewise remain.

Insoluble impurities are objectionable only as diluents. The soluble ones are objectionable in the product if they interfere with subsequent crystallization, as may calcium sulfate; or, if they add color, as may iron compounds; or, if they add unduly to the impurity of the product, as all of them may. Free sulfur may be taken up by oils and their color, taste, and odor altered. The ease with which sulfur may be removed from carbons leaves no justification for its presence. Free acid acts on certain coloring matter possessing the characteristics of indicators, changing their color and in cases affording a false bleaching action. The presence of an excess of acid in carbons applied to sugar may induce inversion. On the other hand, the presence of acid may depress the solubility of the impurity to be removed, and thus be of material aid. Where it increases this solubility it is correspondingly objectionable.

SUMMARY

A simplified method of testing decolorizing carbons has been given.

Results are reported of laboratory and plant-scale tests of kelpchar used as a decolorizing agent applied to numerous materials and new uses are suggested.

Methods of reactivating spent carbons are discussed.

The important characteristics of decolorizing carbons are detailed.

Determination of Monobromated Camphor[1,2,3]

By Elgar O. Eaton

BUREAU OF CHEMISTRY, WASHINGTON, D. C.

The need of quantitative method for determining monobromated camphor arose some time ago in connection with the analysis of tablets, prior to the appearance of Emery's procedure for the estimation of this substance in migraine tablets.[4] The literature available in this laboratory having failed to disclose any finished method directly suited to the problem, attention was directed to a statement made in Schmidt's "Pharmaceutische Chemie,"[5] to the effect that silver oxide decomposes monobromated camphor in the presence of chloroform into silver bromide and other products. Some preliminary experiments showed that the mixture resulting from the addition of 0.5 *N* alcoholic potassium hydroxide to alcoholic silver nitrate, and containing among other things silver oxide, constitutes an ideal solvent for monobromated camphor, and hence a more rational medium in which to bring about the desired reaction, since it eliminates the possibility of chloride formation, as would be the case if chloroform were used.

METHOD

To an amount of the uniformly powdered sample equivalent to about 0.2 g. of monobromated camphor, accurately weighed into a small beaker, add 25 cc. alcohol, warm on the steam bath, filter into a flask, wash both beaker and filter with warm alcohol until all the camphor derivative is removed, add 50 cc. 0.5 *N* alcoholic potassium hydroxide, follow with 25 cc. of alcoholic silver nitrate (0.2 g. in 50 cc. alcohol), connect with a ground-on reflux after the addition of a few glass beads, and boil gently 1.5 hrs., adding at intervals through the condenser the remainder (25 cc.) of the alcoholic silver nitrate. Cool, disconnect, and transfer contents to a large porcelain evaporating dish. Dilute with water to 200 cc. and decant into a beaker, washing the precipitate with water by decantation. Boil the aqueous-alcoholic solution 5 min. with 1 g. of zinc dust in order to clarify it, filter into another beaker, washing thoroughly with water, and add dilute nitric acid to decided acidity and aqueous silver nitrate to complete precipitation. Determine bromides by the usual gravimetric method. (Factor for monobromated camphor = 1.23.)

The special apparatus consists of a 250-cc. flask with ground-on condenser. This is not imperative but if available should be used.

RESULTS

The following results were obtained with this procedure:

SAMPLE	PER CENT
Commercial monobromated camphor....	98.4, 95.8, 96.9, 99.9
Uncoated tablet, labeled 3 grs...........	2.77, 2.77, 2.82
Sugar-coated tablet, labeled 5 grs........	4.71, 4.78

It was found that the addition of more water lowered the results, and that it was advantageous to add the alcoholic silver nitrate in several portions through the condenser to the hot alcoholic potash solution rather than to apply all the silver salt at one time. It is possible that, after the silver oxide becomes agglutinated, the catalytic action, to which the reaction appears to be due, is at an end. It was further shown that potassium bromide is formed and not silver bromide, also that no bromate is produced.

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[1] Received July 13, 1921.

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

[3] This article has been reviewed by Dr. W. O. Emery prior to publication.

[4] THIS JOURNAL, **11** (1919), 756.

[5] II, Vol. 2 (1911), 1393.

Reactions of Accelerators during Vulcanization. IV—Mechanism of the Action of Zinc Compounds[1]

By C. W. Bedford and L. B. Sebrell

Research Laboratories, Goodyear Tire & Rubber Co., Akron, Ohio

In the preceding paper of this series[2] the mechanism of vulcanization was not discussed. The object of the present paper is to present additional data and to consider the mechanism of action of these curing agents.

Five days subsequent to the reading of our last paper Bruni and Romani read a paper[3] before the International Rubber Conference in which the experimental data corroborate and duplicate our work. It is worthy of comment that two sets of workers on opposite sides of the globe should so accurately parallel each other. This parallelism also extends to the two papers,[4] one by Bruni and one by Romani, which were recently abstracted by Schidrowitz.[5] While we gladly acknowledge the work of Bruni as independent, we feel that a few further remarks are necessary.

Bruni questions our knowledge of mercaptobenzothiazole as a sulfur reaction product of thiocarbanilide. We have been working on this as well as on many other sulfur reactions for over six years, and it was through the isolation of mercaptobenzothiazole from the sulfur reaction product of thiocarbanilide that we first became acquainted with the thiazolemercaptans, their disulfides, polysulfides, and zinc salts. These were mentioned in our last paper as being excellent accelerators, some of them at ordinary temperatures. We also mentioned the zinc salt of ethyl xanthate as an accelerator free from nitrogen and were not at that time aware that it had been previously described by Ostromuislensky. We gladly acknowledge his priority as pointed out by Bruni.

Bruni also finds that mercaptobenzothiazole is formed by heating methylenediphenyldiamine with sulfur and has evidently overlooked our earlier paper[6] wherein we stated that the first reaction product of this diamine is thiocarbanilide. Since this is true, the ultimate reaction product should be the same. We verified this prior to January 6, 1917, at which time we applied for our American patents[7] which have recently been issued. The corresponding British patent[8] has been published for some time.[9]

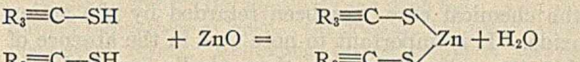
The discovery of tetramethylthiuram disulfide as an accelerator and curing agent is also claimed by Bruni. This accelerator has been on the market in this country for about three years and enjoyed secret commercial use for several years prior to public sale. The availability of its sulfur for vulcanization had been noted by us and by several other investigators, although Bruni was the first to publish the information.

Mechanism of Acceleration

The experimental data published by Bruni exactly duplicate a portion of our work; yet we find that we materially differ from him as to the theory for the mechanism of the vulcanization reactions. We seek, therefore, by the aid of additional data, not to disprove but rather to qualify and enlarge upon his theories. Applied to thiocarbanilide the Bruni mechanism may be represented by the following equations:

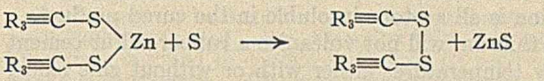
Thiocarbanilide + heat = Phenyl mustard oil + aniline (1)
Phenyl mustard oil + sulfur = Mercaptobenzothiazole (2)
Mercaptobenzothiazole + ZnO = Zinc mercaptide + H_2O (3)
Zinc mercaptide + sulfur = Mercaptobenzothiazole disulfide + ZnS (4)
Disulfide + heat = Monosulfide + sulfur available for vulcanization (5)

The last equation represents the general theory which Bruni applies to thiurams, dioxonthiogens and to other accelerators in general. The proposed mechanism may therefore be represented as follows:



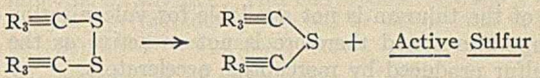
$$\begin{matrix}R_3\equiv C-SH\\ R_3\equiv C-SH\end{matrix} + ZnO = \left.\begin{matrix}R_3\equiv C-S\\ R_3\equiv C-S\end{matrix}\right\rangle Zn + H_2O$$

(6)



$$\left.\begin{matrix}R_3\equiv C-S\\ R_3\equiv C-S\end{matrix}\right\rangle Zn + S \longrightarrow \begin{matrix}R_3\equiv C-S\\ |\\ R_3\equiv C-S\end{matrix} + ZnS$$

(7)

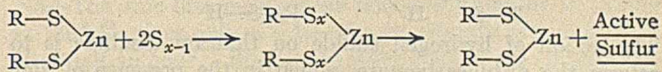


$$\begin{matrix}R_3\equiv C-S\\ |\\ R_3\equiv C-S\end{matrix} \longrightarrow \left.\begin{matrix}R_3\equiv C\\ R_3\equiv C\end{matrix}\right\rangle S + \underline{\text{Active}}\ \underline{\text{Sulfur}}$$

(8)

The theories which the present writers have proposed in the past and now wish to amplify are somewhat different. Using zinc as a representative of all metals which function similarly, we have three variations of the mechanism of vulcanization to propose. All of them are based on our original theory of polysulfides.

1—The action of metallic salts of mercaptans, dithiocarbamates, carbamates, xanthates, thioureas, etc., is represented thus:



$$\left.\begin{matrix}R-S\\ R-S\end{matrix}\right\rangle Zn + 2S_{x-1} \longrightarrow \left.\begin{matrix}R-S_x\\ R-S_x\end{matrix}\right\rangle Zn \longrightarrow \left.\begin{matrix}R-S\\ R-S\end{matrix}\right\rangle Zn + \frac{\text{Active}}{\underline{\text{Sulfur}}}$$

2—The action of inorganic accelerators such as zinc oxide, litharge, lime, etc., also proceeds through polysulfides in absence of organic accelerators which produce carbosulfhydryl groups other than hydrogen sulfide.

$$ZnO + 2H_2S \longrightarrow Zn(SH)_2 + H_2O$$

$$y\ Zn(SH)_2 + (y-1)S \longrightarrow HS-(Zn-S-S)_{y-1}-ZnSH + (y-1)H_2S$$

$$(-Zn-S-S-)_y + y S_{x-2} \longrightarrow (ZnS_x) \longrightarrow (ZnS_2)_y$$

$$\text{or } (ZnS)_y + \frac{\text{Active}}{\underline{\text{Sulfur}}}$$

A differentiation is now made between the active metallic oxides or hydrates as primary or as secondary accelerators. Where they form mercaptides or metallic persulfides their action is that of a primary accelerator. Where they speed the formation of organic sulfhydryl groups on resins, proteins, or added accelerators by removal of hydrogen sulfide, such action is purely secondary. In practically all cases both actions take place simultaneously. There is only one class of organic accelerators which acts both as primary and as secondary accelerators. We reserve the discussion of nitroso accelerators until a later date.

3—Organic accelerators in absence of secondary accelerators function as follows:

$$R-H + S \longrightarrow R-SH$$

$$2RSH + S \longrightarrow R-S-S-R + H_2S$$

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[1] Presented before the Division of Rubber Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] This Journal, **13** (1921), 1034.

[3] *India-Rubber J.*, **62** (1921), 63.

[4] *Giorn. chim. ind. applicata*, **3** (1921), 196.

[5] *India-Rubber J.*, **62** (1921), 89.

[6] Bedford and Scott, This Journal, **12** (1920), 31.

[7] Bedford, U. S. Patents 1,371,662 (1921); 1,371,663 (1921); 1,371,664 (1921).

[8] Brit. Patent 139,857 (1919).

[9] In regard to priority on the subject of causing accelerators to react with sulfur before vulcanization, we may say further that Bruni correctly cites the Peachey patent, Brit. Patent 113,570 (1917), as prior to our British patent of 1919. Peachey specifically patented the sulfur reaction product of *p*-nitrosodimethylaniline as an accelerator and filed his application on August 23, 1917. Our first American patent was filed on January 6, 1917, in which we mentioned the sulfur reaction products used by Peachey (see page 3, line 32, U. S. P. 1,371,662). Through this patent we claim priority for the principle of causing accelerators to react with sulfur before compounding with rubber and specifically for the sulfur reaction products mentioned by Peachey and by Bruni.

$$R—S—S—R + S_{x-2} \longrightarrow R—S_x—R$$
$$R—S_x—R \longrightarrow R—S—S—R + S_{x-2} + \underline{\text{Active}}\ \underline{\text{Sulfur}}$$

Prof. Bruni's mechanism now becomes a corollary to the above equation.

$$R—S—S—R \longrightarrow R—S—R + \underline{\text{Active}}\ \underline{\text{Sulfur}}$$

4—Allowing R to represent either hydrogen, metal, or radical, the entire mechanism of vulcanization with accelerators may be summed up in one equation:

$$R—S_x—R \longrightarrow R—S—R + \underline{\text{Active}}\ \underline{\text{Sulfur}}$$

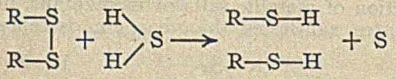
5—Without accelerators we have vulcanization by the "mother" of all polysulfides, *i. e.*, by thio-ozone itself, formed from sulfur dioxide and hydrogen sulfide.

Reactions of Tetramethylthiuram Disulfide

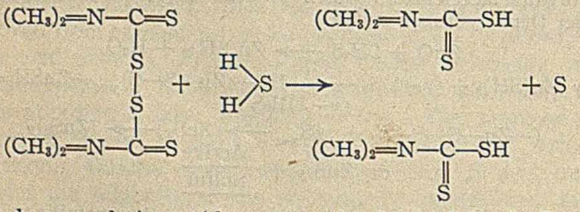
1—Bruni[10] finds that] this thiuram (5 parts) with ZnO (5 parts) will vulcanize rubber (100 parts) in 15 min. at 138° C. The cure will also take place under the same conditions of mix, time, and temperature in the absence of zinc; in fact, either mix will cure in 10 min. We find the same coefficient of vulcanization in 10 min. as in 45 min. The acetone-insoluble sulfur is the same either with or without the zinc oxide, and corresponds very closely to one out of the four sulfur atoms in the thiuram disulfide. Ether-hydrochloric acid, however, removes one-fourth to one-third of the combined sulfur from the zinc stock, showing that it is present as zinc sulfide. Although the zinc stock has the higher modulus usually acquired by the addition of zinc oxide, the chemical cure has been retarded by the action of the oxide. It is important to note that in the absence of zinc oxide the sulfur which is theoretically available for vulcanization is all acetone-insoluble in the cured product.

2—This thiuram will not vulcanize a rubber-sulfur cement at ordinary temperatures either with or without zinc oxide. The sulfur of the thiuram is not available for vulcanization at low temperatures and therefore is not as active as the forms of sulfur produced by mercaptide accelerators.

3—A zinc oxide cement containing thiuram disulfide and sulfur will vulcanize on standing over night if treated with a small amount of hydrogen sulfide. Weyl[11] states that all disulfides, whether aliphatic or aromatic, are easily reduced by alcoholic K_2S or hydrogen sulfide to mercaptans, many at ordinary temperatures and more easily in the presence of bases. Free sulfur is formed.

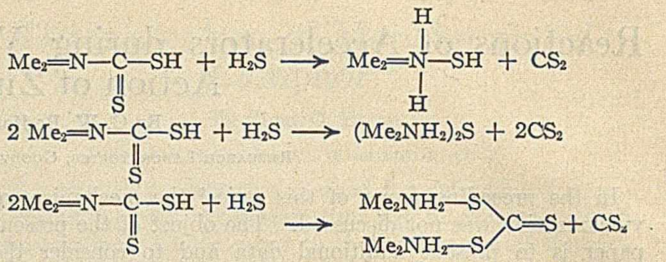


The action of hydrogen sulfide on thiuram disulfide is to reform the dithiocarbamate, which in the presence of zinc oxide again forms the zinc salt. This is a rapid vulcanization agent at ordinary temperature.



In absence of zinc oxide no cure is obtained by hydrogen sulfide and the thiuram disulfide.

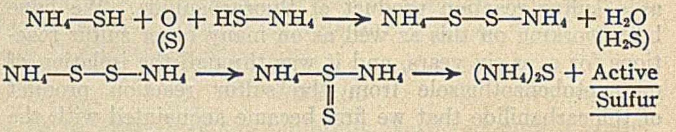
4—Thiuram disulfide in acetone at ordinary temperature reacts with hydrogen sulfide producing a cloudy precipitate of sulfur. The dimethyldithiocarbamic acid, thereby produced, reacts further with hydrogen sulfide to produce methylated ammonium sulfides or trithiocarbamates which at once redissolve the sulfur, and the final result is a deep red polysulfide solution. Some carbon disulfide is set free by these reactions.



$$Me_2{=}N—\underset{\underset{S}{\|}}{C}—SH + H_2S \longrightarrow Me_2{=}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N}}—SH + CS_2$$
$$2\ Me_2{=}N—\underset{\underset{S}{\|}}{C}—SH + H_2S \longrightarrow (Me_2NH_2)_2S + 2CS_2$$

The methylated ammonium trithiocarbonate or sulfide then forms ammonium polysulfide with the free sulfur. Extra sulfur results in a deepening of the red color.

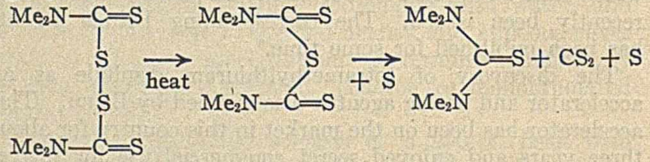
In our last paper we referred to the vulcanization of rubber by Kratz and his co-workers by the use of ammonium sulfide or hydrosulfide and invoked the aid of oxygen to form the disulfide (mono-polysulfide) since no free sulfur was present. We also stated that free sulfur would accomplish the same result. These investigators therefore deserve priority on the vulcanization of rubber by disulfides as far as publication is concerned.[12] The heat vulcanization by their method is the same as for thiuram disulfides.



$$NH_4—SH + \underset{(S)}{O} + HS—NH_4 \longrightarrow NH_4—S—S—NH_4 + \underset{(H_2S)}{H_2O}$$
$$NH_4—S—S—NH_4 \longrightarrow NH_4—\underset{\underset{S}{\|}}{S}—NH_4 \longrightarrow (NH_4)_2S + \underline{\underline{\text{Active Sulfur}}}$$

In the second paper of this series,[13] the statement was made that many accelerators such as hexamethylenetetramine, *p*-phenylenediamine, and aldehyde ammonia function mainly as means for compounding ammonium polysulfides, which they generate by reaction with sulfur during the vulcanization process. A disulfide is simply the first member of the series of polysulfides.

5—Thiuram disulfide heated somewhat above its melting point turns a deep red in color, and retains this color on cooling. The writers are unable to give the exact chemistry of this reaction, but know that some dimethylamine is liberated and that the red liquid is a polysulfide, as shown by the liberation of free sulfur by acids. Romani gives the following equations:



This tetramethylthiourea has been described by Grodski[14] as a base stronger than ammonia, which liberates ammonia from its salts. The deep red solution will not vulcanize a zinc oxide cement according to all of our present tests.

6—Thiuram disulfide heated in aniline also gives a deep red solution. This solution will set a zinc oxide cement within 24 hrs. The carbon disulfide which forms reacts with aniline to produce active dithiocarbamates of zinc.

7—The action of hydrogen sulfide on thiuram disulfide in aniline at ordinary temperature produces a deep red solution. On slight heating, hydrogen sulfide is lost and the color disappears but reappears on again adding the gas. If heated higher, dimethylamine and hydrogen sulfide are lost and the

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[10] *Loc. cit.*

[11] "Methoden der Organische Chemie," p. 243.

[12] We wish to take this opportunity to call attention to what we believe to be the first instance of the use of accelerators. Thomas Rowley, by a British patent (No. 787) in 1881, announced that rubber and sulfur would vulcanize in an atmosphere of ammonia under pressure with less sulfur than is ordinarily required. A time saving was claimed with a product less liable to subsequent deterioration. We believe that this work antedates either the work of Spence or the Bayer Co., and believe that our English brothers may therefore claim the discovery of acceleration.

[13] Scott and Bedford, This Journal, 13 (1921), 125.

[14] *Ber.*, 14 (1881), 2754.

color does not reappear on cooling and again adding the gas. The literature is rich in examples of the replacement of one amine by another in thioureas and dithiocarbamates. The stronger base is usually liberated. In this case we have the disulfide changed to dimethyldithiocarbamic acid with liberation of free sulfur by the hydrogen sulfide. The aniline salt of the acid then forms. Aniline then replaces the dimethylamine to form the aniline salt of phenyldithiocarbamic acid and the dimethylamine reacts with more hydrogen sulfide and sulfur to form the methylated ammonium polysulfides. The latter are broken up by heat with loss of the constituents and reformed by hydrogen sulfide as long as dimethylamine remains in the aniline.

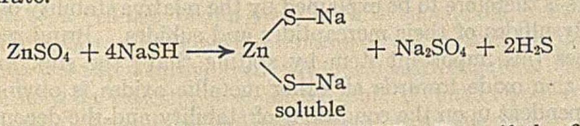
SUMMARY FOR THIURAM DISULFIDES—These disulfides contain sulfur available for vulcanization in heat cures. The presence of zinc oxide gives a higher modulus to the vulcanizate but retards the chemical cure. Thiuram disulfides, used as accelerators with sulfur in heat cures, form alkylated ammonium polysulfides and trithiocarbamates, while in the presence of zinc oxide, dithiocarbamates of zinc are also formed. In this case the zinc seems to accelerate the cure, although chemical data have not been obtained.

For low temperature cures of cements the thiuram disulfide sulfur is inactive. Zinc oxide has no effect. The addition of hydrogen sulfide to the zinc oxide cement containing the disulfide produces dithiocarbamates of zinc, and the cement quickly vulcanizes.

REACTIONS OF DITHIOCARBAMATES

1—Hydrogen sulfide reacts on dimethylamine-dimethyldithiocarbamate in acetone without warming, to produce alkylated ammonium sulfides and trithiocarbamates. The addition of sulfur produces a deep red polysulfide. These combinations have not vulcanized cements at room temperature.

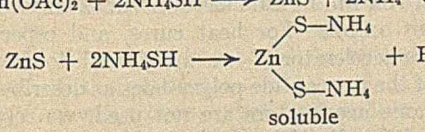
2—Hydrogen sulfide reacts with the zinc salt of dimethyldithiocarbamic acid in aniline at ordinary temperature to produce zinc sulfide as a precipitate. As soon as this precipitate starts to form it redissolves and further hydrogen sulfide does not reform the solid. Heating forms the precipitate again. This phenomenon has its parallel in previously published data. As in the preceding example (No. 1), the carbon disulfide goes to the aniline, and dimethylamine hydrosulfide is formed with excess hydrogen sulfide. Zinc sulfide is soluble in hydrosulfides, as shown by Thomsen,[15] who added a dilute solution of zinc sulfate to a dilute solution of sodium hydrosulfide without getting a precipitate and described the solutions as analogous to the action of caustic in redissolving zinc hydrate.



$$ZnSO_4 + 4NaSH \longrightarrow \underset{\text{soluble}}{Zn\begin{matrix}\diagup S-Na\\ \diagdown S-Na\end{matrix}} + Na_2SO_4 + 2H_2S$$

We find the same reaction with NH_4SH. Even if the first addition of a zinc acetate solution forms a precipitate due to local concentration, this precipitate redissolves. Hydrogen sulfide is liberated.

$$Zn(OAc)_2 + 2NH_4SH \longrightarrow ZnS + 2NH_4-O-Ac$$



$$ZnS + 2NH_4SH \longrightarrow \underset{\text{soluble}}{Zn\begin{matrix}\diagup S-NH_4\\ \diagdown S-NH_4\end{matrix}} + H_2S$$

The re-solution of the zinc sulfide precipitate from the zinc dithiocarbamate in aniline is therefore due to the formation of soluble dimethylammonium dithiozincate, similar to sodium zincate. This aniline solution is bright yellow in color. Warming produces the precipitate again. With sulfur present the solution is a deep red, and this color is also lost if the precipitate is reformed by heating. We have in this case the polysulfide of a thiozincate in solution. Another instance of a soluble polysulfide of a thiozincate is found in the action of zinc acetate on Na_2S_5. With dilute solutions a large amount of the zinc salt may be added without the formation of a precipitate. This will be considered later under inorganic polysulfides. We have several times noted acetone-soluble zinc compounds in the acetone extract of vulcanized rubber stocks which were cured by the use of accelerators.

3—Zinc dithiocarbamate dissolved in aniline with sulfur in the cold and added to a pure gum cement produces a much quicker vulcanization at room temperature than when no aniline is used. The writers attribute this to the solvent action of aniline if the solution has not been heated. They are aware that others in the United States have also observed this action of aniline with zinc dithiocarbamates. In their preceding paper the writers recorded the same action of aniline on a thiocarbanilide-zinc oxide cement. They were later able to vulcanize a cement with thiocarbanilide, zinc oxide and sulfur at room temperature without the use of aniline. The reaction was slower.

4—If a solution of the above salt and sulfur in aniline (zinc salt 10 g.; sulfur 10 g.; aniline 100 g.) be heated on an electric stove, the following reactions occur:

(*a*)—A clear yellow solution results.

(*b*)—At 120° C. the liquid turns a deep red. Any precipitate formed redissolves at once. On cooling, the color is lost and a precipitate forms. Reheating causes complete solution with red color again.

(*c*)—Heated to boiling, the red color is lost and a permanent precipitate is formed. By extraction with hot benzene this precipitate is found to contain as high as 50 per cent of sulfur insoluble in solvents. This corresponds to ZnS_3 or ZnS_4. The inorganic polysulfides of zinc will be shown later to be powerful curing agents in heat cures.

The addition of this red aniline solution to a cement causes vulcanization within a few hours at low temperatures. This the writers believe to be wholly or in part to the zinc salts of polysulfides of alkylated ammonium hydrosulfides.

In forming the aniline solution containing the permanent precipitate, dimethylamine and hydrogen sulfide are lost and thiocarbanilide is formed in solution. If this entire mix be added to a cement no vulcanization takes place after several weeks have passed.

5—The zinc dithiocarbamate boiled with sulfur in xylene at 138° C. gives only a trace of a precipitate of zinc sulfide after half an hour. Boiling for several hours precipitates the zinc, but the reaction is very slow. Both the zinc salt and the sulfur are in solution and the temperature corresponds to these used in heat cures. This is evidence that Prof. Bruni's mechanism of vulcanization through the disulfides is untenable for zinc dithiocarbamates, and also that the solvent action of aniline alone in the previous example is not sufficient to explain the increase in curing power.

In absence of other amines to take up the carbon disulfide, zinc dithiocarbamates do not readily react with sulfur to form zinc sulfide and organic disulfides. There are many cases of mercaptides of zinc, lead, and other metals forming polysulfides by treating with sulfur at ordinary temperatures, both in solution and in the dry state. The temperature factor is very important for these changes and varies greatly for different mercaptides. Even the use of different solvents is an important factor. All the evidence for the great reactivity of mercaptides as accelerators points to mercaptide polysulfides as such.

SUMMARY FOR DITHIOCARBAMATES—For low-temperature vulcanization of cements, zinc is necessary. Either zinc oxide and ammonium dithiocarbamate or the zinc dithiocarbamate may be used. Aniline is a good solvent for the zinc

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[15] *Ber.*, **11** (1878), 2044.

mercaptides and thereby speeds their action. Benzene is the most suitable solvent for the rubber.

In heat cures the zinc dithiocarbamates do not easily react with sulfur to form zinc sulfide except through the further aid of hydrogen sulfide. By the action of rubber resins or proteins in producing hydrogen sulfide the zinc dithiocarbamate is decomposed into the polysulfides of substituted ammonium sulfides and trithiocarbonates, which in the presence of zinc oxide are strong curing agents. On account of the slowness of sulfur in reacting on zinc dithiocarbamates, the authors believe that hydrogen sulfide furnishes the key to a second mechanism of vulcanization by these accelerators. The primary mechanism is through the polysulfides of the zinc salts as such.

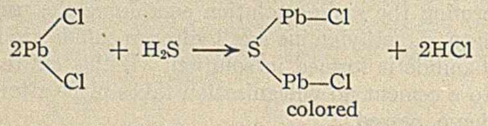
For heat cures the action of aniline is more than that of a solvent for the zinc salt. Zinc sulfides or persulfides are more easily formed and dithiocarbamates of aniline are formed rather than trithiocarbonates.

REACTIONS OF THIOCARBANILIDES

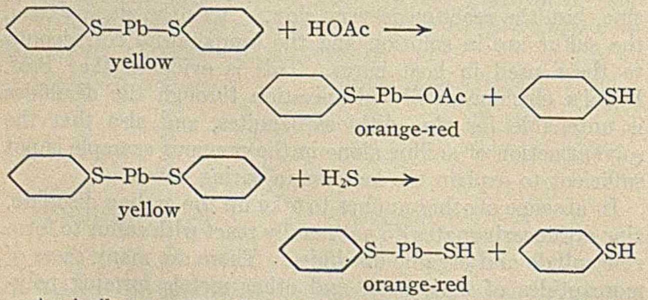
1—In our previous paper we described the zinc mercaptides of thiocarbanilide and their vulcanizing powers in cements at room temperature. The temperatures required for the formation of mercaptobenzothiazole and its disulfide even in the presence of zinc oxide exclude any such mechanism for curing by thiocarbanilide at ordinary temperatures and also for heat cures at 5 lbs. of steam pressure, at which temperature we have found thiocarbanilide and zinc oxide to give a coefficient of 1.7 per cent sulfur combined with the rubber, in 5 min.

2—Litharge and lime also accelerate the curing powers of thiocarbanilide but overcure the rubber faster than when zinc is used. That this cannot be due entirely to the action of litharge, sulfur, resins, and proteins independent from thiocarbanilide is shown by the following data.

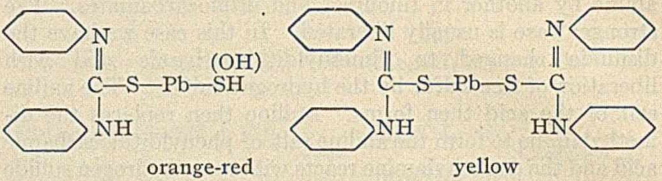
LEAD MERCAPTIDES—Renisch[16] precipitated lead salts in acid solution and obtained the sulfochloride as a red precipitate. Mellor[17] states that the precipitate may be orange, yellow or red, and gives the equation:



We find the same phenomena with lead thiophenol. The normal salt is a bright yellow which changes to a deep orange on adding a trace of acid or hydrogen sulfide.



A similar reaction is obtained with thiocarbanilide and litharge in benzene if chilled to 15° to 20° C. Frequent stirring for a short time produces a deep red mercaptide which is soluble in benzene and may be separated by filtration. Upon slight warming lead sulfide is precipitated from the filtrate. Under certain conditions, the writers have obtained the lead mercaptide as a clear yellow instead of red solution. From the above data they believe that the yellow solution is normal salt, while the usual red product may be called a basic salt containing a hydroxyl or sulfhydryl group on one side of the lead atom.



The addition of sulfur to cold solutions of the lead mercaptide of thiocarbanilide results in a deepening of the red color. This is also true with other yellow mercaptides of lead. With lead thiophenol the color gradually changed from yellow through orange and red, to deeper shades down to the black lead sulfide.

3—The writers have repeated their cement experiments with aniline and carbon bisulfide, thiocarbanilide, etc., using litharge or lime in the place of zinc oxide. In every case the sulfides of lime or litharge form in a few hours and no vulcanization of the cement occurs. If the cements be chilled, the above color changes are easily observed, showing that mercaptides are first formed. By keeping the cements in the ice box we have several times observed a "livering" or partial vulcanization and in one case a permanent gel was formed.

Lead and lime mercaptides are therefore more easily amenable to the formation of disulfides than are the zinc compounds, yet no vulcanization takes place at ordinary temperatures. This is not in accord with Bruni's theory, from which we would expect greater reactivity in this case.

4—The writers have also investigated the curing power of several other lead mercaptides. Lead xanthate is a beautiful maroon compound which changes to lead sulfide before it can be mixed with rubber. The lead salt of phenyldithiocarbamic acid is comparatively stable, and lead mercaptobenzothiazole is more so. The latter will vulcanize cements at room temperatures as does the zinc salt. The cement becomes deep maroon in color, owing to the formation of polysulfides of the salt, and retains this color for weeks after vulcanization has taken place. Lead sulfide forms in a thin layer on the side of the bottle exposed to light but even this does not form for several weeks. The mechanism of vulcanization in this case is through the polysulfides of the mercaptide without the formation of lead sulfide. Moreover the red color cannot be attributed to inorganic lead persulfides, which have been shown by Schiff[18] to be unstable at ordinary temperatures.

The relative curing powers of inorganic accelerators as well as their compatibility or incompatibility with organic accelerators is therefore to be explained by the relative stability of the polysulfides of their mercaptides and sulfides. Bruni recognizes this important item by stating that "the superiority of zinc oxide towards all other metallic oxides is obviously dependent upon the conditions of stability and the decompositions of the various salts and sulfides," but fails to note the importance of the temperature factor or to recognize the metallic polysulfides, both organic and inorganic, as being the important curing agents rather than the organic disulfides.

MECHANISM FOR HIGH TEMPERATURE VULCANIZATION WITHOUT METALLIC OXIDES—For heat cures, and especially for Bruni's "ultra-accelerators," we are forced to invoke the mechanism of the mercaptide polysulfides as described above. Where inorganic accelerators are not used, we rely on the polysulfides of the disulfides until the total available sulfur becomes low and then we call on the disulfide to give up its sulfur. The assumption that disulfides give up half their sulfur to the rubber is further supported by the following references:

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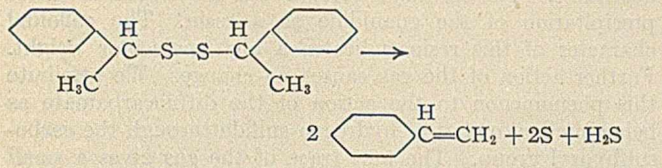
[16] *J. prakt. Chem.*, **13**, 130.

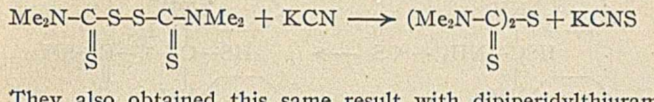
[17] "Modern Inorganic Chemistry," **1919**, 411.

[18] *Ann.*, **115** (1860), 74.

Baumann and Fromm[19] describe the heat decomposition of the disulfide derived from α-phenylethylmercaptan with the liberation of free sulfur.



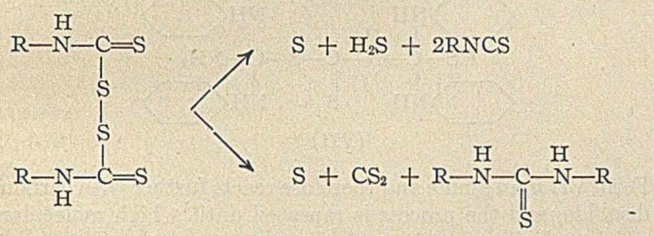
Braun and Stechele[20] obtained a theoretical decomposition of tetramethylthiuram disulfide to monosulfide by warming a suspension of the disulfide in a water-alcohol solution of potassium cyanide.



$$\mathrm{Me_2N{-}\underset{\underset{S}{\|}}{C}{-}S{-}S{-}\underset{\underset{S}{\|}}{C}{-}NMe_2 + KCN \longrightarrow (Me_2N{-}\underset{\underset{S}{\|}}{C})_2{-}S + KCNS}$$

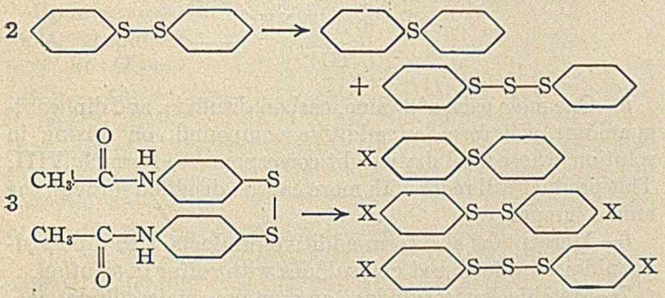
They also obtained this same result with dipiperidylthiuram disulfide, tetrapropylthiuram disulfide and with isothiuram disulfides.

Braun[21] describes the heat decomposition of disubstituted thiuram disulfides by two equations, the first one favoring aliphatic and the second favoring aromatic compounds. Both equations show the liberation of free sulfur.



Braun also mentions[22] the heat decomposition of dixanthogenides with the liberation of free sulfur.

Hinsberg[23] gives an interesting heat decomposition of aromatic disulfides which shows both their liberation of free sulfur as well equaas their ability of forming higher polysulfides.

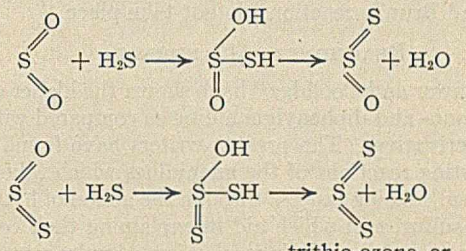


Mercaptobenzothiazole forms a disulfide when heated with sulfur. If extra sulfur is present there is a colloidal polysulfide formed which is deep red in color while hot and cools to a reddish brown resin with a conchoidal fracture. Solvents extract only small amounts of sulfur, and the polysulfide is a rapid curing agent without other free sulfur. Cold caustic soda extracts a small amount of unchanged mercaptans. According to Weyl[24] sodium sulfide forms the mercaptans without the sulfinates. The free mercaptobenzothiazole in absence of zinc oxide is a relatively poor accelerator and the disulfide or its polysulfide is still lower in curing power. This observation is contrary to the Bruni theory that disulfides are the most active form of accelerators.

Research with disulfides should be extended to dithioaniline and other disulfides.

It has frequently been noted that aniline is a stronger accelerator than thiocarbanilide in absence of secondary accelerators. Scott and Bedford proposed a reaction of amino groups with hydrogen sulfide to form derivatives of ammonium polysulfide. Sufficient experimental evidence is still lacking, and the action of organic accelerators in absence of inorganic accelerators is still virgin soil available for pioneering research.

Hydrogen sulfide decomposes many polysulfides and disulfides, such as the thiuram disulfides, with liberation of the sulfur of the hydrogen sulfide. This sulfur may therefore be considered as in the nascent state. When inorganic accelerators are used, they fix this hydrogen sulfide as metallic sulfides, as shown by W. J. Kelly.[25] In absence of these inorganic accelerators there is the possibility that the above described "nascent" sulfur is available for vulcanization. Sufficient experimental evidence is lacking to prove this point. In fact, hydrogen sulfide on nitroso compounds and other inorganic compounds liberates sulfur; yet this reaction will not vulcanize cements at ordinary temperatures. The action of sulfur dioxide and hydrogen sulfide in low-temperature vulcanization has been described as due to nascent sulfur and also as due to the formation of thiozone, which is simply one form of polysulfide sulfur.



trithio-ozone or
polysulfide sulfur

The writers have evidence that the reactivity of the sulfur liberated by Peachey's process is not due to a nascent condition but to a new and active form of sulfur, which to their knowledge has not previously been described. If properly prepared, this sulfur retains its activity in vulcanizing rubber at ordinary temperature in absence of the gases from which it is formed.

If sulfur dioxide and hydrogen sulfide are passed into solvents such as benzene or carbon disulfide, cooled to 10° C. or lower, the liberation of free sulfur begins almost immediately. After sufficient sulfur has been formed one of the two gases is interrupted and the other gas passed in for an hour or longer. The sulfur, so precipitated, is bright yellow in color and on standing changes to plastic sulfur which has the same properties as when formed by pouring molten sulfur into water. On further standing, the product crystallizes.

By pouring off the supernatant liquid and washing the sulfur free from unchanged gas by cold solvent, we find that we have an active form of sulfur which if beaten into a chilled cement will vulcanize the same at low temperatures. The speedy reaction of the two gases at 10° C. or lower to liberate sulfur leads us to believe that none of the intermediate thio acids are stable at these low temperatures. Long treatment with excess of one of the gases and washing with cold solvent removes the remaining gas.

The writers therefore believe that they have isolated a new and active form of sulfur which will vulcanize rubber at low temperatures without the presence of organic or inorganic accelerators and which is trithio-ozone, or the "mother" of polysulfide sulfur itself.

There is no evidence that "nascent" sulfur is active. Further evidence on the liberation of free sulfur in rubber by

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[19] *Ber.*, **28** (1895), 907.

[20] *Ibid.*, **36** (1903), 2275.

[21] *Ibid.*, **35** (1902), 817.

[22] *Ibid.*, **45** (1912), 2188.

[23] *Ibid.*, **43** (1910), 1874.

[24] *Loc. cit.*

[25] "The Determination of True Free Sulfur and True Coefficient of Vulcanization of Vulcanized Rubber—II." Presented at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

various chemical reactions should prove or disprove our theory that the molecular form of the sulfur as liberated is the factor which determines its reactivity rather than the nascent condition of freshly formed sulfur.

SUMMARY ON THIOCARBANILIDES—Thiocarbanilide functions as a mercaptan. Its zinc and lead mercaptides have been described and their polysulfides are believed to be the true curing agents. This reaction is operative for the low-temperature curing of cements as well as in heat cures. Hydrogen sulfide changes mercaptides to metallic sulfides and regenerates the mercaptan which again reacts with the metallic oxide to form the mercaptide.

The action of sulfur on mercaptans to form disulfide polysulfides is apparently inoperative for thiocarbanilide. The action of sulfur on the zinc mercaptide of thiocarbanilide is believed to function only through the formation of mercaptide polysulfides.

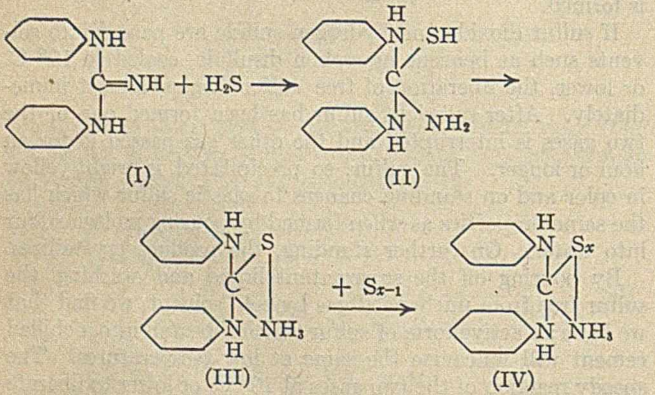
The action of thiocarbanilide to produce phenyl mustard oil and this to produce mercaptobenzothiazole, according to Bruni, is believed to be inoperative except as carried on by sulfur reaction prior to compounding the accelerator. Phenyl mustard oil in a zinc-sulfur-rubber mix is inactive as an accelerator and Bruni's reactions do not take place.

Reactions of Guanidines

Kratz, Flower and Coolidge[26] have shown the higher curing power of mono- and diphenylguanidine as compared with the triphenyl derivative. The present writers have found some very interesting reactions of the guanidines which take place during the vulcanizing process through the action of hydrogen sulfide and sulfur, and which aid in explaining their relative curing powers as well as their mechanism of vulcanization.

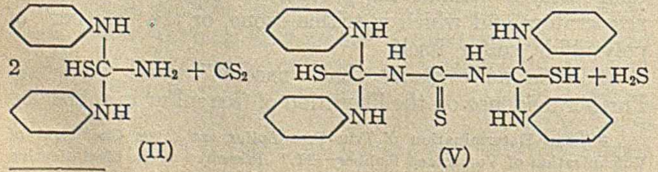
1—With sulfur in benzene at room temperature, triphenylguanidine becomes light red in color if subjected to the action of hydrogen sulfide.

2—Under the same conditions diphenylguanidine gives a much deeper red color. This action is explained by the formation of a peculiar derivative of ammonium sulfide which readily forms polysulfides.

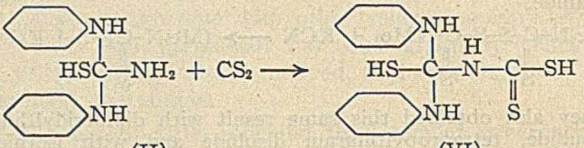


Form III may be considered as a derivative of ammonium sulfide.

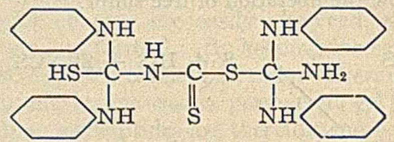
3—The free amino group of Form II is further proved by its reaction with carbon disulfide. A substituted thiourea is formed and the total weight of the reaction product corresponds to the following equation:



4—Further evidence of these reactions is found by passing hydrogen sulfide into a carbon disulfide solution of diphenylguanidine. The first few bubbles of the gas cause a complete precipitation of the guanidine as a resin. The colloidal character of this resin indicates a high molecular weight. Further action of the gas causes no change. We attribute this phenomenon to the action of the dithiocarbamate as being similar to that of hydrogen sulfide through the carbosulfhydryl group. The first trace of the gas gives a small amount of Form II, which forms a dithiocarbamate with carbon disulfide.

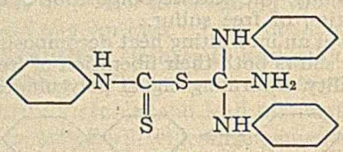


This dithiocarbamate then reacts with a second mole of the guanidine to give Form VII.



(VII)

Form VII is an amine and therefore reacts further with carbon disulfide, and the process is repeated until a high molecular weight is built up and a resin formed.



(VIII)

5—One mole each of aniline, carbon disulfide, and diphenylguanidine will form an additive compound, on mixing in solution, whose total dry weight corresponds to Formula VIII. This product will react with more carbon disulfide through the amino group.

6—Mercaptans also form additive products with diphenylguanidine and form red polysulfides with sulfur in solution.

7—Metallic hydrosulfides, ammonium hydrosulfide, metallic hydrates and oxides give characteristic reactions with the guanidine or Form II.

In all of the above reactions triphenylguanidine is less reactive and in some cases the products are unstable or do not form. The above polysulfides of the guanidines are similar to those of ammonium sulfide and do not cure cements at room temperature. In heat cures diphenylguanidine is more reactive than is triphenylguanidine. The effect of zinc oxide on diphenylguanidine and its curing power is rather peculiar. In many cases the time of cure is not changed by the zinc oxide, while in others it is materially retarded. Kratz has noted the retarding action of zinc oxide on aniline. We have found three classes of organic accelerators based on the effect of metallic oxides. There are accelerators which are aided or retarded by the action of zinc, while there are others which seem to be unaffected.

The above data do not preclude the decomposition of Form III into ammonia and thiocarbanilide in high temperature cures with the corresponding reactions whereby they activate sulfur.

The inactivity of zinc oxide on the curing time of this guanidine at 40 lbs.' steam pressure indicates that this reaction does not take place at this temperature during vulcanization.

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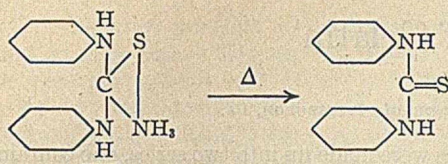
[26] This Journal, 12 (1920), 319.



(III)

SUMMARY ON GUANIDINES—Guanidine accelerators form derivatives of ammonium sulfide by reaction with hydrogen sulfide even at ordinary temperatures. Polysulfides easily form and the aid of metallic oxides is not required except as inorganic fillers. In some cases the action of zinc oxide is that of a retardant. Further research is desirable.

INORGANIC POLYSULFIDES

Schiff[27] studied the polysulfides of a large number of heavy metals other than those of antimony and arsenic. He found most of them to be unstable and obtainable only under special conditions and for a short time, but he stated that the polysulfides of zinc and cadmium do not easily decompose, and can be isolated and manipulated.

In repeating the work of Schiff, the writers have observed the following phenomena: With dilute solutions of zinc salts and sodium pentasulfide a large portion of the zinc solution, preferably the acetate, may be added to the dilute polysulfide solution without causing a precipitate to form. This reaction is similar to the one pointed out by Thomsen.[28]

$Zn(OAc)_2 + 2Na_2S \longrightarrow 2NaOAc + Zn(S{-}Na)_2$ Soluble

$Zn(OAc)_2 + 2Na_2S_5 \longrightarrow 2NaOAc + Zn(S_5{-}Na)_2$ Soluble

Upon further addition of the zinc solution there is formed a precipitate which is colloidal in character and passes through filter paper. The high molecular weight of similar precipitates has been shown by Linder and Picton.[29] We therefore write the next step in the reaction as follows:

$2Zn(S_5{-}Na)_2 + Zn(OAc)_2 \longrightarrow 2NaOAc + Zn(S_5{-}Zn{-}S_5Na)_2$

Upon continuing the addition of the zinc solution up to molar proportions or excess, the precipitate granulates and may be filtered. This precipitate, therefore, consists of $(ZnS_5)_x$ whose formula may be represented as $AcOZn{-}S_5(Zn{-}S_5)_xZn{-}OAc$, or without the final acetate groups if the chain of $-Zn-S_5-$ links be closed. Upon filtering this precipitate, the filtrate is clear, and there is no evidence of colloidal free sulfur. Schiff states that it may be washed with hot water without decomposing the pentasulfide.

The writers have compounded this zinc pentasulfide with rubber, preferably using it as a slightly damp paste and later drying, and have found it a strong curing agent. Figuring four of the sulfurs as available for vulcanization and compounding for 5 per cent of available sulfur on the rubber, they obtained a well-set cure in 45 min., a full cure in from 75 to 90 min., and a distinct overcure in 2 hrs. All cures were at the temperature of 40 lbs. of steam. Five per cent of ordinary sulfur would not give a satisfactory cure in less than 3.5 hrs.

The question of reversibility of the equation $ZnS_5 = ZnS + S_4$ was investigated, in consideration of the fact that rubber cured with the pentasulfide of zinc shows the well-known "sulfuring up" or "bloom." Freshly precipitated zinc sulfide containing no extra sulfur was compounded with sulfur to duplicate the above formula containing 5 per cent sulfur on the rubber. The rapidity of vulcanization was similar to that with pentasulfide, but with lower tensiles. In no case did the sulfide contain free alkali. We find, therefore, that inorganic zinc-sulfur compounds easily form polysulfides which contain active sulfur available for vulcanization purposes, which is far more active than elemental sulfur.

In conclusion the writers wish to call attention to the complicated reactions which attend the vulcanization process by the use of each individual accelerator. In nearly every instance there are two or more mechanisms for the formation of active sulfur and it is as yet impossible to state which reaction predominates. The additional use of inorganic acids further complicates the subject and mixed organic accelerators furnish additional complexity. Further research on each individual accelerator is needed.

The authors believe that they have established the fundamental principles for the science of vulcanization of rubber by sulfur. A few blocks may have been misplaced, but the corner stones seem to be truly set. They are pleased that Prof. Bruni has corroborated their findings and have no desire for a priority polemic.

SUMMARY

1—There is described a new form of sulfur which will vulcanize rubber at low temperatures without the aid of accelerators. This sulfur is believed to be trithio-ozone.

2—Zinc persulfides are shown to be active vulcanization agents and zinc sulfide to be an accelerator when properly prepared. Methods for preparing these active compounds are given.

3—Zinc mercaptides, as well as the mercaptides of other metals, form persulfides without the formation of inorganic sulfides. These mercaptide polysulfides furnish the most active sulfur of all accelerators known to-day. Dithiocarbamates are classed as mercaptides.

4—Thiocarbanilide functions as a mercaptan. Its zinc and lead mercaptides have been described.

5—Basic or mixed mercaptides of polyvalent metals are described which have regular organic mercaptide groups on one side of the metal with sulfhydryl, hydroxy, acidic or other groupings on the other side.

6—The polysulfide of lead mercaptobenzothiazole has been described as a red compound which vulcanizes rubber at ordinary temperatures.

7—New reactions and data on the guanidine accelerators are given. They are classed as "hydrogen sulfide polysulfide accelerators."

8—Nitroso accelerators are reserved for future discussion.

9—Organic disulfides and their polysulfides are shown to be less active curing agents than the corresponding mercaptans or their zinc salts.

10—Further research is needed on vulcanization reactions in the absence of inorganic accelerators, especially for the mechanism of vulcanization by aniline and sulfur.

11—Hydrogen sulfide is shown to be an important factor in the mechanism of vulcanization by many accelerators.

12—All vulcanizing reactions are described as due to some form of polysulfide sulfur. Trithio-ozone, as well as metallic, organo-metallic and organic polysulfides, furnishes sulfur in a more active state than elementary sulfur.

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[27] *Loc. cit.*

[28] *Ber.*, **11** (1878), 2044.

[29] *J. Chem. Soc.*, **61** (1892), 114.

Lectures at Philadelphia College of Pharmacy and Science

Somewhat in line with President Smith's advocacy of popular lectures on chemical subjects, referred to in our November editorials, is the free public lecture course which is being given at the Philadelphia College of Pharmacy and Science. The subjects include:

The Chemistry of Other Worlds
Petroleum and Its Products and Their Modern Uses
Products from Cotton Fields and Forests
Strawberries at the North Pole and Apples at the Equator
Our Bacterial Friends and Enemies
Chemistry in Peace and War
A Thousand and One Odors
Standardized Remedies
How Chemistry Develops the Industries
One Drop of Blood
The Foods of the Next Century
The Raw Materials of the Chemical Industry
Food from the Air
Natural Silk and Artificial Silk

The Swelling and Gelation of Gelatin[1]

By Robert H. Bogue

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In several papers by Martin Fischer and his collaborators[2] it has been shown that the tendency of gelatin to go into solution in mixtures of the salts of polybasic acids increases progressively as the amount of acid or alkali in these mixtures is increased from a given low point. They find further that the highest degree of swelling is obtained in the pure acid solution, that this decreases to a minimum in a solution consisting essentially, for example, of monosodium phosphate, and that the swelling again increases on the alkaline side of this point through the di- and the trisodium phosphates to the pure alkali, at which point it is nearly as high as in the pure acid. In other words, gelatin swells the least, and is not liquefied, in a solution of monosodium phosphate, a solution of about equal parts of monosodium and disodium citrate, and a solution of pure sodium bicarbonate. As the solutions become either more acid or more alkaline the swelling is increased, and they tend ever more strongly to liquefy.

It would seem that the above effects were controlled by the hydrogen-ion concentration of the solution. Patten and Johnson,[3] in repeating a part of the work of Fischer and his collaborators, have shown that the region of least swelling and of least tendency to go into solution corresponds with a pH value of from 4.4 to 5.7. These values correspond reasonably well with the findings of Loeb[4] that the minimum degree of swelling, viscosity, osmotic pressure, alcohol number, and conductivity all fall very close to, or directly at, the isoelectric point, which is for gelatin pH = 4.7.

Another conception which has long been given credence to account for the causes of the alteration in the properties of gelatin under the influence of electrolytes is that the size of the charge on the cation or the anion is the dominant influence. The experiments of Fischer are nonconclusive in this respect, although Fischer himself refers to the changes as being brought about by *acids* and *alkalies*. He avoids a consideration, however, of hydrogen-ion concentration as distinguished from what is generally referred to as acidity or alkalinity.

In connection with some work upon the effect of silicates of sodium on the properties of gelatin, the writer has obtained data which seem to indicate that the variation in hydrogen-ion concentration and the valency of the combined ions may be adequate to account for all variations in properties which are observed.

EXPERIMENTAL

The silicates of sodium[5] which were used consisted of seven of varying composition as follows:

TABLE I—COMPOSITION OF SILICATES OF SODIUM

No.	Per cent Na_2O	Per cent SiO_2	Per cent H_2O	Approximate Molecular Structure
1	7.0	26.9	66.1	$Na_2O.4SiO_2.33H_2O$
2	8.98	30.3	60.72	$Na_2O.3.5SiO_2.23H_2O$
3	11.0	31.2	57.8	$Na_2O.3SiO_2.18H_2O$
4	13.7	32.9	53.4	$Na_2O.2.5SiO_2.13H_2O$
5	17.83	36.45	45.72	$Na_2O.2SiO_2.9H_2O$
6	24.2	38.3	37.5	$Na_2O.1.5SiO_2.5H_2O$
7	26.95	28.85	44.2	$Na_2O.SiO_2.6H_2O$

These silicates were made up into two series, one containing 2 per cent of Na_2O throughout, with consequently varying amounts of SiO_2, and the other containing 4 per cent of SiO_2 throughout, with varying amounts of Na_2O. It has previously been shown[6] that solutions of the silicates of sodium which contain equal amounts of Na_2O by weight, but varying amounts of SiO_2, do not possess the same concentration of hydroxyl ion, but that the latter increases as the ratio of soda to silica in the molecule increases.

The make-up of the two series, together with their pH values, is shown in Table II.

TABLE II—COMPOSITION OF SILICATE SERIES

NUMBER	Per cent Na_2O	Per cent SiO_2	pH (0.01*M*)
		Series 1	
1	2.0	7.7	10.80
2	2.0	6.7	10.90
3	2.0	5.7	11.08
4	2.0	4.8	11.16
5	2.0	4.1	11.50
6	2.0	3.2	11.95
7	2.0	2.1	12.43
8	2.0	0.0	13.57
		Series 2	
1	1.1	4.0	10.68
2	1.2	4.0	10.79
3	1.4	4.0	10.98
4	1.7	4.0	11.11
5	2.0	4.0	11.50
6	2.5	4.0	12.08
7	3.7	4.0	12.62

In the first experiment small portions of the silicates were added in successive stages to the sol of a high-grade gelatin of such concentration that the final product contained always 3 per cent of gelatin. The relative consistency only was measured. The results are tabulated in Tables III and IV.

TABLE III—EFFECT OF SILICATE SERIES 1 ON LIQUEFACTION OF GELATIN
(5 cc. 6 per cent gelatin + 4 cc. water = *a*)

NUMBER	COMPOSITION OF MIXTURE	STATE
1	*a* + 1.0 cc. water (control).	Solid
2	*a* + 0.5 cc. water + 0.5 cc. Silicate 1	Solid
3	*a* + 1.0 cc. Silicate 1	Solid
4	*a* + 0.5 cc. Silicate 1 + 0.5 cc. Silicate 2	Solid
5	*a* + 1.0 cc. Silicate 2	Solid
6	*a* + 0.5 cc. Silicate 2 + 0.5 cc. Silicate 3	Solid
7	*a* + 1.0 cc. Silicate 3	Solid
8	*a* + 0.5 cc. Silicate 3 + 0.5 cc. Silicate 4	Solid
9	*a* + 1.0 cc. Silicate 4	Solid
10	*a* + 0.5 cc. Silicate 4 + 0.5 cc. Silicate 5	Solid
11	*a* + 1.0 cc. Silicate 5	Solid
12	*a* + 0.5 cc. Silicate 5 + 0.5 cc. Silicate 6	Semisolid
13	*a* + 1.0 cc. Silicate 6	Semisolid
14	*a* + 0.5 cc. Silicate 6 + 0.5 cc. Silicate 7	Semisolid
15	*a* + 1.0 cc. Silicate 7	Liquid
16	*a* + 0.5 cc. Silicate 7 + 0.5 cc. Sodium hydroxide 8	Liquid
17	*a* + 1.0 cc. Sodium Hydroxide 8	Liquid

TABLE IV—EFFECT OF SILICATE SERIES 2 ON LIQUEFACTION OF GELATIN
(5 cc. 6 per cent gelatin + 4 cc. water = *a*)

NUMBER	COMPOSITION OF MIXTURE	STATE
1	*a* + 1.0 cc. water (control)	Solid
2	*a* + 0.5 cc. water + 0.5 cc. Silicate 1	Solid
3	*a* + 1.0 cc. Silicate 1	Solid
4	*a* + 0.5 cc. Silicate 1 + 0.5 cc. Silicate 2	Solid
5	*a* + 1.0 cc. Silicate 2	Solid
6	*a* + 0.5 cc. Silicate 2 + 0.5 cc. Silicate 3	Solid
7	*a* + 1.0 cc. Silicate 3	Solid
8	*a* + 0.5 cc. Silicate 3 + 0.5 cc. Silicate 4	Solid
9	*a* + 1.0 cc. Silicate 4	Solid
10	*a* + 0.5 cc. Silicate 4 + 0.5 cc. Silicate 5	Semisolid
11	*a* + 1.0 cc. Silicate 5	Semisolid
12	*a* + 0.5 cc. Silicate 5 + 0.5 cc. Silicate 6	Liquid
13	*a* + 1.0 cc. Silicate 6	Liquid
14	*a* + 0.5 cc. Silicate 6 + 0.5 cc. Silicate 7	Liquid
15	*a* + 1.0 cc. Silicate 7	Liquid

IMPROVED PROCEDURE—In order that more comprehensive data might be obtained a more elaborate procedure was adopted. Cylindrical glass funnels about 25 mm. in diameter and 80 mm. in height were fitted with filter paper, and the outlet tubes were closed by a short sealed piece of rubber tubing. Into these was introduced an excess of the several silicate solutions described, the temperature being about

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[1] Presented before the Division of Physical and Inorganic Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] Fischer, Hooker, Benzinger, and Coffman, *Science*, N. S., **46** (1917), 189; Fischer and Hooker, *J. Am. Chem. Soc.*, **40** (1918), 272; Fischer and Coffman, *Ibid.*, **40** (1919), 303.

[3] *J. Biol. Chem.*, **38** (1919), 179.

[4] *J. Gen. Physiol.*, **1** (1918–19), 39, 237, 363, 483, 559.

[5] The author is indebted to the Philadelphia Quartz Co. for the silicates experimented upon. The analyses of these samples were furnished by William Stericker (Mellon Institute).

[6] R. H. Bogue, *J. Am. Chem. Soc.*, **42** (1920), 2575.

10° C. One-gram portions of the gelatin which had been ground so as to pass a 40-mesh, but retained by a 60-mesh, sieve were poured into each funnel and stirred. After an hour the excess of liquid was drawn off, the gelatin washed by several perfusions of distilled water, and the swelling measured directly in millimeters to which the gelatin rose in the tube. The gelatin was then transferred to small beakers, water was added, and the gelatin brought into solution by warming. Each sample was made up to 100 cc., *e. g.*, a 1 per cent solution, and the viscosity, alcohol number, jelly consistency, and hydrogen-ion concentration were determined.

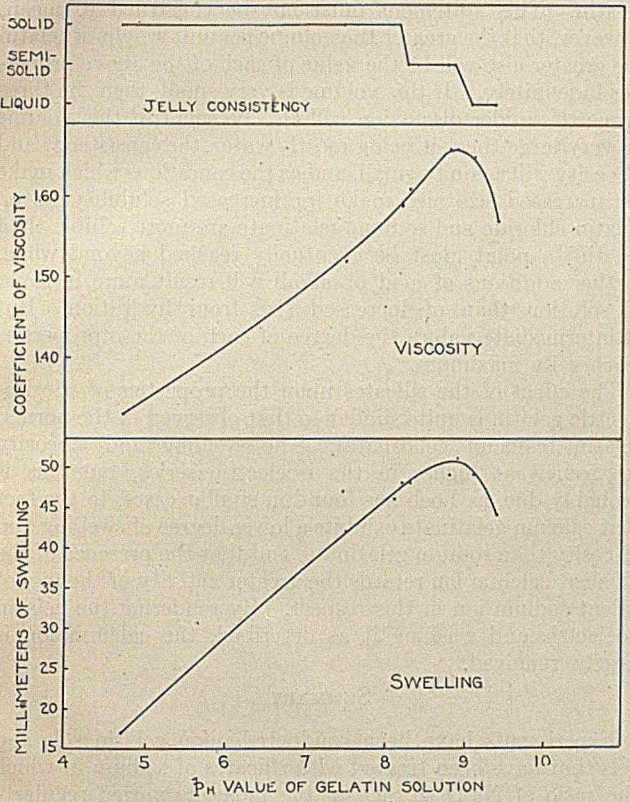

FIG. 1—THE JELLY CONSISTENCY, VISCOSITY, AND SWELLING OF GELATIN AT VARYING pH VALUES. (TABLE VI, SERIES 1)

Viscosity—The viscosity was measured by an Ostwald viscosimeter immersed in a water thermostat set at 35° C. This temperature was selected for the viscosity measurements in order that no complications due to an equilibrium between what C. R. Smith[7] calls the sol form A and gel form B might arise. At 35° the sol form only can exist. The figures given are obtained by dividing the time in seconds for the outflow of the gelatin by the corresponding time for water at the same temperature.

Alcohol number—The alcohol number is taken as the number of cubic centimeters of 95 per cent alcohol which are required to precipitate or produce a definite turbidity in 5 cc. of the gelatin sol at 30° C.

Jelly consistency—The jelly consistency was noted by allowing 10 cc. of the gelatin-silicate mixtures to stand for 12 hrs. at 10° C. Only three degrees of consistency were observed: solid, semisolid, and liquid.

H-ion concentration—The hydrogen-ion concentration was determined by electrometric means. The hydrogen cell was of the type suggested by Clark.[8] Tenth-normal calomel cells, which were made up with great care, were employed. The hydrogen was supplied from a commercial tank and purified by passing through alkaline permanganate, concentrated sulfuric acid, and water containing a little barium chloride. The gas chain and the hydrogen purifying chain were enclosed in an air thermostat set at 30° C. The average deviation during measurements was not greater than ±0.02°. The measurements were made by the use of a Leeds and Northrup type K potentiometer. The value of pH was calculated from the electrode potential by the equation

$$\text{pH} = \frac{\text{E} - 0.337}{0.0601},$$

which was derived from the well-known formula of Nernst:

$$\text{E} = \text{E}_o + \frac{\text{RT}}{n\text{F}} \log_e \text{C},$$

where pH is the log of 1/hydrogen-ion concentration, E the electrode potential at concentration C, E*o* the electrode potential at molar concentration, R the gas constant, T the absolute temperature, *n* the valency of the ion, F the Faraday constant, and C the ionic concentration of the solution.

TESTS ON NORMAL GELATIN—The data obtained by using the gelatin in the normal condition are shown in Table V.

TABLE V—EFFECT OF SILICATES ON PROPERTIES OF NORMAL GELATIN

No.	Per cent Na_2O	Per cent SiO_2	Swelling	Coefficient of Viscosity	Alcohol Number	Jelly Consistency	pH
				Series 1			
0	0.0	0.0	20	1.41	8	Solid	5.8
1	2.0	7.7	37	1.49	23	Solid	7.9
2	2.0	6.7	40	1.51	25	Solid	8.5
3	2.0	5.7	45	1.53	25	Semisolid	8.6
4	2.0	4.8	47	1.58	26	Semisolid	8.7
5	2.0	4.1	47	1.61	25	Semisolid	9.1
6	2.0	3.2	44	1.57	26	Liquid	9.5
7	2.0	2.1	44	1.55	27	Liquid	9.6
8	2.0	0.0	43	1.48	29	Liquid	9.9
				Series 2			
0	0.0	0.0	20	1.41	8	Solid	5.8
1	1.1	4.0	34	1.48	20	Solid	7.5
2	1.2	4.0	38	1.50	22	Solid	7.9
3	1.4	4.0	42	1.52	24	Solid	8.2
4	1.7	4.0	45	1.58	25	Semisolid	8.4
5	2.0	4.0	47	1.61	25	Semisolid	9.1
6	2.5	4.0	46	1.59	27	Liquid	10.0
7	3.7	4.0	43	1.49	30	Liquid	10.8

TESTS ON ISOELECTRIC GELATIN—The above experiments were repeated, but instead of the gelatin in its normal condition, which was essentially calcium gelatinate of a pH of 5.8, the gelatin used was first rendered isoelectric by allowing it to soak for an hour in *N*/128 hydrochloric acid and filtering and washing out the excess of acid by several perfusions with distilled water. The pH value of a 1 per cent solution was found to be 4.7, which is the value of gelatin at its isoelectric point. The data are shown in Table VI.

TABLE VI—EFFECT OF SILICATES ON PROPERTIES OF ISOELECTRIC GELATIN

No.	Per cent Na_2O	Per cent SiO_2	Swelling	Coefficient of Viscosity	Alcohol Number	Jelly Consistency	pH
				Series 1			
0	0.0	0.0	17	1.33	4	Solid	4.7
1	2.0	7.7	42	1.52	24	Solid	7.5
2	2.0	6.7	46	1.58	25	Solid	8.1
3	2.0	5.7	48	1.59	25	Solid	8.2
4	2.0	4.8	48	1.61	26	Semisolid	8.3
5	2.0	4.1	49	1.66	25	Semisolid	8.8
6	2.0	3.2	51	1.66	26	Semisolid	8.9
7	2.0	2.1	49	1.65	30	Liquid	9.1
8	2.0	0.0	44	1.57	32	Liquid	9.4
				Series 2			
0	0.0	0.0	17	1.33	4	Solid	4.7
1	1.1	4.0	39	1.47	23	Solid	7.1
2	1.2	4.0	41	1.49	24	Solid	7.5
3	1.4	4.0	44	1.56	24	Solid	7.8
4	1.7	4.0	46	1.58	25	Solid	8.1
5	2.0	4.0	49	1.66	25	Semisolid	8.7
6	2.5	4.0	48	1.64	30	Semisolid	9.6
7	3.7	4.0	46	1.59	35	Liquid	10.4

In Fig. 1, the jelly consistency, viscosity, and swelling of Series 1 in Table VI are plotted against the pH values.

DISCUSSION

An inspection of the data presented in the several tables and in the figure brings out many points that are of interest. The swelling is found to progress regularly in Series 1 with decreasing silica content, the percentage of soda present being held constant, and in Series 2 with increasing soda

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[7] *J. Am. Chem. Soc.*, **41** (1919), 135; THIS JOURNAL, **12** (1920), 878.

[8] *J. Biol. Chem.*, **23** (1915), 475.

content, the silica in this case being kept constant. This increase in swelling does not continue throughout the entire extent of the series, however, but reaches a maximum beyond which it drops slightly. The coefficient of viscosity is found to behave in an entirely similar manner, as would be expected from the findings previously reported[9] which have shown that solution and viscosity are parallel functions, and swelling is a measure of solvation. If the hydrogen-ion concentration were not simultaneously determined it would be assumed that, in Series 1, the variation in swelling and viscosity were directly attributable to the regular variation in the percentage of silica present, since the soda content remains constant.

But the pH values are found to increase regularly also, and this increase cannot conceivably be attributed to the decrease in silica content *per se*, because the silicic acids have many times been shown to be un-ionized. The only conclusion which may be drawn to account for the increase in the pH value is that as the content of silicic acid in the molecule of the sodium silicates decreases the sodium hydroxide actually present in an ionized condition increases. And this in turn may be brought about only by a continually increasing degree of hydrolysis of the silicates with increasing ratio $Na_2O:SiO_2$. Furthermore, the differences in degree of hydrolytic dissociation on passing through the silicate series must be considerable in order to account for the wide variation in pH, *e. g.*, in Table VI, Series 2, from No. 1 (pH=7.1) to No. 7 (pH=10.4). These results are in complete accord with, and therefore tend to confirm, the conclusions reported in an earlier paper,[10] to the effect that the hydrolysis of the silicates of sodium increases as the ratio of Na_2O to SiO_2 in the molecule increases.

The alcohol number is found to rise regularly with increasing pH, and might conceivably be utilized for the purpose of roughly locating the hydrogen-ion concentration of a solution of gelatin.

The jelly consistency is solid at the lower pH values, but in the neighborhood of pH=8.5 a softening is observed, while at a pH of about 9.5 the gelatin will no longer gel at 10°. The relation of the jelly consistency to the swelling and the viscosity should be especially observed. At the point where the maximum swelling and viscosity are attained the jelly is no longer firm, but has become soft. This is well illustrated in Fig. 1. On further increases in pH, swelling and viscosity begin to decline, and the gelatin, at the concentration used, remains liquid.

This has an important bearing on the explanation of the mechanism of gelation. As the gelatin is brought into the presence of increasing quantities of sodium hyroxide, constantly increasing amounts of gelatin will, according to Loeb[4] be converted into sodium gelatinate. This gelatinate is shown to possess a strong tendency towards solvation, *e. g.*, it swells to a considerable extent. But it also is much more soluble, according to Loeb, than gelatin *per se* and so will not gel under the conditions of our experiment.

But may gelation, and precipitation or coagulation, be regarded as identical? In other words, is gelation dependent primarily upon solubility? There is no doubt that gelatin at its isoelectric point is actually much less soluble than under any other electrical condition. A white, almost granular, precipitate may be obtained by bringing gelatin to that condition. But the writer has data which show that the consistency of the jelly under those conditions may actually be less than at slight intervals on either side of that point. Gelation appears rather to be due to an increase in the solvation or *hydration* of the dispersed particles while true precipitation and coagulation take place only under conditions of excessive *dehydration*. That solvation and viscosity run parallel has already been shown,[9] and the fact that the viscosity at 30° begins to drop when the liquid at 10° will no longer solidify is significant. Swelling is known to be increased by low temperatures, and viscosity is also increased by low temperatures. Gelation is similarly influenced, which means that solvation is much greater at low than at high temperatures. All of our data confirm this point of view.

Since the volume occupied by the dispersed phase is very nearly defined by the degree of solvation, the size of the molecule, *e. g.*, the volume occupied by unit weight of dispersed phase, will be the determining factor in both the degree of swelling, the viscosity, and the jelly consistency of the gelatin. This statement must not be construed to mean, however, that the greater the volume per unit weight of gelatin the greater also will be the value of each of the above properties indefinitely. If this volume is very small, then the three properties under discussion will also be small; if this volume be very large then, it being mostly water, the consistency and viscosity will again be small, and as the conditions which make for increased size also make for increased solubility (*e. g.*, gelatin chloride and sodium gelatinate are more soluble than gelatin) a point must be eventually reached beyond which further additions of acid or alkali will result more in favor of solution than of increased size from hydration. But at intermediate values the degree of each of these properties reaches its maximum.

The effect of the silicates upon the properties of the isoelectric gelatin is quite similar to that observed in the normal gelatin (calcium gelatinate). The swelling and viscosity are somewhat higher in the isoelectric series, but this is probably due, as Loeb has found in similar cases, to the fact that calcium gelatinate exhibits a lower degree of swelling and viscosity than sodium gelatinate, and that the presence of the divalent calcium ion retards the greater activity of the monovalent sodium ion in this respect. By rendering the gelatin isoelectric and washing it as described, the calcium ion is largely removed.

SUMMARY

Experiments have been conducted upon gelatin sols and gels that have been treated with silicates of sodium in which the ratio of Na_2O to SiO_2 in the molecule varied regularly from 1:4 to 1:1. The solutions were made up so that the actual amount of Na_2O was constant in one series, while the actual amount of SiO_2 was constant in the other series. The degree of swelling, viscosity, alcohol number, and pH value were determined in each series, both upon the normal gelatin, which was essentially calcium gelatinate of a pH of 5.8, and upon the gelatin which had been rendered isoelectric and had a pH value of 4.7.

The data obtained show that the swelling and the viscosity increase, in Series 1, with a decrease in the silica content, the percentage of soda being held constant. The pH value is shown to increase constantly, however, as the ratio $Na_2O:SiO_2$ increases. This is due to an increase in the degree of hydrolysis of the silicates. The variation in the above-mentioned properties appears to be dependent upon the pH value, rather than upon the changing silica content. This is further evidenced by the similar behavior of Series 2, in which the silica content remains constant.

The swelling and viscosity reach their maximum value at a pH of about 8.5, and decrease slightly at higher values. The jelly consistency, however, is solid at pH values between 4.7 and 8.0, but at 8.5 it becomes soft, and liquefies at 9.0 and above. This affords the basis of an argument which concludes that gelation is due to and dependent upon the tendency of the substance to become solvated, the volume occupied by unit weight of dispersed phase being the determining factor. When this volume is very small or very

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[9] R. H. Bogue, *J. Am. Chem. Soc.*, **43** (1921), 1764.

[10] *Ibid.*, **42** (1920), 2575.

large the jelly consistency will be small, and, at intermediate values of volume per unit weight, the jelly consistency will reach its maximum.

The results upon isoelectric gelatin are similar to those obtained with normal gelatin, except that higher degrees of swelling and viscosity are attained, because of the absence of the retarding divalent calcium ion.

The alcohol number is found to rise regularly with increasing pH, and it is suggested that this value may be utilized for rough measurements of pH.

The Chemical Changes Involved during Infection and Decay of Wood and Wood Pulp[1]

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A knowledge of the chemical composition of woods and pulps, linked with a study of the changes in composition after infection[2] with specific organisms of molds and wood-destroyers, is of considerable importance in that it throws further light on the astonishing losses sustained through the decay of wood and pulp and in the pulping and conversion into paper of such infected wood and pulp.

A mere study of the organisms of decay, without a thorough investigation of the chemical changes involved, would help but little in solving the problem, because an infected log or lap of pulp may look more or less sound and yet contain wood-destroying fungi which have chemically changed the cellulose, rendering it very much less resistant. By the study of the chemical changes involved, the progress of decay may easily be followed, and the cause of the large losses in pulping infected woods may also be explained.

The methods of analysis, with the exception of the determinations of lignin,[3] solubility in 7.14 per cent sodium hydroxide[4] (α-, β-, and γ-celluloses),[5] and copper number[6] were those described by A. W. Schorger[7] in the "Analysis of Some American Woods." The methods used were chosen with the purpose of following the progress of decay of wood and pulps, and of obtaining data, if possible, which would aid in ascertaining the chemical changes which these substances undergo during decay. It was also hoped to explain the effects of decay on the yield, quality, and pulping characteristics of wood by the mechanical, sulfite, and soda processes.

The cellulose content of the woods and pulps is undoubtedly the constant of most vital importance in the manufacture of paper. This value was therefore determined directly by the Cross and Bevan method, and the nature and progress of decomposition of the cellulose derived from sound and decayed material were studied. Data regarding the latter were obtained by determining the resistance toward chemical reagents, such as the copper number, and the percentages of α-, β-, and γ-celluloses.

The percentage of lignin or noncellulose materials is of importance in the manufacture of chemical pulp; therefore a knowledge of its rate of decomposition relative to that of cellulose would determine whether or not the organisms of decay produced a uniform degradation or selective action on woods and pulps.

The comparison of the solubility in hot and cold water of the sound and decayed woods and pulps would be a direct measure of the losses sustained through the use of decayed materials. These constants would also indicate the extent of decay, as Rose and Lisse have pointed out that decay is associated with increasing molecular simplicity.

During decay wood breaks down to a considerable extent into substances which are almost entirely soluble in alkali.[2] The solubility of the sound and decayed woods and pulps in strong (7.14 per cent $NaOH$) and weak (1 per cent $NaOH$) alkali would be a measure of the progress of decay and also show the hydrolytic action of the organisms of decay. This value would also tend to explain the results obtained in pulping decayed woods by the soda process.

Since the reducing properties of wood and pulp are increased during decay, due partly to the increase in the percentage of the less stable or less resistant celluloses, *viz.*, β- and γ-, and other substances, the copper number was determined. It also seemed desirable to show the relation between the ether-soluble content, the ash, the pentosan, and methylpentosan contents of sound and decayed woods and pulps. The moisture content was determined in order to make the calculations of all results for comparative purposes on the oven-dry (105° C.) or moisture-free basis.

Through the courtesy of a large number of mills coöperating with the Forest Products Laboratory, a number of shipments of sound and infected woods and pulps were received for chemical and pulping studies and for isolation of the typical organisms causing the decay.

The woods studied were spruce, balsam, hemlock, and aspen, representing various stages of decay, determined microscopically.

Comparison of Sound and Infected Spruce Woods and Pulps Derived from Them by Mechanical, Sulfite, and Soda Processes

The sample of fresh sound spruce wood used as a standard of comparison was obtained from the Marathon Paper Mills Co., Rothschild, Wis. The infected spruce woods, representing various stages of decay, as determined by the eye, were carefully selected from the following sources:

1—Very slightly infected, containing some mycelium (determined microscopically), from Cloquet, Minn.

2—Slightly infected, taken from the top of a pile of logs at the Marathon Paper Mills Co., Rothschild, Wis.

3—Wood considerably more infected, taken from the bottom of a pile of logs at the Marathon Paper Mills Co.

4—Very badly infected wood, such as would be rejected for pulping purposes, obtained from the Wausau Paper Mills Co., Brokaw, Wis.

Samples of these woods were shipped to the Forest Products Laboratory for chemical analysis and pulping trials, while some of the wood was made into mechanical pulps on experimental mill runs. The results of the pulping trials will be given in a later publication.[8]

In order to establish the percentage of cellulose as a standard for comparison, and the relation of this constituent to

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[1] Presented before the Section of Cellulose Chemistry at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26–29, 1921.

[2] It has been shown by Rose and Lisse that wood undergoes a chemical change during decay. This Journal, **9** (1917), 284.

[3] Ost and Wilkening, *Chem.-Ztg.*, **461** (1910); Cross and Bevan, "Researches on Cellulose," **III** (1905–10), 39.

[4] Ordnance Department, U. S. A., *Pamphlet* **450** (1918), 16.

[5] Cross and Bevan, "Paper Making," **1916**, 97; Schwalbe, "Chemie der Cellulose," **1911**, 637.

[6] Schwalbe, *Ibid.*, 625.

[7] This Journal, **9** (1917), 556.

[8] Otto Kress, C. J. Humphrey, C. A. Richards, M. W. Bray, and J. A. Staidl, "Deterioration of Wood Pulp and Pulpwood."

TABLE I—RESULTS[1] OF THE CHEMICAL ANALYSES OF SAMPLES OF SOUND (WHITE SPRUCE) WOOD FROM VARIOUS PARTS OF NORTH AMERICA

No.	COMPANY; LOCATION; LOCATION WHERE WOOD WAS GROWN; REMARKS	Moisture	Lignin	Cellulose	Ether-Soluble	Alcohol-Soluble	Annual Rings	RESULTS OF MICROSCOPIC ANALYSIS
....	Sound white spruce (Schorger) from Mellon, Wis.	...	...	61.85	1.36	..	..	Reported as sound
2549	Sound white spruce, Cloquet, Minn.	12.18	30.60	54.65	1.58	..	..	......
Id & g	Pejepscot from cut 10 mi. north of Brunswick, Me.	4.26	26.85	59.70	0.69	0.82	18	Sound
II-A	Northern Paper Mills, Green Bay, Wis. Cl. white spruce	5.02	29.50	57.50	0.15	1.71	53	Considerable mycelium
III-A & bx	Fletcher Paper Co., Alpena, Mich.	4.24	27.90	58.10	0.96	1.07	27	An occasional thread of mycelium
IV-A	S. D. Warren Co., Cumberland Mills, Me.	4.48	26.93	60.15	0.64	0.84	75	Sound
V-A	Marathon Paper Mills, Rothschild, Wis. Fresh sound Wisconsin spruce	3.17	28.30	58.58	1.24	0.83	80	Sound
VI-A	Groveton Paper Mills Co., Groveton, N. H. Spruce woods	5.02	28.12	60.75	0.86	1.10	47	Sound
VII-C	Port Huron Sulphite & Paper Co., Port Huron, Mich. White spruce from Edmunton, Alberta, Canada	3.38	26.89	61.70	0.72	0.41	64	Occasional thread of mycelium
VIII-B	Riordon Co., Ltd., Hawkesbury, Ont.	4.51	28.00	61.10	0.71	1.07	110	Occasional thread of mycelium
IX-A	Hammermill Paper Co., Erie, Pa. White spruce from Ft. William, Canada	3.62	27.60	59.30	0.71	1.17	85	Sound
XB	Laurentide Co., Ltd., Grand Mere, Que., Canada. White spruce from this region	4.98	28.10	60.55	1.53	0.95	40	Sound
XI-A	Abitibi Pulp & Paper Co., Iroquois Falls, Ont. Secured from the bush	5.60	28.41	57.35	1.79	1.56	48	......
XIII-B	Price Bros. Co., Ltd., Kenogami, Que. White spruce. Middle of tree	5.05	27.42	60.95	1.58	0.94	23	Sound

[1] Calculations were made on oven-dry weight of samples of wood.

lignin or noncellulose in sound spruce wood, these constants were determined on a large number of samples obtained from various parts of the United States and Canada.

These samples of sound wood were first examined microscopically by an independent investigator in order to determine their soundness. Slides were made of samples taken from the center of the tree to the circumference. The annual rings were also carefully counted. In Table I are given the results of several determinations made on the samples of wood, together with the locality from which they came.

It was found that the cellulose and lignin content of sound spruce woods varied considerably, depending upon the location in which they were grown. The cellulose content of the samples of spruce woods grown in the northeastern part of the United States and in Canada was much higher than in those grown in Minnesota and Wisconsin. The sample of spruce wood from Mellon, Wis., analyzed by A. W. Schorger[7] showed a very high cellulose content (61.85 per cent); however, this sample was not prepared for analysis in the manner described in this paper. It may also be noted that the spruce wood secured from Edmunton, Alberta, Canada, by the Port Huron Sulphite and Paper Company of Port Huron, Mich., gave the highest cellulose content, although it contained an occasional thread of mycelium or decay. However, since the pulping trials and other chemical studies were made on infected woods from Wisconsin, it seemed advisable not to take the averages of the analytical constants obtained from all of the sound spruce woods, but to use a sound Wisconsin spruce wood as a standard for comparison. The sample of fresh "sound white spruce," from the Marathon Paper Mills Co., Rothschild, Wis., was chosen as a standard for sound spruce, with which other results from the analyses of decayed wood are to be compared, because it was found not to contain any infection or decayed materials. The data on check analyses are given in Table II.

TABLE II—RESULTS OF ANALYSIS OF SOUND WHITE SPRUCE WOOD FROM ROTHSCHILD, WISCONSIN

Sample No.	Cold-Water-Soluble	Hot-Water-Soluble	Ether-Soluble	1 Per cent NaOH	7.14 Per cent NaOH	Copper No.	Lignin	Cellulose	α-Cellulose	β-Cellulose	γ-Cellulose	Pentosan	Methyl-pentosan	Ash	Moisture
V-A	2.25	3.83	...	8.80	18.91	...	...	58.50	63.55	10.37	26.08	11.88	1.88	0.17	3.17
V-A	2.30	3.90	1.24	8.83	18.90	4.14	28.30	58.40	...	...	...	...	...	...	...
Av.	2.28	3.87	1.24	8.82	18.90	4.14	28.30	58.50	63.55	10.37	26.08	11.88	1.88	0.17	3.17

TABLE III—RESULTS OF ANALYSIS OF SOUND AND INFECTED SPRUCE WOODS

KIND OF WOOD (SPRUCE)	Cold-Water-Soluble	Hot-Water-Soluble	Ether-Soluble	1 Per cent NaOH	7.14 Per cent NaOH	Copper No.	Lignin	Cellulose	α-Cellulose	β-Cellulose	γ-Cellulose	Pentosan	Methyl-pentosan	Ash
Sound spruce V-A, Rothschild, Wis.	2.25	3.83	...	8.80	18.91	4.14	...	58.58	63.55	10.37	26.08	11.88	1.88	0.17
Average	2.30	3.90	1.24	8.83	18.80	...	28.30	58.40	...	...	...	...	...	...
White spruce No. 2549, Cloquet, Minn. Very slightly infected	3.47	5.61	1.58	15.07	24.00	5.55	30.60	54.60	...	...	...	...	...	0.38
Slightly infected No. 2545 Marathon, top of pile, mill run	4.19	6.39	1.71	20.64	28.54	7.74	30.51	54.18	42.86	37.68	19.46	11.31	1.63	1.37
Infected No. 2546 Marathon, bottom of pile	5.54	9.75	1.38	39.92	49.28	17.48	35.21	46.90	27.75	61.45	10.80	9.45	2.66	0.75
Badly infected spruce No. 2541 Brokaw	6.58	11.92	1.47	44.00	62.36	23.57	38.20	42.00	17.00	74.60	8.40	8.50	3.77	0.61
Dead head spruce No. 2556, Sartell, Minn.	1.41	1.34	0.59	12.00	19.70	5.97	30.96	59.5	60.00	16.10	23.90	9.81	2.84	0.45

DISCUSSION OF THE ANALYSES OF SOUND AND DECAYED SPRUCE WOODS

In Table III are listed the more important chemical constants of the five typical spruce woods described above. There are also included in this table the data on the analysis of a "dead head" or water-logged sample of spruce wood.

The cellulose content of the wood decreases very considerably with increased decay. Taking the extremes of the sound and infected wood, we find such results as 59.50 and 42.00 per cent, respectively, in the total cellulose content for Wisconsin woods. Although the difference in the cellulose content is comparatively large in the decayed woods as compared with the sound, far more indicative of the amount of decay is the fact that the cellulose obtained from the decayed woods is not as stable or as resistant toward chemical reagents as that obtained from sound woods. Practically 60 per cent of the cellulose from sound wood is stable, or the so-called α-cellulose, whereas, only 17 per cent of the small cellulose content of decayed wood is α-cellulose. This ratio of one-fifth as much stable cellulose in the decayed wood as in the sound, and the low chemical resistance of the unstable celluloses found in the decayed woods, would tend to explain the small yields obtained from pulping decayed woods, especially in the soda and sulfate processes. As the process of decay progresses, there is a very marked increase in the less stable or β-cellulose. This appears to be due either to the metabolism of the organisms of decay or to the action of enzymes, produced by these organisms, on the cellulose. The increase in β-cellulose in extremely decayed over sound woods is approximately 60 per cent of the cellulose. This very large

TABLE IV—RESULTS OF ANALYSIS OF THE CORRESPONDING "SULFITE PULPS" FROM SPRUCE LISTED IN TABLE II

KIND OF WOOD	Cold-Water-Soluble	Hot-Water-Soluble	Ether	1 Per cent NaOH	7.14 Per cent NaOH	Copper No.	Lignin	Cellulose	α-Cellulose	β-Cellulose	γ-Cellulose	Pentosan	Methylpentosan	Ash
No. 2561 paper from sound white spruce, typical	0.15	0.00	1.12	11.02	20.53	3.05	1.26	97.25	87.50	3.19	9.31	3.55	0.89	0.29
No. 2547 paper from No. 2545 Marathon (top of pile) wood	0.00	0.00	1.59	10.85	24.89	2.66	2.80	96.17	75.83	17.85	6.32	4.61	0.60	0.57
No. 2548 paper from No. 2546 Marathon (bottom of pile) wood	0.00	0.00	1.01	13.46	31.39	3.78	2.19	96.18	72.96	22.00	5.04	3.69	1.47	0.50
No. 2555 paper from No. 2541 Brokaw infected wood	0.32	5.00	0.91	31.90	52.80	9.05	1.73	94.44	46.05	48.62	5.33	2.97	1.43	0.81
No. 2560 Nekoosa-Edwards wood comparable with No. 2547 or Marathon (top of pile)	0.37	0.00	1.36	14.32	28.20	3.87	1.58	96.50	79.40	11.40	9.20	4.25	0.94	0.33

TABLE V—RESULTS OF ANALYSES OF "SODA PULPS" FROM SOME OF THE SPRUCE WOODS

KIND OF PULP	Cold-Water-Soluble	Hot-Water-Soluble	Ether	1 Per cent NaOH	7.14 Per cent NaOH	Copper No.	Lignin	Cellulose	α-Cellulose	β-Cellulose	γ-Cellulose	Pentosan	Methylpentosan	Ash
No. 2559 paper from infected Nekoosa-Edwards spruce	0.86	0.19	1.02	3.23	6.59	2.58	9.64	89.42	57.10	39.10	3.80	7.80	0.70	1.17
No. 2557 paper infected Brokaw wood No. 2541	0.65	0.00	0.72	7.01	13.64	7.92	38.32	56.43	23.36	69.66	6.98	4.58	2.77	2.08

difference in extreme cases of decay points out very clearly how the progress of decay of spruce may be observed by this determination.

RESULTS OF THE CHEMICAL ANALYSIS OF PULPS MADE FROM SOUND AND DECAYED SPRUCE BY THE SULFITE PROCESS

These spruce woods, together with a sample of infected wood from Port Edwards, Wis., were separately subjected to pulping by the sulfite process, in the small digester at the Forest Products Laboratory. The pulp was run into waterleaf paper on the small experimental paper machine and the samples thus obtained were chemically analyzed, by the same methods of procedure as in the case of the woods.

It will be noted in Table IV that the cellulose content of pulp made from these woods by the sulfite process decreased with increased decay. But the difference is not so marked as in the woods themselves. There is a difference of only about 3 per cent in the most extreme cases. The α-cellulose, however, indicates again how far the decay had advanced in the woods previous to pulping. There is only one-half as much α-cellulose in pulp made from the badly rotted wood as in the pulp made from sound wood, or, in other words, the decrease is from 87.50 per cent to 46.05 per cent.

There is a great difference in the β-cellulose content of waterleaf pulp made from sound and decayed woods. In pulps made from sound wood, the β-cellulose is only 3 per cent of the total cellulose, while it is 48.62 per cent of the total cellulose in paper made from decayed wood. The proportion of γ-cellulose in the total cellulose content remains practically constant in pulps made from sound and decayed woods. This would tend to show that the γ-cellulose had been practically removed by the drastic treatment of the woods during the pulping process. The amount of γ-cellulose obtained in the determinations is probably due to the action of the alkali on the original "Cross and Bevan" cellulose. The fact that a second treatment of the α-cellulose with 17.5 per cent sodium hydroxide gives an additional loss of 5 per cent (as proved by the authors and also shown by C. G. Schwalbe and Becker[9]) would tend to show that a small amount of γ-cellulose is possibly formed by the action of the alkali, even though it is completely removed during the pulping process. The additional fact that γ-cellulose is easily hydrolyzed also points to the fact that γ-cellulose was practically removed by the pulping process.

CELLULOSE DETERMINATIONS—In studying the pulping characteristics of sound and decayed woods by the soda process (data of which will be given in a later publication), it was found that the pulp made from badly rotted wood (Sample 2541, Table III) was very raw (brash and dirty). This was because the wood neutralized or made inactive practically all of the alkali before the cook had reached completion. It may be pointed out here that there is a tremendous loss in chemicals when decayed wood is pulped by the soda process. This point will be taken up in greater detail in the discussion of the results of the action of dilute and strong alkali solutions on sound and decayed woods and pulps.

It will be noted in Table V that the pulp made from badly rotted wood by the soda process has a very low cellulose content (56.43 per cent) as compared with pulp from only partly decayed wood (89.42 per cent).

RESULTS OF CHEMICAL ANALYSIS OF PULPS MADE FROM SOUND AND DECAYED SPRUCE BY GROUNDWOOD PROCESS

Two samples of spruce wood, one representing a practically sound Wisconsin spruce ground daily at one of the large Wisconsin mills, and the other representing badly rotted wood taken from the bottom of a pile of logs, were subjected to pulping by the groundwood process at one of the coöperating mills.

These samples, together with a sample of sound pulp, were inoculated with a wood-destroying fungus and stored for 6 mo. in a constant temperature and humidity room before analysis. The data in Table VI show that the cellulose content of sound groundwood pulp is practically the same as that of pulp made from badly rotted wood, *e. g.*, 60 and 59.69 per cent, respectively. These results may appear surprising at first. However, if the small yield (78.5 per cent) obtained and also the value of the pulps resulting from the use of badly rotted woods, as compared to that of sound wood, is taken into consideration, one can easily see the tremendous losses which must be sustained by the mills from the use of decayed woods.

The cellulose content remains practically constant because of the large percentage of cold- and hot-water-soluble products found in the rotted woods. These values make up the large amounts of material found in the "white water" which is a direct loss to the manufacturer.

Sample 26 of groundwood pulp (Table VI) made from sound spruce wood infected with a wood-destroying fungus gave a very decided decrease in the cellulose value, *e. g.*, from 60.00 per cent to 43.00 per cent. S. A. Mahood and D. E. Cable[10] have indicated that the cellulose content of infected groundwood pulp is reduced. The cellulose content of the two pulps made from sound and infected woods, when stored in the fungus pit for 6 mo., showed a greater decrease in the case of the pulps made from wood that was already infected than that made from sound wood. This fact, together with the evidence shown in Table VI, brings out more plainly the losses involved in using infected wood, especially in cases where the pulp is to be stored for any length of time.

The α-, β-, and γ-celluloses in these pulps, made from sound and infected woods, remain practically constant, while pulp that has been infected and stored for 6 mo. after manufacture shows a large decrease in α- and γ-cellulose and a very decided increase in β-cellulose.

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[9] *Paper*, **27** (1921), No. 25, 21.

[10] "A Chemical Investigation of Sound and Infected Groundwood Pulp," *Paper*, **25** (1920), No. 24, 11.

Table VI—Results of Analyses of the Corresponding "Groundwood Pulps" from Woods in Table III

Kind of Pulp	Cold-Water-Soluble	Hot-Water-Soluble	Ether	1 Per cent NaOH	7.14 Per cent NaOH	Copper No.	Lignin	Cellulose	α-Cellulose	β-Cellulose	γ-Cellulose	Pentosan	Methypentosan
No. 2544 sound groundwood corresponding to No. 2545 Marathon wood (top of pile)	0.00	1.00	0.41	10.13	18.28	4.44	31.00	60.00	60.53	24.48	14.99	11.96	2.01
No. 2558 paper groundwood Marathon (bottom of pile) No. 2546	0.68	1.45	0.786	17.72	27.43	6.63	29.74	59.69	58.69	26.71	20.60	10.37	2.65
No. 26 groundwood pulp infected with wood destroyers and stored for 6 mo. in sterile bottles	6.94	11.06	0.16	47.40	62.80	23.90	35.30	43.00	31.35	63.20	5.45	8.44	3.04

General Discussion of Constants Obtained by Complete Chemical Analysis of Sound and Decayed Spruce Woods and Pulps Made Therefrom by the Three Processes

CELLULOSE—The data obtained from the complete analysis of sound and infected woods and pulps indicate quite clearly that the wood and pulp in most cases of extreme decay breaks down, as might be expected, by a more or less selective action of the organisms.[11] That the organisms, especially the wood destroyers, attack the cellulose to a larger extent than the noncellulosic material is shown by the large decrease in cellulose and the apparent increase in the noncellulosic material or lignin. The words "apparent increase" are used because the lignin content remains nearly constant during decay, if the loss in weight of the decayed wood is taken into consideration and the results of the lignin determinations are based on the weight of the original sound wood. In other words, the actual weight of lignin obtained from a definite weight of sound wood remains practically the same after the wood has decayed. This selective action on the cellulose is especially marked in the case of badly decayed groundwood pulps inoculated with wood destroyers. The data indicate plainly that as the decay progresses the percentage of cellulose decreases, but far more indicative of the progress of decay is the decrease in the amount of the α- or stable cellulose, and the very decided increase in the percentages of the β- or less stable cellulose. The decrease in the amount of γ-cellulose would show that the cellulose is broken down by the process of decay into the less stable or less resistant β- and γ-celluloses. But since γ-cellulose occurs in smaller amounts in decayed woods than in sound wood and pulp, it would appear that the γ-cellulose is a transition form of cellulose and is broken down into simpler compounds much more rapidly than it is formed by the action of the organisms of decay. It would appear, from the foregoing statements, that fungus cellulose is composed mainly of the two less stable celluloses, *e. g.*, β- and γ-, since these two celluloses and their cleavage products are most abundant in decayed woods and pulps.

LIGNIN—The results in Table I show that the lignin content or the noncellulosic material of spruce wood, as determined by a modification of the Ostand Wilkening[12] method, bears a more or less direct relation to the cellulose content in sound spruce woods. In other words, the ratio of lignin to cellulose is practically constant. This relation appears to be independent of the locality where the woods were grown, or the rate of growth or the age of the tree. However, in infected woods (Table III) this relation does not hold in all cases, as was shown in the discussion under cellulose. The extreme case of sound and badly rotted wood shows an increase of 10 per cent in lignin.

The lignin content of the sulfite pulps made from sound and infected woods remains nearly constant and depends upon the cooking conditions applied in reducing the wood to pulp. This may also be said of the lignin remaining in the pulps made by the soda and sulfate processes. The high lignin content of 38.32 per cent in soda pulp from the badly rotted wood is a result of the raw cook, due to the fact that the wood neutralized the alkali, practically at the beginning of the operation. The slight increase in lignin content in infected groundwood pulp is due to the larger hot- and cold-water-soluble materials in the decayed wood.

HOT- AND COLD-WATER-SOLUBLE CONSTANTS—These constants increase to a very great extent with the increase in decay of wood and pulp. Mahood and Cable[11] found that the water-soluble content of groundwood pulp increased as a result of infection. Taking for example the extremes of the sound and infected wood, there are such differences as 3.83 and 11.92 per cent hot-water-soluble material and 2.25 and 6.58 per cent cold-water-soluble material. If one takes into consideration the tremendous loss of practically 12.00 per cent of the total wood, when pulping infected woods, one can see what this means to the manufacturer. The greatest losses occur in the groundwood process. A mill run on sound and infected spruce showed yield figures on a weight basis of 84.5 and 78.5 per cent, respectively, and on a cord basis a yield of 390 lbs. more per cord of sound wood than were obtained per cord of infected wood. Aside from these actual losses there is a very decided further loss from the decrease in quality of the stock made from infected wood, which, however, cannot be accurately estimated. In Table VI (Sample 26) it is shown that another 11 per cent hot-water-soluble loss is sustained when infected pulp, stored for 6 mo., is reduced to paper.

ETHER-SOLUBLE MATERIAL—According to the data on both spruce woods and pulps, the ether-soluble material, consisting of resins, waxes, etc., does not change materially with increased decay; hence, this determination is not a criterion of the progress of decay.

ALKALI-SOLUBLE MATERIAL—The values obtained upon treating the woods and pulps with solutions of 1 per cent and 7.15 per cent sodium hydroxide show, in general, that the infected woods are less resistant to alkaline reagents. There are very decided increases in solubility with the progress of decay, when sound and infected woods and pulps made from them by the sulfite, soda, and groundwood processes are treated with the two concentrations of alkali. Such differences as 18.91 and 62.36 per cent strong-alkali-soluble were found in sound and infected wood, respectively. The increase in alkali solubility with increase of decay was almost as striking in the case of sulfite pulps made from these woods.

In reducing the badly rotted wood to soda pulp, under the same cooking conditions as were used for sound wood, the alkali liquor was neutralized or made inactive practically at the beginning of the cook. This resulted in a very raw cook. These results are confirmed by E. Sutermeister in a recent publication.[13] The resulting pulp, as would be expected, gave a very high alkali solubility compared with that obtained from pulp made from slightly infected wood.

The alkali solubility values, obtained on groundwood pulp made from these woods, showed an increase with increased decay. These values, however, are not as high as those resulting from direct treatment of the woods. This wide variation is accounted for in the fact that in the one case the analysis was made on waterleaf paper made from the pulp and in the other on the wood. In the drastic treat-

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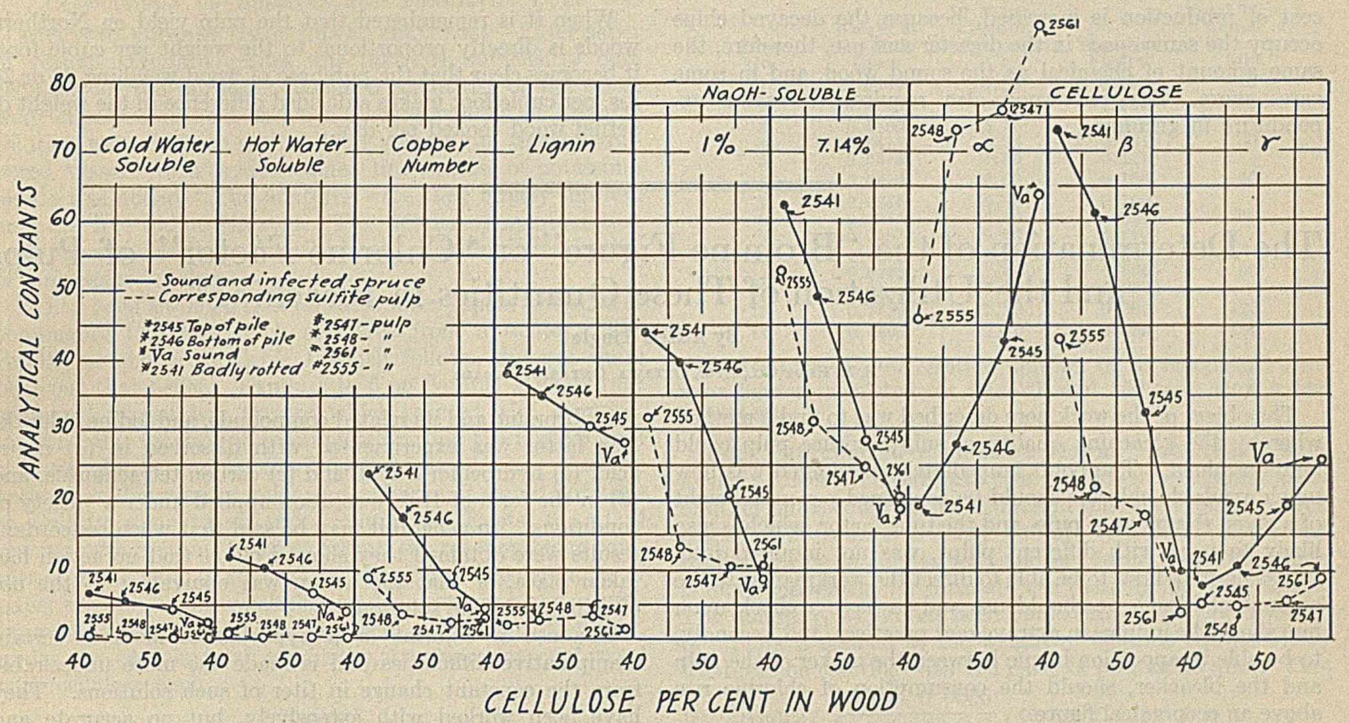
[11] This is also shown in the work of B. Johnsen and R. W. Hovey, *Paper*, **21** (1918), No. 23, 46.

[12] *Chem.-Ztg.*, **34** (1910), 461; Cross and Bevan, "Researches on Cellulose," III (1905–10), 39.

[13] "Decay of Pulpwood and Its Effects in the Soda Process," *Pulp Paper Mag. Can.*, **19** (1921), 733.



Analytical Constants for Sound and Infected Spruce and Corresponding Sulfite Pulp

ment of beating and screening and repeated washings, the finer particles which show the greatest solubility in alkali are removed.

The extremely high value of 62.80 per cent strong-alkali-soluble, obtained from groundwood pulp (Sample 26, Table VI) infected with a wood-destroying fungus and stored for 6 mo. in sterile bottles at constant temperature and humidity, again shows a direct comparison between sound and infected woods and pulps.

copper number—This value is a measure of the reducing power of the woods and pulps. The data show a large increase in this value with increased decay in the woods. The difference in this value for pulps is not nearly as marked except in the case of infected groundwood pulp, where the copper number is as large as is obtained from badly rotted spruce wood. The large copper values in the decayed woods and pulps are due to the cleavage products formed by the action of the organisms of decay, and possibly to some extent to the increase in lignin.[14]

pentosans and methylpentosans—The yields of pentosans obtained from the sound and infected spruce woods appear to decrease with the progress of decay, while the methylpentosan content increases with decay. The percentages obtained from pulps made from sound and decayed spruce wood give no uniform values from which conclusions might be drawn.

Although the values of these chemical constants are a measure of the content of pentosans which are obtained by the Tollens method,[15] a number of compounds introduce an error in this determination. Oxycellulose, oils or waxes, and fatty decomposition products[16] yield furfural, the error of which is difficult to eliminate. Although a correction to lessen this error has been worked out, it may be seen that the difficulty encountered lies in obtaining an accurate knowledge of amounts of each one of the compounds which introduce the error.

ash—The results of this determination are of little value, because the mineral content of woods remains practically unchanged during decay.

Relation of Analytical Constants to Per cent Cellulose

The results given in the figure show at a glance the large losses in woods and pulps due to infection and decay, and indicate how the chemical constants increase or decrease with the progress of decay.

The cellulose content of woods and pulps is undoubtedly the constant of most vital importance in the manufacture of paper. This value has, therefore, been used as a basis for plotting the other analytical constants.

Conclusions

The conclusions from the chemical standpoint which may be drawn from this work are that in all cases the infected woods produce less pulp per unit weight of wood than the sound woods.

The inferiority of the infected woods over the sound woods are:

1—The cold- and hot-water-soluble materials increase during decay and are a direct loss to the mills.

2—Higher alkali-soluble materials are found, showing a lower resistance to the action of chemical reagents. This would be very noticeable in a soda or sulfate mill, because more alkali than would be necessary for sound wood would be required to accomplish the same result.

3—There is an increase in copper number showing that infected wood contains a greater amount of reducing compounds.

4—In most cases of extreme decay, the rate of degradation of lignin and cellulose is selective and not uniform.

5—Lower percentage of α- or stable cellulose, higher percentage of β- or less stable cellulose.

The large losses sustained in converting infected woods into pulps, together with the additional losses of further converting these pulps (made from infected woods which undergo further decomposition when stored) into paper, have been pointed out.

The paper made from decayed woods and pulps is dirty, brash, and has very little strength. It requires more sizing, offers difficulty in sticking to the couch and press rolls, and foams excessively.

The yield of finished paper is greatly reduced, while the

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[14] E. Heuser, "Determination of Lignin," *Paper*, **27** (1921), No. 23, p. 24.

[15] Ellett and Tollens, *J. Landw.*, **53** (1905), 20.

[16] Browne, "Handbook of Sugar Analysis," 452.

cost of production is increased, because the decayed chips occupy the same space in the digester and use, therefore, the same amount of chemical as the sound wood, and in some cases more. Decayed wood also requires the same expenditure in grinding.

When it is remembered that the pulp yield on Northern woods is directly proportional to the weight per cubic foot, it becomes clear that the purchase of wood weighing 28 or 24 lbs. per cubic foot makes a decided difference in the weight of actual wood cooked per day.

The Determination of the "Bromine Figure" or "Chlorine Factor" of Pulp, and the Utilization of These Quantities in Bleaching[1,2]

By Alfred Tingle

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The object of the work here described was to find a method whereby the bleaching quality of sulfite spruce pulp could be determined. The point immediately considered was how much available chlorine should be consumed per unit weight of a given shipment of pulp, and the time factor, which is also likely to vary with different pulps, was not inquired into. It was desired, first, to be able to direct the workman as to the amount of bleach he should use and to have a check upon him should he indulge in extravagant practices, and, secondly, to be able to apportion blame between the maker of the pulp and the bleacher, should the consumption of chlorine rise above an economical figure.

This first object has only partly been attained at present. Owing to the fact that the pulp must be dried before any result can be obtained, the process consumes much time when applied to routine control work. It can, also, be used only by a man versed in careful analytical procedure.

The second object has been fully attained, to judge by the results in this laboratory and mill. Its general utility and final reliability can, however, not be settled by work done in a single laboratory, where of necessity the pulps examined are of only a few types. The work is now published in the hope that it may be duplicated elsewhere, receiving criticism and, if necessary, condemnation as the result of extended experience.

Preliminary Considerations

CHOICE OF REAGENTS—There seemed to be three possible classes of reagent by which the chlorine-consuming power of a pulp might be measured, *viz.*, (1) compounds which react specifically with lignone, and supposed to give condensation products, (2) oxidizing agents, and (3) halogens or halogen-producing compounds.

Cross and Bevan's phloroglucinol reaction might be considered as a type of the first class. It was dismissed as too tedious and probably not sufficiently sensitive. Preliminary experiments showed that nothing could be based on the absorption of an aniline salt from its solution by lignone. The quantity of amine thus withdrawn is small in proportion to the lignone present, and the action is possibly one of solid solution rather than chemical combination.

In Class 2, potassium ferricyanide was tried, while mixtures of potassium permanganate or dichromate with hydrochloric acid may be considered as belonging to either Class 2 or 3, according to the concentration of the solutions used. In all three cases it was found that under experimental conditions leading to the attack of lignone, cellulose was also attacked, generally to a marked degree; if action was so moderated as to leave cellulose unacted upon, the lignone remained also little attacked.

More definitely in Class 3 come chlorine and the hypochlorites, bromine and its related compounds, and iodine chloride. The latter was experimented with dissolved in (*a*) acetic acid, (*b*) hydrochloric acid, and (*c*) carbon tetrachloride, and (*d*) in the form of Hubl's solution applied under a variety of conditions. In general it may be said that when concordant results were obtained they showed either that no action had taken place, or that the action was equivalent to the use of ordinary iodine solution.

The use of chlorine or a hypochlorite involves certain manipulative difficulties and is made the more undesirable from the constant change in titer of such solutions. They have been worked with extensively, but no accurate and accepted method involving their use has yet been evolved.

Bromine does not present quite so many difficulties at first sight. While the titer of bromine water does not remain constant, a solution of bromine in alkali will, over considerable periods, give the same amount of bromine when acidified. Thus what is equivalent to a permanent standard solution of bromine can easily be prepared, though it can be used only in acid media. The relative extent of action of bromine on lignone and cellulose is not well known, and experiments made to elucidate this point were not at first concordant.

THE MEANS OF OVERCOMING DISCREPANCIES—As experiments were continued it became apparent that discordant results had a purely mechanical origin. Liquid reagents were acting upon a solid pulp; a solid, too, which had in some cases been rendered very nonabsorbent in the drying process to which it had been subjected. In some cases reaction did not proceed throughout the mass, while in others the reacting liquid held in the pores of the solid differed in composition from the main volume. Experiments were then made, in the course of which the cellulose was completely dissolved before addition of the reagent, and concordant results became the rule.

The solvent chosen was a mixture of 9 volumes HCl (sp. gr. 1.19) to which was added 1 volume H_2SO_4 (sp. gr. 1.84). The mixture could be made before being added to the pulp, but in some cases solution was better effected by first saturating and disintegrating the pulp with hydrochloric acid, then adding the requisite amount of sulfuric acid, which formed a gelatinous but clear solution. When water was added, cellulose was precipitated from this solution in such a fine state of division that it was readily penetrated by reagents.

Any chemical change in the cellulose which may accompany these physical changes is not important in the present work so long as the new products are, like the cellulose, unattacked by the reagents used in determining the lignone.

Experiments made with hypochlorites, even after the adoption of this solvent, continued to give discrepant results. This was attributed, at least in part, to the mechanical loss of chlorine, which could be avoided only by using elaborate apparatus. Bromine was not subject to this difficulty and experiments were continued with that reagent.

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[1] Presented before the Section of Cellulose Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] Received May 28, 1921.

INTERACTION OF BROMINE AND DISSOLVED PULP[3]

ACTION OF BROMINE ON DISSOLVED CELLULOSE—Filter paper of various standard grades was taken as sufficiently pure cellulose for the purpose. Weighed quantities of the paper were dissolved in acid and a measured volume of bromine solution was added to each. After standing in tightly stoppered vessels for a predetermined time, excess of potassium iodide was added. The mixtures were then largely diluted, and the free iodine titrated. The details of manipulation were the same as those described below for the investigation of unbleached pulps.

It had been assumed that all these filter papers would be of thoroughly bleached stock and free from antichlor. The results, as shown in Table I which follows, did not quite bear out that belief. Expts. 1 to 5 on Sample A show that some constituent was present which reacted with bromine, but that this reaction was completed within the first 90 min. and was almost completed within the first 40 min. Had the action been between bromine and cellulose, it would not have so quickly come to an end. Sample B (Expts. 6 and 7) reacted with bromine to a less extent, the reaction being completed in 30 min. or less. The remaining three samples of paper seem to be purer cellulose and showed no reaction with bromine in 30 min. or more. It seems a safe conclusion that, under the experimental conditions, bromine does not react with cellulose itself.

TABLE I

Expt. No.	Weight of Filter Paper Gram	Time of Action of Bromine Min.	0.1 N Bromine Solution Consumed Cc.	Sample of Filter Paper Used
1	0.6025	40	0.6	A
2	0.6635	60	0.7	
3	0.6685	90	0.8	
4	0.6635	120	0.8	
5	0.6953	150	0.8	
6	0.5878	30	0.3	B
7	0.5840	90	0.3	
8	0.5210	30	0.0	C
9	0.5458	40	0.0	
10	0.5300	60	0.0	
11	0.5730	120	0.1	
12	0.6356	30	0.0	D
13	0.6413	30	0.0	E

ACTION OF BROMINE ON UNBLEACHED SULFITE SPRUCE PULP—Experiments were made in a manner similar to the foregoing, substituting an unbleached sulfite spruce pulp for the "pure" cellulose. Samples were in every case taken from the same small sheet of pulp, the only variation in the experiments being the time factor. The results were calculated to a common basis for which the term "bromine figure" is suggested. This is defined as the weight in grams of pulp which reacts with 1 cc. of 0.1 N bromine solution. The "bromine figure" calculated from each determination is shown in the fourth column of Table II. It should be remarked that where several determinations have been made for a given time of action, they have been made on different occasions and under as widely different circumstances as the method of manipulation can permit.

A study of these figures led to the following conclusions:

1—More than 50 per cent of the reaction takes place in the first 10 min.

2—After 20 to 30 min. there is a pause in the changes which occur. It seems as though a definite stage in the reaction were reached, and as though no further bromine was consumed till this stage was completed.

3—*For this 30-min. time interval all determinations on the same pulp agree very closely.*

4—After the stage which is reached in 30 min. the reaction becomes more irregular. Determinations made at the end of a 60-min. period show poor agreement *inter se.*

TABLE II

Expt. No.	Weight of Dry Pulp Gram	0.1 N Bromine Solution Consumed Cc.	"Bromine Figure"	Total Time of Action of Bromine Min.
1	0.6086	5.15	0.118	10
2	0.5745	5.15	0.111	20
3	0.6460	5.75	0.112	30
4	0.6413	5.75	0.111	
5	0.6278	5.65	0.111	
6	0.6390	6.00	0.106	40
7	0.6245	5.85	0.106	60
8	0.6345	6.60	0.096	
9	0.7257	6.60	0.110	
10	0.6970	7.20	0.096	90
11	0.6925	7.00	0.099	
12	0.7170	7.20	0.099	
13	0.7520	7.80	0.096	120
14	0.6865	7.10	0.096	150

5—After 90 min. the reaction appears to be complete. Bromine figures calculated for 90, 120, and 150 min. show a fair agreement.

THE "THIRTY-MINUTE BROMINE FIGURE" AND THE "CHLORINE FACTOR" CONSIDERED AS CONSTANTS—Examination of other pulps confirms the deduction that the bromine which reacts in 30 min. is a fairly definite constant. Analytical results can be calculated into another form, however, which is more convenient for ultimate use than the bromine figure. The quantity, which has been named the "Chlorine Factor" of a pulp, is defined as the weight of chlorine equivalent to the bromine reacting with 100 parts of pulp in 30 min. This is obviously $\frac{100 \times 0.0035}{\text{bromine figure}}$, or more directly

$$\frac{100 \times 0.0035 \times \text{cc. of } 0.1\ N \text{ Br consumed}}{\text{weight of pulp sample}}.$$

The results of determinations of these constants on six pulps having very different histories are given in Table III and show the extent of agreement which may be expected.

TABLE III

Expt. No.	Weight of Dry Pulp Gram	0.1 N Bromine Solution Consumed Cc.	"30-Minute Bromine Figure"	"Chlorine Factor"	Sample No.
1	0.6135	3.60	0.1704	2.083	A
2	0.7160	4.20	0.1704	2.082	
3	0.6570	3.30	0.1990	1.783	B
4	0.6490	3.30	0.1966	1.805	
5	0.5267	4.70	0.1120	3.168	C
6	0.6880	5.90	0.1166	3.044	
7	0.7575	6.80	0.1114	3.186	D
8	0.7795	7.10	0.1098	3.233	
9	0.7722	4.40	0.1755	2.023	E
10	0.7347	4.20	0.1749	2.029	
11	0.6278	5.65	0.1111	3.194	F
12	0.6413	5.75	0.1112	3.183	
13	0.6460	5.75	0.1123	3.159	

The determinations on Sample C do not agree as closely as they should, but in setting forth this work no eliminations have been made except where a known fault of manipulation has led to obvious error.

The difference between the determinations on Sample D amounts to 0.047 in the chlorine factor. When the practical application of the constant is explained, it will be seen that this difference has slight significance.

UTILIZATION OF THE "CHLORINE FACTOR"

It is obvious enough that the chlorine factor is not the weight of chlorine required to bleach 100 parts of pulp. The experience of this mill is that it does bear a simple and definite relation to the latter quantity.

It is now suggested that for a well-washed pulp the weight of chlorine required to bleach 100 lbs. dry weight = chlorine factor × K.

It may be found that K varies according to the practice of different mills. As bleaching is carried out at the mill where these experiments were made, the value determined is 3.

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[3] In the following experiments it must be understood that by "decinormal bromine solution" is meant a solution of bromine in dilute alkali, of such strength that when added to an acid medium it liberates the amount of bromine contained in the same volume of decinormal bromine solution.

Thus, a certain pulp was found to have consumed 6.03 lbs. of chlorine per 100 lbs. of dry material, in the ordinary run of mill practice, excess of bleach being added and the amount of this excess determined. The same washed pulp showed a chlorine factor 2.026, so that the calculated weight of chlorine required to bleach 100 lbs. was 6.078 lbs. Agreement of theory and mill practice could not well be closer.

It need hardly be said that bad methods such as negligent washing, excessive temperature, etc., will affect the apparent value of K. Whether its value will be the same in every well-conducted mill can be decided only by the extended observations of many competent observers. It would be of great interest to know also whether this method is applicable to pulps of entirely different types made from different woods and by different processes. It is too early to speculate as to whether the fact that $K=3$ (at least for certain bleaching methods) has any theoretical significance, but if this value is found to be a general one, a theoretical reason might be suggested.

Detailed Description of Analytical Method

PREPARATION OF BROMINE SOLUTION—Add 8 g. of bromine to 100 cc. *N* NaOH solution, agitate till solution is complete, then boil. When cool, dilute to 1 liter. Standardize by adding potassium iodide to a known volume, acidifying with hydrochloric acid and titrating the liberated iodine against 0.1 *N* sodium thiosulfate solution.

The above product remains for weeks without appreciable change in strength and when run into an acid solution is equivalent to a 0.1 *N* solution of bromine.

PREPARATION OF "ACID SOLVENT"—Into a flask containing 450 cc. of hydrochloric acid (sp. gr. 1.19) pour slowly 50 cc. of sulfuric acid (sp. gr. 1.84). Mix thoroughly and allow to cool. This mixture will generally gelatinize and dissolve pulp in a few minutes. Sometimes, especially when the pulp has not been evenly compressed, it is better dissolved by adding the acids separately and successively in the reaction vessel, allowing the hydrochloric acid to disintegrate the pulp before the sulfuric acid is added.

ANALYTICAL PROCEDURE—Weigh the dry pulp (0.6 to 0.75 g.) into a dry flask or bottle (about 200 cc.) having a well-ground glass stopper. Add 30 cc. of the "acid solvent" described above and agitate till solution is complete, or add 27 cc. of hydrochloric acid (sp. gr. 1.19), shake till the pulp is disintegrated, add 3 cc. of sulfuric acid (sp. gr. 1.84), and shake again. It is essential at this stage that the solution be quite free from hard, unchanged cores of pulp. When uniformity has been obtained, add a measured volume (20 or 25 cc.) of the alkaline 0.1 *N* bromine solution, shake well, and allow to stand for 30 min. with occasional gentle agitation. Check the reaction by adding 2 g. of potassium iodide dissolved in about 25 cc. of water and shaking well. Dilute as largely as the capacity of the reaction vessel renders convenient, and titrate with 0.1 *N* sodium thiosulfate. Toward the end of the titration starch paste may be added advantageously, but disappearance of the blue color is *not* a sign that the end-point has been reached. There remains a little iodine dissolved in the finely divided cellulose, to which it gives a reddish brown tint. The thiosulfate should be added very slowly toward the end, and each addition should be followed by prolonged and very vigorous shaking. Finally the red tint of the cellulose precipitate disappears, leaving a cream-colored or white suspension. This, the true end-point, can be read within 0.1 cc. after a little practice, and back-titration with 0.1 *N* iodine solution can be resorted to in case it is overrun. Persistence of blue or purple spots after all other color has disappeared is due to the pulp not having been thoroughly disintegrated by the acid solvent. The titration will be untrustworthy in proportion as these spots are large and numerous; the iodine which they contain leaches out only slowly and somewhat imperfectly—too slowly to make a good titration possible.

CALCULATION OF RESULTS—This is best shown by an actual example.

Weight of dry pulp = 0.7722 g.
Volume of alkaline bromine solution = 20.0 cc.
Standardization showed 20 cc. bromine solution = 21.1 cc. 0.1 *N* $Na_2S_2O_3$
Buret reading after titration of pulp = 16.8 cc. 0.1 *N* $Na_2S_2O_3$
Bromine consumed by pulp = 4.3 cc. 0.1 *N* solution

$$\text{"Bromine figure"} = \frac{0.7722}{4.3} = 0.1796$$

$$\text{and "Chlorine factor"} = \frac{4.3 \times 0.00355 \times 100}{0.7722} = 1.977$$

Summary

1—The extent to which bromine solutions, approximately decinormal, act on cellulose and on unbleached sulfite spruce pulp has been investigated.

2—It is found that accurate measurements are possible only when the material is brought into solution, *e. g.*, by certain mineral acids, before treatment with bromine.

3—Under these circumstances there is no reaction between bromine and cellulose within 30 min.

4—Reaction between bromine and pulp (containing lignone) seems to proceed in definite steps, one of which is completed within 30 min.

5—From measurements of this action, a quantity is found which bears a definite and simple relation to the chlorine consumption in bleaching.

6—The method of manipulation is described in detail.

Civil Service Commission Announcements

The United States Civil Service Commission has announced the following examinations to fill vacancies in the Bureau of Standards: Junior aid at \$720 to \$840, laboratory apprentice at \$540, laboratory assistant junior grade at \$1000, senior aid at \$900, engineer at \$2800 to \$4000, associate engineer at \$2000 to \$2800, assistant engineer at \$1500 to \$1800, technologist at \$2800 to \$4000, associate technologist at \$2000 to \$2800, and assistant technologist at \$1500 to \$2000. On account of the needs of the Service, applications will be received until further notice. Papers will be rated as received and certification made if the needs of the Service require.

On January 11, March 8, and May 17, 1922, examinations will be given to fill the following vacancies in the Bureau of Standards: Junior engineer at \$1200 to \$1500, and junior technologist at \$1200 to \$1500.

On January 11, 1922, the following examinations will be given to fill vacancies in the Chemical Warfare Service, Edgewood Arsenal, Md.: Chemical laboratorian at \$1200 to \$1500, chemist at \$3600 to \$5000, associate chemist at \$2500 to \$3600, and assistant chemist at \$1800 to \$2500.

For further details in regard to these examinations, application should be made to the U. S. Civil Service Commission, Washington, D. C.

Short Course in Ceramic Engineering

The regular biennial two weeks' short course in Ceramic Engineering will be given next January at the University of Illinois, between the dates of January 23 and February 4. The subjects covered will include elementary physics and chemistry; the origin, classification, winning and refining, and testing of clays; the shaping, drying, and burning of clay products; bodies and glazes; the technology of glass; refractories and refractory products; kiln construction; coal and gas fuels; engines and boilers, dynamos and motors, equipment control; pyrometry; drafting and reading of drawings; and business law.

The complete program will be ready for distribution early in January and copies may be secured by addressing the Department of Ceramic Engineering, University of Illinois, Urbana, Ill. The course is open to all who are interested and can be taken to advantage by any one having a common school education. There are no tuition fees.

Effect of Adding Various Chemicals to Wood Previous to Distillation[1]

By L. F. Hawley

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This investigation is a continuation of Palmer's work on "The Effect of Catalyzers on the Yield of Products in the Destructive Distillation of Birch."[2] A new title has been chosen since it is not wished to imply that the action in all cases is truly catalytic and since it is not intended to limit the work to one species of wood.

Aside from Palmer's work, in which the wood was treated with phosphoric acid, the only publication on the subject is a recent short note[3] without details, in which it is stated that when wood is distilled in the presence of three or more parts of lime the acid yield (in form of acetone) is greatly increased. Nothing is said about an effect on the yields of alcohol.

Different distillation methods from those used by Palmer were used in the present study in order to develop a simpler process and one which could be used for maintaining an even mixture of sawdust with insoluble materials such as lime. The sawdust was mixed with the solid material if an insoluble chemical was used or was saturated with a solution of the chemical, then dried if necessary, and pressed into briquets 2 in. in diameter and about 1 in. in thickness. These briquets were distilled in a tube furnace under sufficient mechanical pressure to prevent them from falling apart, and the products were collected and analyzed in the usual manner. This general method of distillation had been used in a previous investigation and was found to be simple and satisfactory.[4]

SILVER MAPLE SAWDUST

PHOSPHORIC ACID—The results of several trials with phosphoric acid are shown in Table I. With wood treated with three different concentrations of the acid (0.5, 1, and 1.5), there was a slight decrease in the yield of alcohol and a slight increase in the yield of acid as compared with untreated wood, although the increase and decrease did not follow a regular order according to the amount of acid used. The increase in yield of acid was not sufficient to make phosphoric acid treatment a promising process, especially since the alcohol was slightly decreased. The only distillation of wood treated with phosphoric acid in which a large yield of acid was obtained reported by Palmer was made by distillation under high pressure, a condition which could not be readily obtained in commercial-sized apparatus. Apparently, the use of phosphoric acid under ordinary conditions of pressure is not promising.

LIME—Lime was tested, mixed with the sawdust both in the form of dry lime and milk of lime. The only noticeable effect of small percentages of lime was a decrease in the amount of acetic acid. With larger proportions of lime, as shown in Table I, there was a noticeable increase in the alcohol yield. This alcohol yield was determined by the specific gravity of a fraction of the distillate after redistillation with alkali and acid. It was, therefore, not a determination of pure methyl alcohol, but included also acetone and other materials with low gravities. Contrary to expectation, this increase in total alcohol, constituents was not due to an increase in the acetone content. Acetone determinations were made in all cases with the results varying only between 0.01 and 0.05 per cent, which is not sufficient to require any further discussion. This corresponds with Bassett's statement that large acetone yields were obtained only when three times as much lime as wood was used.

TABLE I—SAWDUST TREATED AND BRIQUETTED

CATALYST		Alcohol	Acetic	
Chemical	Per cent	Per cent	Per cent	REMARKS
		MAPLE		
......	..	1.61	5.22	Av. of 4 runs
H_3PO_4	0.5	1.51	5.67	Av. of 2 runs
H_3PO_4	1.0	1.24	5.39	
H_3PO_4	1.5	1.55	5.40	
$Ca(OH)_2 \Leftrightarrow 60\%$ CaO		2.45	0.48	
CaO	60	1.94	0.65	
$CaCO_3 \Leftrightarrow 40\%$ CaO		2.08	4.69	
$CaCO_3 \Leftrightarrow 20\%$ CaO		1.95	5.13	Av. of 2 runs
$CaCO_3 \Leftrightarrow 10\%$ CaO		1.80	5.20	
Na_2CO_3	20	0.84	0.21	
Na_2CO_3	10	2.00	2.40	Av. of 2 runs
Na_2CO_3	5	1.72	3.40	Av. of 3 runs
Na_2CO_3	3	2.06	4.25	Av. of 3 runs
Na_2CO_3	1.5	2.39	5.26	Av. of 3 runs
Na_2CO_3	1.0	1.94	5.02	Av. of 2 runs
Na_2CO_3	0.5	1.61	5.32	Av. of 2 runs
Na_2SiO_3	1	1.78	4.87	
Na_2SiO_3	3	2.21	5.77	
MgO	5	1.57	5.22	
MgO	10	1.65	4.11	
		WHITE OAK		
......	..	1.17	4.91	Av. of 2 runs
Na_2CO_3	0.5	2.58	5.09	
Na_2CO_3	1.0	1.99	3.86	Av. of 2 runs
Na_2CO_3	1.5	2.47	3.40	
Fe_2O_3	10	1.16	3.78	
Fe_2O_3	5	1.08	4.37	
MgO	20	1.21	3.57	
MgO	5	1.14	2.77	
$MgCl_2$	10	0.49	..	
$MgCl_2$	20	0.36	..	

The results obtained with lime are very interesting in the large yields of wood alcohol obtained, but the greatly decreased yields of acid make the method unpromising.

CALCIUM CARBONATE—Several runs were made with calcium carbonate instead of calcium hydroxide in an attempt to maintain the high alcohol yields without decreasing the acid. With large amounts of calcium carbonate high yields of alcohol were obtained with only slightly decreased acid yields. With smaller amounts of carbonate the yields of acid were about normal while the alcohol yields were still increased to some extent. However, the amount of carbonate required to obtain satisfactory results was so great that the value of the charcoal was seriously diminished. Only in cases where the charcoal was not considered of much value or where it might be used as fuel in the near vicinity of the plant might this process be promising.

It might be supposed that the lime or carbonate was partly transformed into calcium acetate during the first part of the distillation and, if the temperature was not great enough to decompose it, a residue of calcium acetate might be left with the charcoal. This was tested out in several cases, but not more than a slight trace of calcium acetate was found in the charcoal.

SODIUM CARBONATE—The first few distillations with large amounts of sodium carbonate material were unsatisfactory. The distillations were rather violent at times and low yields of both alcohol and acid were obtained. This is shown in Table I, where the use of 20 per cent sodium carbonate gives very unpromising results. With 10 per cent, however, a slightly increased yield of alcohol was obtained, although the acid was still low. The amount of carbonate was gradually decreased, until with 1.5 per cent a large increase in alcohol was obtained without any decrease of acid. Smaller amounts of carbonate were not so satisfactory, although even with 1 per cent a considerable increase in alcohol was obtained. These effects of sodium carbonate on the reaction of the decomposition of wood by heat are difficult to explain, especially the frequent increase of acid yields due to an alkaline treatment. In several cases the charcoal was

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[1] Presented before the Section of Cellulose Chemistry at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

[2] THIS JOURNAL, 10 (1918), 264.

[3] H. P. Bassett, *Chem. Met. Eng.*, 20 (1919), 190.

[4] Hawley, THIS JOURNAL, 13 (1921), 301.

leached and the soluble salt examined. More than 20 per cent of the sodium was never found in the form of acetate, and this acetate never amounted to more than 0.3 per cent of acetic acid on the weight of the wood distilled.

SODIUM SILICATE—Sodium silicate acts as a mild alkali similar to sodium carbonate. Similar results were obtained, although slightly larger amounts of silicate were apparently required to give the same increase in yields.

MAGNESIUM OXIDE—Magnesium oxide was used in concentrations of 5 and 10 per cent without appreciable increases in yields of either alcohol or acid.

White Oak Sawdust

All of these distillations were made with the same lot of sawdust from silver maple. The rest of the results reported in Table I were on white oak sawdust, and in comparing these with previous results it should be noted that the blank runs with oak where no chemical was used gave considerably lower yields, especially of alcohol. Sodium carbonate seems to have an even greater effect on the alcohol yields of oak than on those of maple. With as little as 0.5 per cent of sodium carbonate, one distillation gave double the yield of alcohol and slightly increased yields of acetate. The results obtained with 1 and 1.5 per cent were not so satisfactory, especially on account of the small acid yields, but high alcohol yields were obtained in both cases.

Iron oxide mixed with the sawdust in 5 and 10 per cent proportions did not show any promising results. The same was found in connection with the use of magnesium oxide and magnesium chloride. In the case of the latter chemical, high acid yields were recorded but tests showed that there was chloride present in this acid.

These results obtained with briquetted sawdust indicated that sodium carbonate was the most favorable chemical for further tests, both on account of its cheapness and its effect on the yields of alcohol. Further experiments were, therefore, carried out with this chemical upon wood in larger sizes.

Tests on Blocks of Wood

Blocks of white oak and maple wood 6 in. long were treated with a solution of sodium carbonate under 100 lbs. pressure so that a fairly uniform penetration of the solution was obtained. In the case of the maple blocks the distribution of the solution was especially complete. In the oak blocks, however, it was only the sapwood where penetration to the center was obtained, the heartwood showing only a slight penetration of perhaps 0.5 in. The blocks were distilled in the oil-jacketed retort in which previous wood distillation experiments have been made, and the results were compared with some of the same blocks which were distilled without previous chemical treatment. Table II shows the results of these distillations. In the case of the oak blocks a 50 per cent increase in wood alcohol was obtained with no decrease in the acetic acid in one series of runs (with 1.03 per cent carbonate), with a slight decrease in the other series (with 0.52 per cent carbonate). It is difficult to account for this decrease in acid where a smaller amount of sodium carbonate was used, but since all of the results given in the table were obtained from average figures on two distillations the results cannot be very inaccurate. In the case of the maple blocks there was a pronounced increase of alcohol (with 0.68 per cent and with 1.12 per cent carbonate), but in both series of runs the acetic acid was very considerably decreased. The question of the decrease in acid yields needs to be studied further since the results were erratic. In some distillations a slight increase appeared, while in other runs there was a very considerable decrease in acid.

Table II—Blocks of Wood Treated with Sodium Carbonate

Sodium Carbonate	Treatment	Settled Tar	Dissolved Tar	Pyroligneous Acid	Charcoal	Gas	Total Tar	Acetic Acid	Wood Alcohol
Per cent		Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
				Oak					
..	......	4.2	7.5	32.6	46.6	16.7	11.7	5.56	1.20
0.52	Pressure	5.1	5.5	32.5	42.5	20.0	10.5	4.71	1.85
1.03	Pressure	5.1	4.7	31.2	42.3	21.5	9.7	5.58	1.79
1.26	Soaked	5.2	6.7	32.1	43.4	19.4	11.9	5.66	1.40
				Maple					
..	......	5.0	9.0	38.8	38.7	17.5	14.0	7.65	1.67
0.68	Pressure	6.3	4.0	35.8	36.3	21.4	10.3	5.52	2.09
1.12	Pressure	6.7	8.2	38.8	38.9	15.7	14.7	6.74	2.16
3.15	Soaked	6.2	5.4	30.2	37.1	24.8	12.7	4.35	1.80

In order to show the effect of the sodium carbonate when not well distributed throughout the wood, runs were made on both oak and maple blocks which had simply been soaked in a solution of sodium carbonate without the application of pressure. The penetration was very slight at the ends of the blocks, and on the sides there was hardly more than a wet surface. The results of the distillation show that it is necessary to have all parts of the wood in contact with the chemical at the time of distillation in order to obtain the best results. Although in all cases there was a slight increase in alcohol from the soaked blocks, this increase was much less than in the case of pressure treated blocks or of briquetted sawdust.

The complete data on these runs with blocks are given in Table II, but little information of value can be obtained from the figures on the products other than acetic acid and wood alcohol. A variation in the relative amounts of pyroligneous acid, charcoal, and gas can be obtained by variation in the maximum temperature to which the charcoal is heated. Since this maximum temperature cannot be readily controlled in the apparatus used, the variations in these three products cannot be controlled and the percentage yield cannot be taken as an indication of the effect of the sodium carbonate.

Discussion of Application

It can be seen from these results that sodium carbonate previous to distillation can best be used in connection with processes for the distillation of sawdust. Since there are no processes of this kind in operation it has been impossible to test out the application of this principle on a commercial scale. It is very likely, however, that some sawdust distillation plants may be in operation in the near future.

It would probably be impossible to treat the ordinary distillation wood with sodium carbonate solution in such a way as to obtain much benefit therefrom. Most wood is distilled in 4-ft. lengths, and even with a pressure treatment it would be difficult to obtain an even distribution of the carbonate solution throughout such large sticks of wood. There are, however, a few commercial wood distillation plants which are using blocks because they are better suited for their artificial drying process than the ordinary 4-ft. sticks of wood. It is possible that these plants could submit their blocks to a pressure treatment with sodium carbonate solution before the wood goes to the driers and obtain thereby sufficiently increased yields of alcohol to make the process profitable. It is very likely that the value of the wood alcohol from wood distillation will be much greater than that of the acetic acid, so that any slight decrease in acid yield will not be a very great detriment to this process. If the commercial value of acetic acid products continues as low as it is at the present time, it is also possible that wood distillation plants will not attempt to recover acetic acid but will distil the alcohol from the pyroligneous acid and let the rest of the products go to waste. In this case the slightly diminished yields of acid would be of no disadvantage.

Other chemicals are being tested, and the effect of the distribution of the chemical is being determined. It is also hoped that an early opportunity will be afforded for trying out on a commercial scale the distillation of wood treated with sodium carbonate.

Effect of Change of Acidity upon the Rate of Diffusion of Tan Liquor into Gelatin Jelly[1,2]

By John Arthur Wilson and Erwin J. Kern

Laboratories of A. F. Gallun & Sons Co., Milwaukee, Wisconsin

Thomas[3] has shown that the rate of diffusion of tanning extracts into gelatin jelly is usually greater the greater the ratio of nontannin to tannin in the extract. Thus for typical samples he found the rate of diffusion increasing in the order quebracho, hemlock bark, larch bark, oak bark, chestnut wood, gambier, sumac. This is also the order for decreasing astringency or rate of combination of hide and tanning material. The same order is roughly borne out in experiments dealing with the rate of diffusion into cowhide.

Our explanation of the fact that nontannins increase the rate of diffusion of the tannins into hide is as follows: Tannins and certain nontannins form compounds with the hide substance, but the hide-tannin compound is very stable, while the hide-nontannin compound is considerably dissociated. The nontannins, having a much smaller molecular weight than the tannins, diffuse more rapidly into the hide. When the slowly moving tannin reaches a point where it would combine with hide substance, it cannot do so because the point is already occupied by nontannin. Tannin that would otherwise have combined with hide substance near the surface of the hide is thus enabled to proceed into the interior and the measured rate of penetration is thereby increased. This action is more marked the greater the concentration of nontannin capable of combining with hide substance. The hide-tannin compound being much the more stable, tannin replaces nontannin as the hide-nontannin compound hydrolyzes.

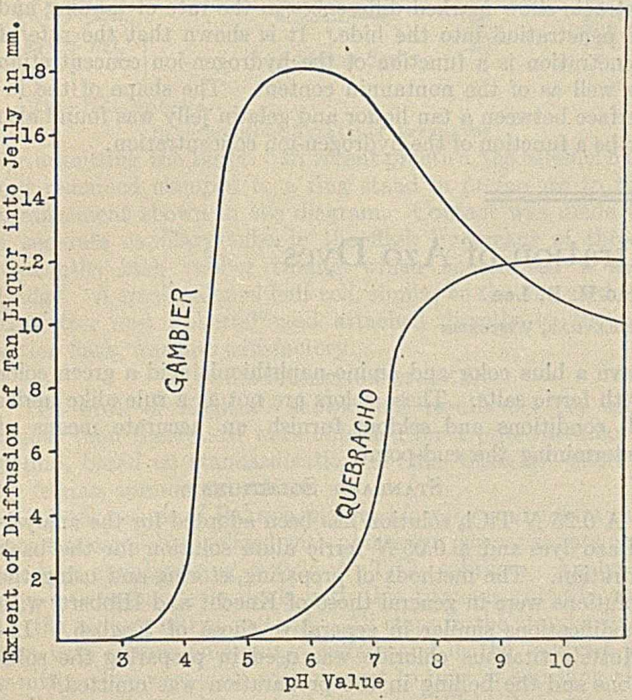

Fig. 1—Showing Rate of Diffusion of a Tan Liquor into Gelatin Jelly as a Function of the Hydrogen-Ion Concentration

According to the Procter-Wilson theory[4] of vegetable tanning, the rate of tanning, and also of the combination of hide and certain nontannins, can be decreased either by increasing the electrolyte concentration or by lowering the positive electrical charge which hide substance possesses in acid solution, which can be accomplished by decreasing the acidity. We should therefore expect the constituents of a tan liquor, both tannin and nontannin, to penetrate hide substance more rapidly as the acidity of the tan liquor is decreased to the isoelectric point of hide substance.

Thomas prepared a 5 per cent dispersion of gelatin in hot water containing 0.1 per cent ferric chloride and poured it into a series of test tubes to three-quarters of their capacity. When the dispersions had set to jelly, equal volumes of solutions of different extracts were poured on top of the jellies, which were then placed in an ice box. All of the extract solutions were made to contain 1 per cent of dry solid matter. Tannin and some nontannins react with ferric chloride giving a dark blue or black color which served to indicate the extent of the penetration. In 96 hrs. the gambier had penetrated 18.0 mm., as against only 4.8 mm. by the quebracho. It was of course the extent of penetration by the nontannins that was measured, as these diffuse the more rapidly.

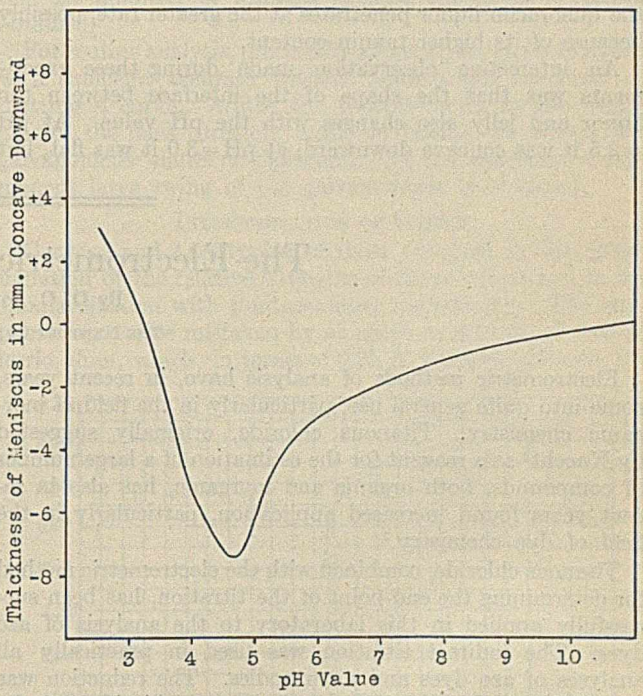

Fig. 2—Indicating Change of Shape of Interface between Tan Liquor and Gelatin Jelly as a Function of the Hydrogen-Ion Concentration

A large volume of a dispersion of gelatin in dilute ferric chloride solution was treated with tartaric acid until its pH value was reduced to 2.5, as determined by the hydrogen electrode. Equal portions were then treated with sodium hydroxide to give the desired pH values, which ranged from 2.5 to 11.0. Dilutions were such that the final dispersions contained 5 per cent of gelatin and 0.1 per cent of ferric chloride, as in the experiments of Thomas.

Gambier and quebracho extracts were selected for the test which showed by analysis:

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[1] Presented before the Division of Leather Chemistry at the 62nd Meeting of the American Chemical Society, New York City, September 6 to 10, 1921.

[2] Received August 15, 1921.

[3] *J. Am. Leather Chem. Assn.*, **15** (1920), 593.

[4] *J. Chem. Soc.*, **109** (1916), 1327.

	Gambier Per cent	Quebracho Per cent
Water	48.84	19.41
Insoluble	7.58	9.50
Nontannin	36.14	27.06
Tannin[1]	7.44	44.03

[1] Wilson-Kern method, THIS JOURNAL, **12** (1920), 465.

Solutions of these extracts were treated with tartaric acid to give a pH value of 2.5. Equal portions were then treated with sodium hydroxide to give a series of pH values the same as in the series of jellies. Each final liquor contained 1 g. of dry solids of the original extract per 100 cc.

The gelatin dispersions were poured into test tubes and allowed to set. On each was poured a given volume of tan liquor having the same pH value as the jelly. Both the quebracho and gambier series were run in duplicate. They were kept in the ice box and examined at intervals for 96 hrs.

The extent of the diffusion of the tan liquors into the jellies is shown in Fig. 1, the measurements being taken after 96 hrs. In each case the duplicate series were practically identical.

Gambier, which has a high ratio of nontannin to tannin, begins to penetrate at a pH value of 3.0 and reaches its maximum rate at pH = 6.0. Quebracho, on the other hand, scarcely shows any penetration until pH = 4.7, the isoelectric point of gelatin, is reached. At pH values greater than 9, however, the quebracho liquor penetrates at the greater rate, possibly because of its higher tannin content.

An interesting observation made during these experiments was that the shape of the interface between tan liquor and jelly also changes with the pH value. At pH = 2.5 it was concave downward, at pH = 3.0 it was flat, but with increasing pH value it became concave upward with the thickness of the meniscus increasing to a maximum of 7.5 mm. at pH = 4.7 and then decreasing until the interface again became flat at pH = 11.0. The thickness of the meniscus as a function of the pH value is shown in Fig. 2. This change in shape of the interface appears to be related to the swelling of gelatin. The point of minimum in the curve in Fig. 2 occurs at the isoelectric point of gelatin, pH = 4.7, while the curve slopes upward towards the points of maximum swelling of gelatin, pH = 2.4 and pH = 11.7, for the external solution. The measurements recorded are those for the gambier series, but the quebracho series showed practically the same effect.

Studies have also been made of the effect of change of acidity upon the rate of diffusion of tan liquors into cowhide. With increasing pH values up to about 8 there is a distinct increase in rate of diffusion, but because of the flaccid nature of hide at pH = 8 it is difficult to make accurate measurements of the rate of diffusion. At pH values below 3 and above 11 the hide swells considerably and becomes rubbery and distorted.

SUMMARY

As ordinarily used in tanning, gambier and quebracho extracts show marked differences in the rate of tanning and of penetration into the hide. It is shown that the rate of penetration is a function of the hydrogen-ion concentration as well as of the nontannin content. The shape of the interface between a tan liquor and gelatin jelly was found also to be a function of the hydrogen-ion concentration.

The Electrometric Titration of Azo Dyes[1]

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Electrometric methods of analysis have, in recent years, come into quite general use, particularly in the field of inorganic chemistry. Titanous chloride, originally suggested by Knecht[2] as a reagent for the estimation of a large number of compounds, both organic and inorganic, has also in recent years found increased application, particularly in the field of dye chemistry.[3]

Titanous chloride, combined with the electrometric method for determining the end-point of the titration, has been successfully applied in this laboratory to the analysis of azo dyes. The indirect titration was used in practically all analyses of azo dyes and nitro bodies. The reduction was made with an excess of standard titanous chloride and the excess was determined by titration with ferric alum.

In the former titanous chloride methods, involving the use of a thiocyanate indicator, the end-point was sometimes difficult to determine with accuracy on account of the turbidity of the solution, the presence of insoluble reduction products, or the masking of the end-point by the color of the solution itself. Thiocyanate was not satisfactory as an outside indicator, because the titrations were carried out in an atmosphere of carbon dioxide and because the solutions themselves were often of a pink color.

The reduction products of some azo dyes produce, with ferric salts, characteristic colors, which sometimes furnished indications of the end-point.[4] For example, diamino-H-acid gave a blue color and amino-naphthionic acid a green color with ferric salts. These colors are not as a rule alike under all conditions and seldom furnish an accurate means of determining the end-point.

STANDARD SOLUTIONS

A 0.25 *N* $TiCl_3$ solution has been adopted for the analysis of azo dyes and a 0.05 *N* ferric alum solution for the back titration. The methods of preparing, storing and using the solutions were in general those of Knecht and Hibbert[5] with modifications similar in general to those of English.[6] LaMotte's titanous chloride was used in preparing the solutions and the boiling in the preparation was omitted.[7]

APPARATUS

For the application of the electrometric method to oxidimetric reactions, reference is made to the work of Hostetter and Roberts.[8] Wendt's electrotitration apparatus, with slight modifications in the calomel half cell and the addition of a reversing switch, was used in this work. Any modifications in the electrometric apparatus in its application to oxidimetric reactions as published by Roberts[9] will also find application here.

The electrometric apparatus used in conjunction with titanous chloride is shown in the accompanying diagram. Carbon dioxide from a drum was used for maintaining an oxygen-free atmosphere in the reaction flask, which consisted of a 250-cc. Pyrex extraction flask with a 3-hole rubber stop-

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[1] Presented before the Division of Dye Chemistry at the 62nd Meeting of the American Chemical Society, New York, September 6 to 10, 1921.

[2] Knecht and Hibbert, "New Reduction Methods in Volumetric Analysis," 1918.

[3] F. English, THIS JOURNAL, **12** (1920), 994.

[4] Arthur G. Green, "Analysis of Dyestuffs," 2nd Ed., 117.

[5] *Loc. cit.*

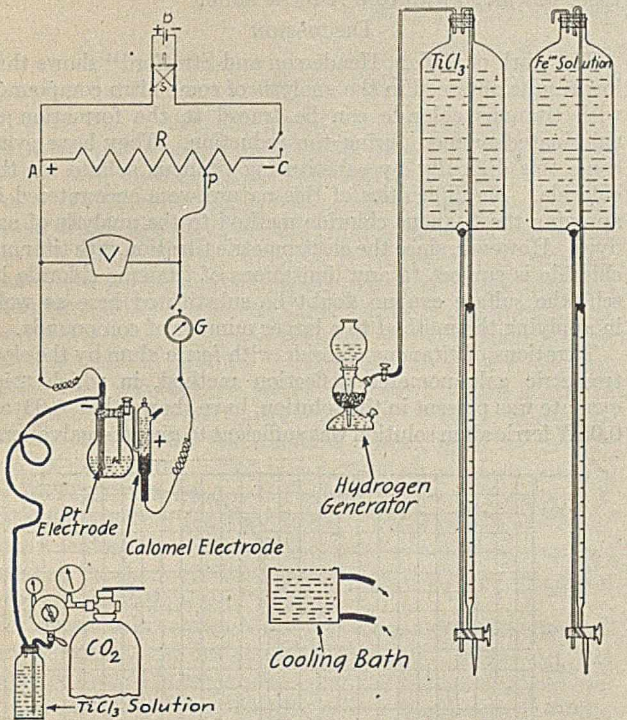
[6] *Loc. cit.*

[7] *J. Am. Chem. Soc.*, **43** (1921), 91.

[8] *Ibid.*, **41** (1919), 1337.

[9] *Ibid.*, **41** (1919), 1358.

per. Two holes were for the platinum electrode and capillary tube of the calomel half cell, respectively, and the third for admitting the buret. In recent practice, the calomel half cell remained clamped to a ring stand in preference to the arrangement shown in the diagram. Contact was made to a separate capillary tube in the flask by means of three-sixteenths inch rubber tubing which constituted a salt bridge. A small calomel half cell, similar to the one used by Hostetter and Roberts[10] and attached directly to the reaction flask, was also satisfactory.



ELECTROMETRIC TITRATION APPARATUS

STANDARDIZATION OF $TiCl_3$

The work of English[11] shows that results 0.4 per cent higher than theoretical were obtained for a pure nitro compound, based on standardization of the titanous chloride by ferrous ammonium sulfate.

A fresh sample of Baker's analyzed ferrous ammonium sulfate was carefully oxidized with potassium permanganate and used in standardizing a 0.25 *N* $TiCl_3$ solution. Analyses of *p*-nitroaniline were made with this titanous chloride and by the sodium nitrite method. All steps in the standardization with ferrous ammonium sulfate and in the analyses of *p*-nitroaniline were alike with respect to time of expelling air, boiling, cooling, volume of solution, etc. Table I shows analyses of *p*-nitroaniline by the two methods.

TABLE I

SAMPLE	With $TiCl_3$ Per cent	With $NaNO_2$ Per cent
I	99.67	99.55
	99.75	99.55
AVERAGE	99.71	99.55
II	99.02	99.11
	98.95	99.08
AVERAGE	98.98	99.09

The analyses by sodium nitrite were made at different times with different standard solutions. Compared with the results by sodium nitrite, ferrous ammonium sulfate and *p*-nitroaniline are equally good standards when used under the same conditions.

Fifty cc. of stock solution of *p*-nitroaniline containing 4 g. per liter were used for each standardization. Sublimed *m*-nitroaniline was also found satisfactory as a standard.

ANALYTICAL PROCEDURE

Weigh a sample of the finely powdered dye, approximately 1 g. and seldom less than 0.5 g., sufficient in quantity to require for reduction 30 to 45 cc. of 0.25 *N* titanous chloride. Transfer the sample, which is usually in the form of the soda salt, to the reaction flask, add 25 cc. distilled water, cover loosely, and place the flask on a steam bath for about 10 min. to dissolve or at least soften the particles. Add 25 cc. of 40 per cent sulfuric acid, stopper the flask, and pass a current of CO_2 through for 5 min.; then add the required amount (35 to 50 cc.) of titanous chloride (at least 5 cc. 0.25 *N* $TiCl_3$ in excess of that required for reduction are added). Boil for 5 min. and cool to 30° C. in a bath of running water. Titrate back the excess of titanous chloride with ferric alum. The titration is made in approximately the same volume as in the standardization.

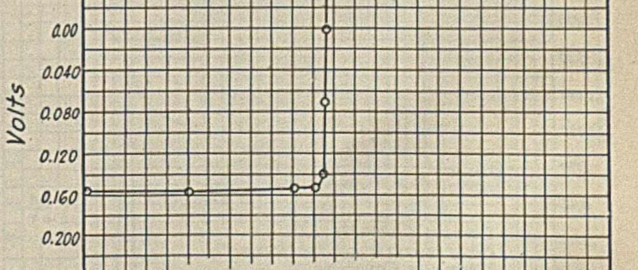
The back titration is conducted as follows: Adjust the potentiometer and read voltages for each addition of ferric alum. Add the latter at first in 5-cc. portions, gradually decreasing to 0.1 cc. or less. When passing over the end-point, reverse the poles in the usual manner and again read voltages as additions of ferric alum become larger.

Plot volts as ordinates against cc. ferric alum solution as abscissas and determine the end-point from the curve. From this the quantity of titanous chloride consumed is readily obtained.

For routine analysis, practically all azo dyes can be analyzed with sufficient accuracy without reading the voltmeter or plotting a curve. Adjust the potentiometer at the beginning of the back titration, until, on closing the circuit, the galvanometer shows no deflection. At the end-point a permanent large swing of the galvanometer is obtained.

INTERPRETATION OF CURVES

Curves 1 and 2 are typical of those obtained in the determination of the relative strengths of the solutions and in the standardization with *p*-nitroaniline, respectively. The end-points cannot be mistaken by as much as 0.10 cc. of 0.05 *N* ferric alum, which, in terms of 0.25 *N* titanous chloride, in-



Curve #1
Electrometric Titration of
Titanous Chloride and
Ferric Alum Solutions
End Point, 81.57 cc.

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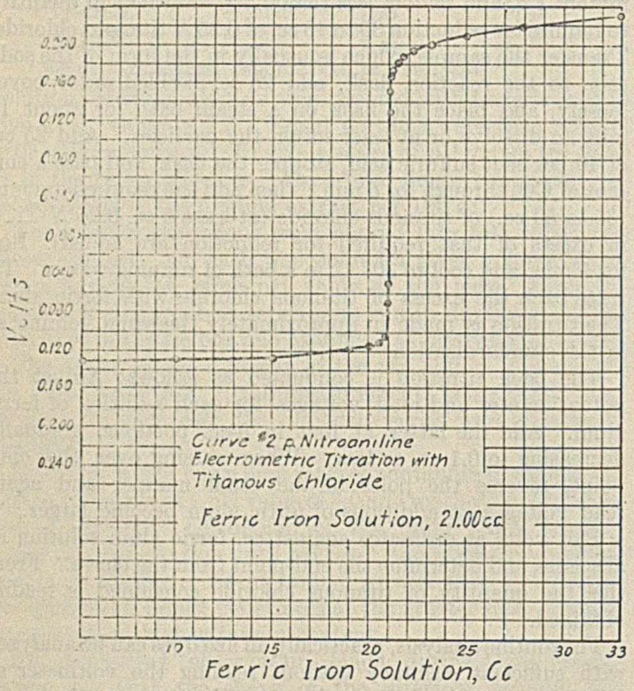
[10] *Loc. cit.*, 1340.

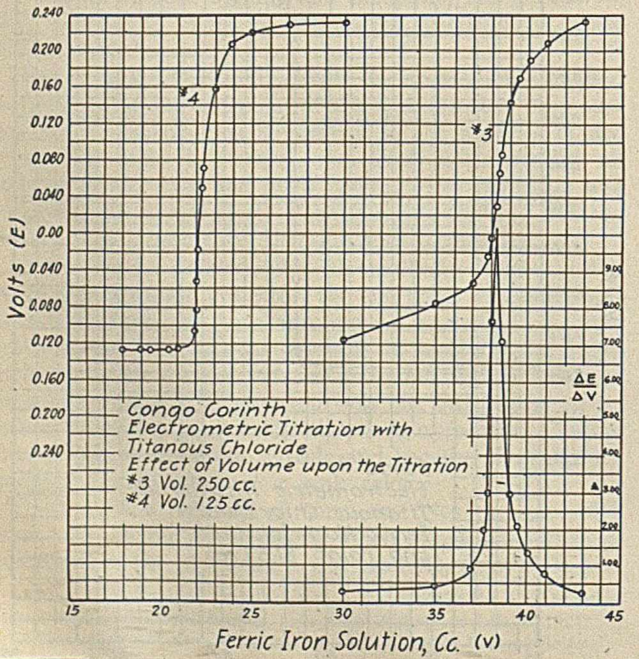
[11] *Loc. cit.*, 995.

troduces as error less than 0.05 per cent in the analysis. Curves 3 and 4 were obtained with Congo Corinth. Curve 4 is typical of those obtained in the most improved practice and was obtained using a 1.0 g. sample, 0.25 N titanous chloride, and a volume at the end-point of 125 cc. Curve 3 was obtained with 0.15 N titanous chloride, a 0.5 g. sample, and a volume of 250 cc. Curves with different slopes, obtained under different conditions, have in all cases indicated the same end-point with sufficient accuracy.



In Curve 3 is shown the application of the method used by Hostetter and Roberts[12] in which the coincidence of the curves, obtained by plotting $\Delta E/\Delta V$ against V, indicates the true end-point.

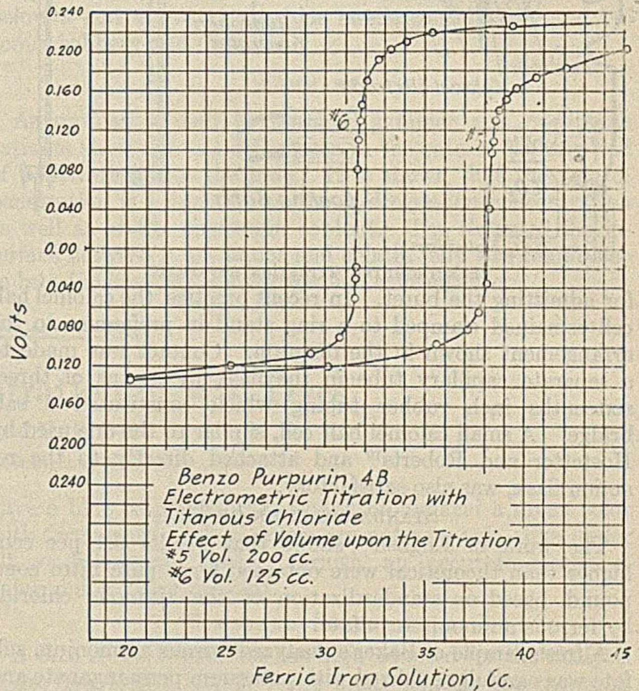
Curves 5 and 6, typical of Benzo Purpurine 4B, show again a slight difference in favor of Curve 6 with the smaller volume. Curve 5 was obtained with 0.15 N titanous chloride and a 0.5 g. sample; Curve 6 with a 1.0 g. sample and 0.25 N titanous chloride. The back titration in both cases was made with 0.05 N ferric alum.



Discussion

The work of Callan, Henderson and Strafford[13] shows that low results obtained in the analysis of some nitro compounds with titanous chloride can be traced to the formation of chlorinated amines during the reduction. They have overcome this difficulty by substituting titanous sulfate for the chloride. No difficulties of this nature were encountered in applying the titanous chloride method to the analysis of azo dyes. However, since the electrometric titration with titanous chloride is subject to any limitations of titanous chloride itself, the sulfate can no doubt be substituted here as well, in applying the method to a larger number of compounds.

Titrations of titanous chloride with ferric alum by the electrometric galvanometer deflection method, in which thiocyanate was present in the solution, have shown that 0.03 cc. 0.05 N ferric alum solution was sufficient to give the galvanometer pointer a decided and permanent swing and at the same time to change the solution from colorless to a decided pink.



The electrometric titration is valuable as a means of accurately analyzing a larger number of azo dyes for the control of process yields than could be accomplished by previous methods.

Summary

1—The difficulties encountered in the analysis of azo dyes with titanous chloride by previous methods are enumerated.

2—An analytical procedure is described whereby the electrometric method of following oxidimetric reactions is used in conjunction with titanous chloride for the successful analysis of azo dyes and nitro compounds.

3—A modified electrometric apparatus adapted for use with titanous chloride is described.

4—Typical curves for obtaining the end-point are shown.

Acknowledgment

Acknowledgment is made to Mr. E. V. Romain of this laboratory for assistance in obtaining data in the development of this paper.

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[12] *Loc. cit.*, 1341.

[13] *J. Soc. Chem. Ind.*, **39** (1920), 86*t*.

Comparison of the Various Corn Products Starches as Shown by the Bingham-Greene Plastometer[1]

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

Research Laboratory, Corn Products Refining Co., Edgewater, New Jersey

Up to the present the method of determining the flow characteristics of starch and dextrin pastes was the so-called fluidity test, described in the original communication by H. Buel.[2] The fluidity funnel is simply a 4-in. glass funnel with a stem drawn to a point so that if 125 cc. of water are poured into the funnel 105 cc. run out in 70 sec. The different funnels are of only approximately the same dimensions and are calibrated in terms of one of the funnels for pastes made of 5 and 7.5 g. of starch. For starches of low fluidity, 5 g. of starch are stirred with 10 cc. of water, 90 cc. of 1 per cent caustic soda solution are added, and the mixture is stirred for 3 min. and allowed to stand 0.5 hr. The cc. flowing in 70 sec., corrected to the standard funnel, give the fluidity term as used above. The thin boiling starches are sold on the fluidity specifications—2 F should give a 20 fluidity, 9 F a 90 fluidity within practical limits. This method, of course, is not scientific and, although it is good as a control, does not enable all the characteristics of a paste to be studied, especially at the concentrations used in practice.

In order to investigate the physical characteristics of starches, gums, and dextrins, Carl Bergquist, chemist of this company, worked in conjunction with the Bureau of Standards on this investigation. This paper is a continuation of the investigations carried on by Herschel and Bergquist,[3] and for the theory involved and the description of the apparatus used reference should be made to the original paper. Herschel and Bergquist have found that viscosity or plasticity plays a very important part in the practical application of starch and dextrin pastes, together with their chemical composition and concentration. The present investigators have endeavored to obtain such results as would enable the starch users to know the particular properties of the different grades of corn starches manufactured. This would facilitate matching of products used for a particular purpose.

It will only be necessary to define a few of the terms and empirical equations used. With viscous substances the flow through capillary tubes (neglecting the correction for kinetic energy and the correction for the resistance outside the capillary) is Poiseuille's formula

$$n = \frac{\pi g r^4 p t}{8 v l}$$

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

or the fluidity is $= \frac{1}{n} = \frac{8l}{\pi g r^4} \frac{V}{pt}$.

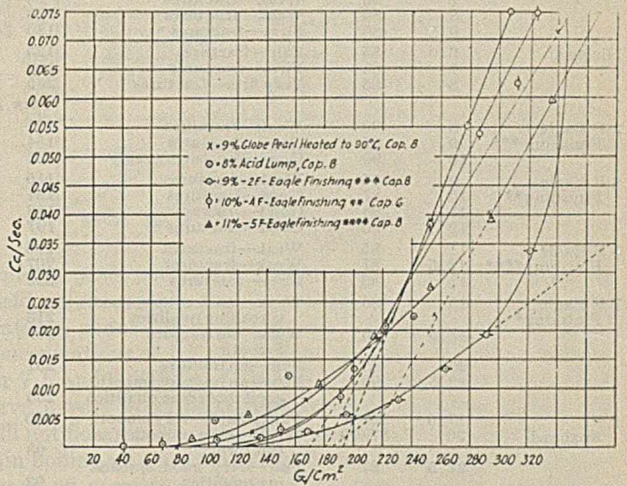
Where $\frac{8l}{\pi g r^4}$ is a constant, K, for a given capillary, K can be determined by calculation from the dimensions or by direct determination with a heavy oil of known viscosity.

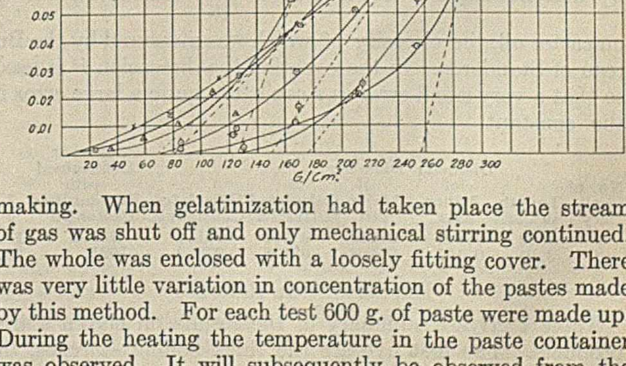
The flow for viscous materials, therefore, is proportional to the pressure. With plastic substances there is no flow until the pressure or shearing force has exceeded a certain definite value. The terms used with these materials are rigidity, R, and mobility instead of viscosity and fluidity.

$$\text{Mobility} = \frac{1}{\text{R}} = \frac{\text{KQ}}{p-f}$$

where f is the intercept of the asymptotes or tangent to the curve with the pressure axis. The term f in c. g. s. units is called by Bingham "yield shear value."[4]

The apparatus and method of procedure were the same as described in the article by Herschel and Bergquist. In order to be able to duplicate results the method of making pastes was kept as uniform as possible. A mechanical stirring arrangement which rotated at about 12 r. p. m. was used. This eliminated as far as possible variations due to changes in the rate of stirring. This mixing was not sufficient to keep the starch suspended until gelatinization was completed. However, since it was not desirable to increase the rate of stirring after the paste was gelatinized, a fairly slow stream of inert gas was bubbled through hot water and brought into the bottom of the paste kettle in the early stages of the paste making. When gelatinization had taken place the stream of gas was shut off and only mechanical stirring continued. The whole was enclosed with a loosely fitting cover. There was very little variation in concentration of the pastes made by this method. For each test 600 g. of paste were made up. During the heating the temperature in the paste container was observed. It will subsequently be observed from the





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[1] Presented before the Section of Sugar Chemistry and Technology at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] *8th Internat. Cong. of Applied Chem.*, XIII, 63.

[3] This Journal, **13** (1921), 703.

[4] Bureau of Standards, *Scientific Paper* **278**.

Table I—Plastometer Results

Description of Starch Sample	Paste Per cent Dry Substance	Temperature to Which Paste Was Heated ° C.	Consistency of Cold Paste	Capillary 6				Capillary 8			
				Yield G. per Sq. Cm.	Dynes per Sq. Cm.	Mobility	Rigidity $\frac{1}{\text{Mobility}}$	Yield G. per Sq. Cm.	Dynes per Sq. Cm.	Mobility	Rigidity $\frac{1}{\text{Mobility}}$
				Thick Boiling Starches							
Globe Pearl	7	87	Sloppy—fractures	76	74,600	1.530	0.665	167	164,000	4.67	0.214
	8	90–95	Firm—fractures	221	216,800	0.153	6.54	260	255,000	0.152	6.58
	9	85–87	Firm (weaker than 8 per cent)—fractures	257	252,000	0.494	2.02	255	250,000	0.306	3.25
	8	85	Slightly weak—fractures	106	103,900	0.490	2.04	101	99,000	0.353	2.83
	9	85	Slightly weak—fractures	164	161,000	0.482	2.07	170	166,500	0.428	2.33
Special Molding	7	85	Sloppy—fractures	85	83,400	1.129	0.886	146	143,000	2.236	0.448
	8	85	Weak—fractures	116	113,800	0.385	2.58	176	172,500	0.664	1.51
	9	87	Firm—fractures	210	206,000	0.368	2.72	265	260,000	0.283	3.53
Buffalo	7	85	Slightly weak—fractures	120	117,800	1.600	0.625	126	123,300	1.390	0.720
	8	85	Good—fractures	232	227,600	1.158	0.864	254	249,000	1.435	0.697
	9	85	Good—fractures	250	245,000	0.673	1.48	Flow too slow			
Acid Lump	6	86	Weak—fractures	94	92,100	2.63	0.380	96	94,000	1.31	0.764
	7	85	Weak—fractures	76	74,500	0.870	1.15	93	91,200	0.473	2.11
	8	85	Weak—fractures	135	132,200	0.596	1.68	194	190,000	0.683	1.48
	9	86	Firm—fractures	180	176,500	0.543	1.84	241	236,000	0.766	1.30
Niagara	6	85	Fair—fractures	125	122,500	0.701	1.43	151	148,000	0.759	1.32
	7	85	Firm—fractures	160	157,000	0.355	2.82	192	188,200	0.307	3.76
	8	85	Very firm—fractures	265	260,000	0.0520	19.20	226	221,600	0.0443	22.50
				Thin Boiling Starches							
2 F Eagle Finishing ***	8	90	Weak—fractures	121	118,500	0.492	2.03	170	166,800	0.597	1.63
	9	87	Good—fractures	154	151,000	0.249	4.01	186	182,200	0.192	5.20
	10	90	Good—fractures evenly	172	168,500	0.0323	30.9	201	197,000	0.0266	37.60
4 F Eagle Finishing**	9	85	Weak—fractures	115	112,800	0.474	2.11	127	124,200	0.820	1.22
	10	87	Good—fractures	181	177,200	0.134	7.46	184	180,500	0.105	9.52
	11	86	Good—fractures	183	179,500	0.0876	11.40	209	205,000	0.043	23.20
	12	90	Good—fractures	197	193,000	0.00880	113.80	...	.....	.....	.....
5 F Eagle Finishing****	11	85	Weak—fractures	185	181,500	0.725	1.38	210	206,000	0.483	2.06
	12.5	87	Weak—fractures	207	203,000	0.124	8.06	272	266,200	0.149	6.72
	15	85	Firm—fractures	225	221,000	0.0119	88.00	...	.....	.....	.....
7 F Eagle Finishing*	15	85	Weak—no fracture, good spreading qualities	213	209,000	0.543	1.84	230	225,600	0.256	3.91
	17.5	90	Weak—no fracture Smooth	207	203,000	0.270	3.71	235	230,400	0.214	4.67
	20	85	Fair—no fracture	231	227,000	0.0123	81.30	...	.....	.....	.....
	22.5	90	Fair—no fracture smooth —good spreading qualities	230	226,000	0.00436	230.40	...	.....	.....	.....
9 F Foxhead	17.5	85–87	Fairly fluid—very smooth	60	58,800	0.595	1.68	83	81,400	0.543	1.84
	20	87–90	Weak—very smooth (no fracture)	93	91,100	0.236	4.24	120	117,500	0.188	5.32
	22.5	87	Fair—very good spreading qualities	92	90,000	0.101	9.90	96	94,200	0.056	17.80
	25	87	Weak—very good spreading qualities	131	128,500	0.0720	13.90	171	167,500	0.0575	17.40
	27.5	87	Little weak—very good spreading qualities	177	173,500	0.0116	86.200	177	173,500	0.00810	123.50
	30	85	Fair—very good spreading power	196	192,000	0.00285	351.00	...	.....	.....	.....
	32.5	85–87	Fair consistency—no fracture—good spreading qualities	207	203,000	0.000883	1131.00	...	.....	.....	.....
				Mazam							
	35	95	Fairly fluid	82	80,400	0.506	1.98	69	67,600	0.442	2.26

data that, in order to get results comparable one with another, it is very important to have the final temperature the same for all the starch pastes. After the 0.5-hr. heating at 85° C. or other temperatures as noted, the pastes were poured through cheese-cloth to remove any lumps which might clog the capillaries, and allowed to cool down slowly to 25° C. until the next day. The upper layer of paste was rejected. Conditions for the treatment of successive samples still need to be made more uniform.

The capillaries were measured by the Bureau of Standards. The constant K used for investigations was the one obtained by determining the constant $K = \frac{p}{Qn}$ from determinations on castor oil, the viscosity of which was measured by the Bureau of Standards. In the equation the dimension r^4 is used, so that a very small error in r can cause quite a large error in the constant.

No. of Capillary	Length in Cm.	Diameter of Minor Axis	Diameter of Major Axis	Calculated Diameter	Calculated Constant K	Constant Determined with Standardized Castor Oil	$\frac{1}{d}$
6	2.62	0.146	0.152	0.149	221.4	256.5	17.5
8	3.01	0.105	0.108	0.106	972.9	1025.	28.3

Experimental Results

Table I gives a summary of the results on eleven starch products. The first five are the thick boiling starches, the next five are the thin boiling starches, and the last, Mazam, a partly dextrinized starch containing 4 to 6 per cent of reducing sugars. The column "consistency of cold paste" gives the molding quality of the paste.

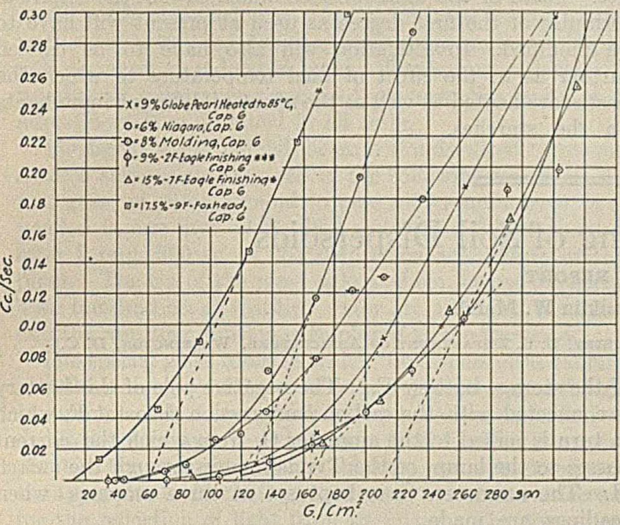
The sets of curves give the experimental results of a certain concentration of each starch on the two capillaries used. In making the tests, about three concentrations were tested that would come within the upper and lower limits for best flow through the plastometer. Since starch users have been accustomed to the term fluidity, the values of the mobilities were included in the tabulation.

The chemical differences of the ten starches are given in Table II.

Table II

No.	Name of Starch	Moisture Per cent	Acidity Per cent	Alkalinity Per cent	Soluble Per cent	Protein Per cent	Fluidity
1	Globe Pearl	10.38	0.06	..	0.09	0.54	..
2	Buffalo	10.45	0.09	..	0.20	0.47	..
3	Special Molding	10.92	0.07	..	0.35	0.46	..
4	Acid Lump	11.68	0.08	..	0.22	0.43	..
5	Niagara	11.61	..	0.04	0.62	0.56	..
6	2 F Eagle Fin.***	11.83	0.07	..	0.33	0.40	22.5
7	4 F Eagle Fin.**	9.98	0.07	..	.34	0.43	46.0
8	5 F Eagle Fin.****	10.10	0.08	..	.84	0.44	57.5
9	7 F Eagle Fin.*	10.15	0.08	..	2.19	0.40	71.5
10	9 F Foxhead	9.85	0.10	..	1.25	0.47	94.0
11	Mazam	8.16	..	..	99.0	..	

GLOBE PEARL STARCH—The variations in the results obtained are attributable to the fact that the final temperature to which the paste was heated varied to some extent. Two samples of pastes of 8 per cent on dry substance were made up in identically the same way except that one was heated to 90° to 95° C., the other to 85° only. The paste obtained from the 90° temperature was very firm, giving a yield value with capillary 6 of 221 g. per sq. cm. and a mobility of 0.153.



The 8 per cent paste kept at 85° C. had a yield value of 106 g. per sq. cm. and a mobility of 0.490. Its consistency was weak. A 9 per cent concentration heated to 87° gave a slightly higher yield value than the 8 per cent heated only to 85° C. The mobility of this 9 per cent paste was almost three times as high as that of the 8 per cent heated to 90° C., which under normal conditions should have been reversed. These variations really existed in the pastes because the 9 per cent paste was much weaker than the 8 per cent. The determined dry substance on these pastes checked the concentrations given. A 9 per cent paste heated to 85° C. gave a lower yield and about the same mobility as the 9 per cent heated to 87° C. However, the 9 per cent paste heated to 85° gave a higher yield value than the 8 per cent paste heated to 85° C., which is consistent. Both pastes heated to 85° C. were weak. Globe Pearl pastes of this concentration should give firm pastes and evidently it may be best to heat these pastes to 90° C. rather than to 85° so as to make sure that gelatinization is complete. This slowness of gelatinization is noticed with some materials more than with others. The character of the curves is regular, the flow being directly proportional to the increase of pressure (at the higher pressures).

BUFFALO STARCH—The curves are very consistent, being typical plastic flow curves. Even when the yield value is high, the mobility is also comparatively high.

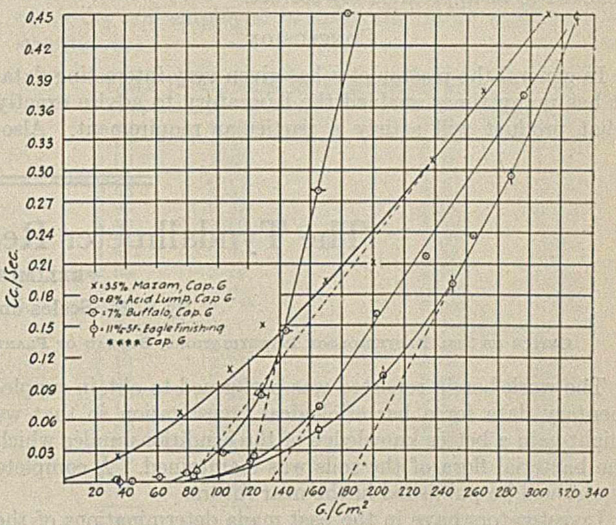
SPECIAL MOLDING STARCH—Gives fairly regular curves.

ACID LUMP STARCH—The curves are regular plastic flow curves. Results are consistent.

All of the acid starches give mobilities that are from 2.00 to 0.300, depending on the concentration. The mobilities as determined by the two capillaries seldom check, usually being lower with the smaller capillary, sometimes only one-half of the value obtained with the larger capillary.

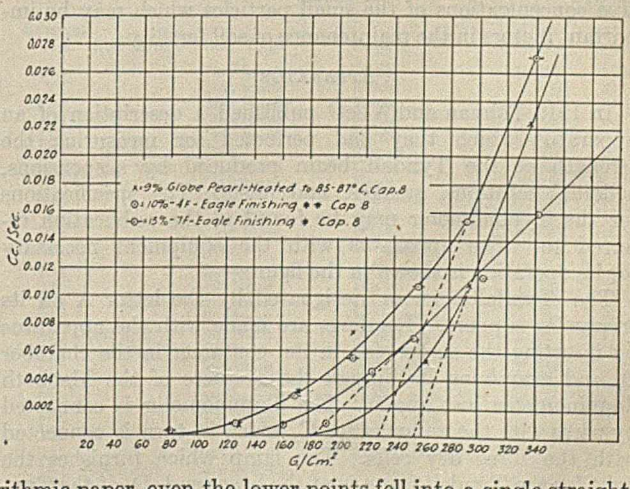
NIAGARA STARCH (a slightly alkaline starch)—The curves are very good type curves, the flow at higher pressures being directly proportional to the increase of pressure. The mobilities in the 3 cases for the 2 different capillaries check almost within experimental error. The mobilities go to 0.05 on the 8 per cent concentration. The yields are much higher than corresponding concentrations of 8 per cent acid starches.

THIN BOILING STARCHES—The characteristics of 7 F and 9 F were much different from those of the other starches. They never became firm enough to give a fracture similar to the other starches. 9 F especially gives a smooth uniform paste of very good spreading power. 2 F gives a very firm paste with 9 per cent concentration, 4 F with 11 per cent, 5 F with 15 per cent, 7 F pastes become fair in consistency at 20 per cent concentration but never firm; 9 F becomes fair with 22.5 per cent concentration and remains a smooth uniform paste even up to 35 per cent. With 7 F starch the yield values remain about the same at the different concentrations, about 220 g. per sq. cm. The mobilities of higher concentrations of 7 F and 9 F are very low, 0.0123 to 0.00436 for 7 F and 0.00285 to 0.000883 for 9 F, showing that pastes have a very good body and excellent covering power, and will not flow easily. The characteristics of the more modified thin boiling starches make them very desirable for sizing purposes, on account of the large concentrations in which they can be used and other characteristics such as low mobility and fairly high yield value.



Yield values for the different thin boiling starches are higher for the smaller capillaries. The mobilities are lower for the smaller capillary, sometimes checking to within experimental error and sometimes one-half as large.

The thin boiling starches give results that make it difficult to obtain the yield and mobility values, because even at the highest pressures the increase of flow appears to be some function of the pressure. Comparison of these starches will have to be made with the use of other mathematical equations. When some of these curves were plotted on logarithmic paper, even the lower points fell into a single straight line, showing that the flow is some function of the pressure even at the lower pressures. Herschel and Bergquist point out that a slight difference in weighting of points will cause a great variation in the yield and that in reality nearly all points were on the curved part of the graph. They claim there is a lack of accurate formulas. The same was found



true with these results. In most cases different possibilities were weighted and the most logical values taken. These are believed to be approximately correct.

Conclusion

In general the plastometer has given very interesting data. It has many times enabled the laboratory to advise exactly what product will satisfy a particular requirement. Also, it has been used in conjunction with the chemical analysis to tell what product would exactly match a submitted product. Some of the data obtained indicated that the empirical formulas of the first degree as used at present will have to be modified. Investigation will also have to be carried further as to the effect of final temperature to which the pastes are heated as well as the effect of different ingredients on the starches.

The Tyndallmeter Reading of Soil Dispersoids[1]

PRELIMINARY REPORT

By F. M. Scales and Franklin W. Marsh

Office of Soil Bacteriology Investigations, Bureau of Plant Industry, U. S. Department of Agriculture, Washington, D. C.

The work herein reported was performed to obtain supplementary data for a bacteriological investigation so that we might gain a better knowledge of the conditions under which the bacterial flora of the soils was maintained. A complete report will be published in the near future.

Investigators have in the past made determinations of the dispersoid content of soils by the water-vapor adsorption, dye or gas adsorption, and suspension methods. The first two usually require a modification of procedure for each soil type and on this account are not well adapted for the study of a variety of soils. The suspension method gives the most promise and, if a satisfactory procedure can be developed, ought to yield fairly close results.

In this investigation a suspension method was employed in order to obtain a measure of the concentration of the disperse phase in a soil by means of a Tyndallmeter. The suspensions from the naturally moist soils were examined for dispersoid content after they had stood for 24 hrs. No attempt was made to determine the size of the organic or inorganic particles in the disperse system but, if it is assumed that the size of the particles left in suspension after 24 hrs.' settling was approximately the same for the different soils, the strength of the Tyndall beam may be taken as roughly proportional to the concentration of dispersed material.[2]

In any case, since all the suspensions were prepared by a uniform procedure, the factors obtained bear sufficient relation to each other to furnish a good index of the comparative concentrations of the small particles which may be important factors in the maintenance of soil fertility.

Apparatus

In 1919 Tolman and Vliet[3] published a description of an apparatus which they had perfected for measuring the strength of the Tyndall beam produced by suspensions, colloidal solutions, smokes, and mists. The specifications for the Tyndallmeter may be found in the publication referred to. The apparatus with the equipment necessary for its operation is shown in the figure.

The Tyndallmeter is designated by the letter A on its triangular support. Readings are made with the apparatus by inserting the suspension in its container in the chamber B, and examining it through the eyepiece of the Macbeth illuminometer just above. The illuminometer is connected by wires with the milammeter C, which in turn is connected with the three dry cells. The lamp which furnishes the light for the Tyndall beam is at the lower end, D, of the Tyndallmeter and is connected by a wire with the positive pole of the storage battery E. The negative pole of this battery is connected with the carbon compression rheostat F, which in turn is joined to the ammeter G, from which the current passes to the lamp of the Tyndallmeter through the switch H. The ammeter G is kept set at three amperes when readings are made.

The wooden horse which has been employed for the support of the Tyndallmeter is simple in construction but very convenient for adjusting the apparatus to any angle that suits the observer.

Although all readings of soil dispersoids in the Tyndallmeter are made in a dark room, it is found very trying to the eyes to determine the end-point, owing to the difficulty of matching the intensity of the lights when the colors are different. A screen placed in the eyepiece makes the readings much easier to obtain. It is prepared essentially as described by Crabtree[4] by clearing an unexposed Hammer photographic dry plate in a regular hypo solution and then thoroughly washing and drying it. The plate, gelatin side up, is put in a developing tray containing a filtered solution of 0.1 per cent of Aniline Brown and allowed to adsorb the color for 10 min. The tray should be tilted back and forth for a short time when the plate is first immersed and then at intervals, as this procedure tends to make a more uniformly colored plate. At the end of this time the plate is rinsed for 1 min. in ice cold water and dried where it will be free from dust. The plate is cut in small squares, and three thicknesses are placed in the eyepiece. A test with and without the screen showed that more uniform readings were obtained with it.

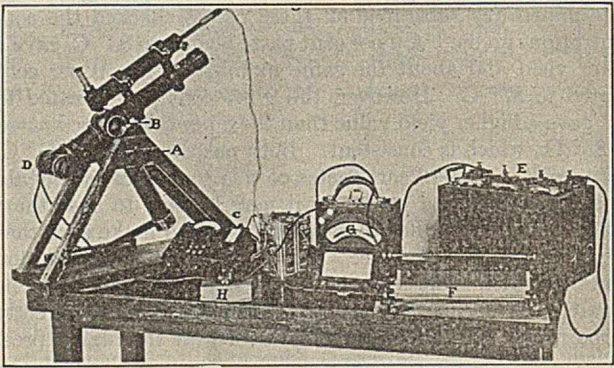


Fig. 1

Standardization

It is necessary to standardize the light of the illuminometer and that for the Tyndall beam.

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[1] Received August 3, 1921.

[2] R. C. Tolman, L. H. Reyerson, E. B. Vliet, R. H. Gerke, and A. P. Brooks, "The Relation between Intensity of Tyndall Beam and Concentration of Suspensions and Smokes," *J. Am. Chem. Soc.*, **41** (1919), 300.

[3] "A Tyndallmeter for the Examination of Disperse Systems," *J. Am. Chem. Soc.*, **41** (1919), 297.

[4] "How to Make, Fit and Use Light Filters," *Amateur Photographer and Photographic News*, **49** (1909), 173.

The illuminometer light is standardized with the apparatus made for that purpose by Leeds and Northrup Co. Since the standardization has been described by Tolman and Vliet it will not be repeated here. In our work the lamp is adjusted so that the actual number of apparent foot candles is only one-half as many as indicated by the illuminometer scale. The number of mil-amperes required to keep the lamp at this adjustment is maintained in all tests.

The light for the Tyndall beam is standardized by means of a silica suspension prepared in the following manner: One-half gram of silica, ground to pass a 200-mesh sieve, is suspended in one liter of distilled water in a 2-liter flask, and after 2 min. 300 cc. of the suspension are withdrawn by a pipet. The tip of the pipet is kept 2 cm. below the surface. Two hundred cc. of distilled water are added to the 300 cc. and the resulting dilution is employed as the standard.

The special glass tubes in which the dispersoid is examined are 12 cm. long by 4.3 cm. in outside diameter and the glass is approximately 1 mm. thick. The tubes are first filled with distilled water and closed with a 1-hole rubber stopper to prevent the inclusion of air bubbles, and are examined in the apparatus to determine whether any correction is necessary for the reflection of light from the glass. The correction is so small that it has been ignored. The silica standard is then placed in the tube and ten consecutive readings made by each of the two observers. Five readings should be made by approaching the end-point from the zero and five from the maximum end of the scale as described by Tolman and Vliet. This standard solution is kept in a well-sealed flask and employed for the frequent standardization of the apparatus.

METHODS

The soil samples are passed through a 7-mesh sieve to remove plant tissue and small stones and to produce a uniform texture, and they are then thoroughly mixed. The sifting and mixing are done as rapidly as possible to prevent loss of moisture by evaporation. The moisture content of the soil is then determined by air-drying two 25-g. quantities from each sample.

When the percentage of moisture is known, four portions are weighed out from a sample so that each one is equivalent to 5 g. of air-dry soil. These portions are placed in 1-liter Erlenmeyer flasks, and 500 cc. of distilled water are added. The flasks are stoppered and shaken vigorously for 5 min. and allowed to stand for 1 min., when 50 cc. of the suspension are withdrawn from each with a pipet by inserting the tip 2 cm. below the surface. The four 50-cc. aliquot portions are run into a 2-liter Erlenmeyer flask and diluted, if necessary, with a measured quantity of distilled water so as to give a reading between 1 and 10 on the Tyndallmeter scale. The investigator will soon find that he can readily estimate the concentration between these points. If the suspension is more disperse than desired a second 50 cc. from each flask may be added to it. The composite suspension is shaken vigorously for 1 min. and allowed to stand 24 hrs. At the end of this time all but 200 cc. of the supernatant suspension is siphoned into a flask and well shaken for 1 min. to insure uniformity. Two of the special tubes are filled with the suspension and read in the Tyndallmeter. A similarly prepared composite suspension is also read as a check on the first one.

The factor for the concentration of the disperse system is obtained by converting the actual apparent foot candle reading to the theoretical value for 1 g. of air-dry soil. The formula employed for this purpose is

$$X = \frac{vdr}{2w}$$

where X is the factor for the concentration of dispersoid per gram of air-dry soil; v is the total volume of the final suspension; d is the quotient of the initial total volume, generally 2000, by the aliquot taken for the final suspension, usually 200; r is the Tyndallmeter reading; w is the weight in grams of air-dry soil employed to make the initial total volume of suspension.

TABLE I—READINGS OF SUSPENSIONS FROM SOIL 32

	Suspension A_1		Suspension B_1	
	3.00	2.60	3.02	2.91
	2.98	2.55	3.07	2.79
	2.90	2.65	3.10	3.03
	2.90	2.80	2.90	3.13
	2.95	2.65	3.05	2.93
	2.90	2.85	2.88	2.75
	2.80	2.69	3.05	3.00
	2.85	2.90	3.00	2.80
	2.91	2.70	3.00	2.91
	2.85	2.79	2.97	3.04
Av.	2.904	2.718	3.004	2.929
	Suspension A_2		Suspension B_2	
	3.02	2.87	3.15	3.10
	3.10	2.79	3.04	2.85
	2.85	2.84	2.94	2.85
	2.85	2.91	2.95	3.05
	3.10	2.71	2.96	3.07
	2.90	3.09	3.00	2.91
	2.98	3.02	3.10	3.20
	2.88	2.78	3.11	3.02
	2.85	2.85	3.00	2.77
	2.85	2.90	2.95	2.97
Av.	2.938	2.876	3.020	2.979

DATA

The factor for the concentration of disperse phase obtained by the method outlined has been determined in thirty-one soils of different agricultural values. The first eight (6 to 13, inclusive) were kindly sent in by Dr. A. W. Sampson of the Great Basin Experiment Station, Ephraim, Utah. They are soils that have been overgrazed and are now supporting weed growth in different stages of succession. The soils numbered 31 to 34, inclusive, were collected by the junior author as representatives of types used in Massachusetts cranberry bogs. For all the remaining samples from different parts of the country our thanks are due to Dr. C. F. Marbut, in charge of Soil Survey Investigations, Bureau of Soils, U. S. Department of Agriculture.

Most of the soils gave duplicate suspensions that checked very closely, but a few, on account of their nature, gave suspensions showing greater differences. In Table I is given an example of the results that may be obtained by carefully following the procedure outlined.

TABLE II

SAMPLE No.	Soil Group	Soil Type	Source	Mean Reading	Dispersoid Concentration Factor
10	Clay and clay loam	Clay loam	Utah	1.016	191
7		Clay loam	Utah	1.685	211
12		Clay loam	Utah	1.117	356
9		Clay loam	Utah	1.031	387
11		Clay loam	Utah	1.656	621
25		Clay	Texas	2.850	712
8		Clay loam	Utah	3.063	1532
13		Clay loam	Utah	5.538	2077
30		Clay	Alabama	7.380	3690
6		Clay loam	Utah	8.230	4115
26		Clay loam	Utah	14.390	7195
24		Clay	Texas	22.840	22840
18	Silt and silt loam	Loam	Indiana	1.634	82
28		Silt loam	Idaho	1.113	223
20		Silt loam	N. Dakota	2.631	263
21		Silt loam	N. Dakota	5.558	278
37		Silt loam	Idaho	3.577	711
14		Silt loam	Kentucky	2.178	1089
17		Silt loam	Nebraska	7.519	2820
15		Silt loam	Kentucky	8.196	4057
22		Silt loam	New York	11.150	5575
27		Silt loam	N. Carolina	12.600	6300
16		Silt loam	Nebraska	14.620	7500
33	Sand and sandy loam	Sand	Massachusetts	Trace	Trace
19		Sandy loam	Indiana	1.085	51
29		Sand	Alabama	1.470	74
36		Sand	Michigan	4.730	237
35		Sandy loam	Michigan	1.316	329
31	Bogland	Sandy muck	Massachusetts	Trace	Trace
34		Bogland	Massachusetts	1.510	76
32		Woodland muck	Massachusetts	2.920	439

The average reading of Suspensions A_1 and A_2 is 2.859; of Suspensions B_1 and B_2, 2.984. The mean of these readings is 2.922, and the variation of the averages from this is 2.2 per cent.

In Table II are the results obtained from the thirty-one soils. It will be noticed that the mean readings do not increase in the same order as the dispersoid concentration factors. This difference is due to the fact that the mean readings were made with dilutions of dispersoid that varied for the different soils.

An examination of the readings obtained with these soils shows that the average error from the mean is 2.54 per cent. In obtaining this figure the results of five soils are omitted on account of abnormally high percentage errors. No effort was made to get closer checks on these samples, because four of the factors were so low and one so high that an exact check would not in any case have altered the relative values of the soils.

The relation of these dispersoid concentration factors to the other data that have been obtained will be discussed in a future report.

SUMMARY

A procedure is given for obtaining by means of a Tyndallmeter a factor for the concentration of dispersoid in a soil.

The Determination of Glycerol in the Presence of Sugars[1]

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The accurate estimation of glycerol in transparent soaps is attended with difficulty on account of the cane sugar which is almost invariably present.

AVAILABLE METHODS FOR GLYCEROL ANALYSIS

It is obvious that the sugar will oxidize, in part at least, and give rise to uncertain results if an attempt is made to determine glycerol by the Hehner method,[2] in which the sample is oxidized with potassium dichromate in acid solution. The acetin method of Benedikt and Cantor[3] is open to the objection that sugars, having numerous hydroxyl groups, are acetylated by acetic anhydride in much the same manner as glycerol.[4]

The alkaline permanganate method of Benedikt and Zsigmondy[5] should theoretically work on a mixture of glycerol and sugar, since it depends on the supposition that glycerol only is oxidized to oxalic acid by potassium permanganate in alkaline solution. As a matter of fact, however, invert sugar was subsequently found to be quantitatively oxidized to oxalic acid by this method. A test made in our laboratory showed that an amount of oxalic acid equivalent to practically 100 per cent of the theoretical quantity was produced when pure invert sugar was subjected to oxidation with alkaline permanganate in the usual way. This method as applied to straight glycerol analyses has been adversely criticized by Lewkowitsch[6] and by Allen.[7] Experiments in our laboratory have indicated that the method gives low results on crude and C. P. glycerols. The method is tedious and cumbersome, and a more convenient method capable of giving better results on glycerol was therefore sought. The isopropyl iodide method of Zeisel and Fanto[8] was not considered because it has been sharply criticized by Lewkowitsch,[9] and is moreover complicated, tedious, and of doubtful accuracy in presence of sugar.

The most usual method of determining glycerol in the presence of sugar is of course that of Donath and Mayrhofer,[10] or one of its various modifications, in which the sample is treated with lime or baryta to render the sugars insoluble, and the glycerol is extracted from the nearly dry mixture with various solvents. Any chemist who has ever tried this method cannot but have been impressed with its tediousness, many chances of losses, and resultant inaccuracy.

The method of Cook,[11] which is really an adaption of the Shukoff and Schestakoff[12] method for the determination of glycerol in meat and meat extracts, would not appear to be applicable in the presence of sugar since it is, in effect, merely an acetone extraction of the sample which has been dehydrated by mixing with sand and anhydrous sodium sulfate, and does not render sugar insoluble if present. Methods such as precipitation of glycerol with copper sulfate,[13] distillation of glycerol *in vacuo* from a solution containing sugar or salts,[14] distillation *in vacuo* with the aid of sandalwood oil[15] or precipitation as sodium glyceride[16] were examined and found inapplicable to the present problem.

EXPERIMENTS WITH THE DONATH AND MAYRHOFER METHOD

An attempt was made to apply this method to the present problem, using known weights of pure sugars and glycerol of known purity. Glycerol is normally determined in a sample of soap by cracking with dilute sulfuric acid and determining glycerol in the acid filtrate by the dichromate or acetin methods. In the case of a transparent soap containing cane sugar, the acid filtrate would contain the sugar in the form of invert sugar. Hence in the experiments known equal weights of pure dextrose and pure levulose, *i. e.*, invert sugar, were used.

These results showed that continued extraction with acetone gradually dissolved the sugars. The difficulty of determining when extraction was complete and of removing all of the solvent without losing glycerol was so great and the results were so unreliable that no further work was done with the method.

QUANTITATIVE OXIDATION OF SUGAR AND GLYCEROL BY POTASSIUM DICHROMATE IN ACID SOLUTION

It seemed to the authors that it should be possible to oxidize a mixture of sugar and glycerol quantitatively with dichromate. Since the sugar in such a mixture could be readily determined by a method like that of Munson and Walker[17] it would be possible to calculate the glycerol.

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[1] Received January 26, 1921.

[2] *J. Soc. Chem. Ind.*, **17** (1898), 330.

[3] *Ibid.*, **7** (1888), 696.

[4] The acetin method was applied in our research laboratory to 0.5 g. of invert sugar. As dextrose and levulose both contain five hydroxyl groups a pentacetate might be expected to form under suitable conditions. It was found that invert sugar apparently took on 4($C_2H_2O_3$) groups, or, as is more likely, acetylated to a mixture of acetates, whose net average was a tetracetate, since the above quantity of invert sugar gave a recovery of 95.3 per cent on the assumption that tetracetates were formed.

[5] *J. Soc. Chem. Ind.*, **5** (1885), 610.

[6] "Oils, Fats and Waxes," 5th Ed., I, 447.

[7] "Commercial Organic Analysis," 4th Ed., XI, 457.

[8] *Z. landw. Versuchw.*, **5** (1902), 729.

[9] *Loc. cit.*, I, 450.

[10] *Z. anal. Chem.*, **20** (1881), 383.

[11] *J. Assoc. Official Agr. Chem.*, **1** (1915), 279.

[12] *Z. angew. Chem.*, **18** (1905), 294.

[13] *C. A.*, **6** (1912), 1072.

[14] *Ibid.*, **8** (1914), 772.

[15] *J. Am. Pharm. Assoc.*, **4** (1915), 75.

[16] *C. A.*, **11** (1917), 216.

[17] *J. Am. Chem. Soc.*, **28** (1906), 663; **29** (1907), 541; **34** (1912), 202.

Expt. I—Donath and Mayrhofer Method

Solvent: Equal parts, absolute alcohol and ethyl ether.

Conditions: Mixture of 0.125 g. dextrose, 0.125 g. levulose, 0.25 g. C. P. glycerol (96.23 per cent), and 25 cc. water, evaporated at 60° C. nearly to dryness, after addition of 0.750 g. hydrated lime, and sand. Residue extracted with successive portions of ether-alcohol, which was evaporated at low temperature, and glycerol in residue determined by dichromate method.

Recovery of Glycerol:

Test	Per cent
I	54.0
II	81.97
III	91.66

Expt. II—Donath and Mayrhofer Method

Solvent: Redistilled acetone.

Conditions: Test I—Same weight of materials as used in Expt. I; residue extracted with successive portions of solvent in the evaporating dish; glycerol determined by dichromate method. Test II—Same weight of materials as in Test I; dried residue extracted in Soxhlet extractor for 10 hrs.

Recovery of Glycerol:

Test	Per cent
I	67.4
II	164.1

Potassium dichromate should act upon invert sugar in acid solution according to the following balanced equation:

$$\underset{181.26}{C_6H_{12}O_6} + \underset{1176.8}{4\,K_2Cr_2O_7} + 16H_2SO_4 = 6\,CO_2 + 4Cr_2(SO_4)_3 + 4\,K_2SO_4 + 22\,H_2O$$

The regular Hehner or dichromate method for glycerol uses a potassium dichromate solution containing 74.552 g. per liter (1.5204 *N*), of which 1 cc. is equivalent to 0.0100 g. of glycerol. According to the above equation, 1 cc. of a 1.5204 *N* dichromate solution should be equivalent to 0.01142 g. of invert sugar.

It was found by experiment that the Hehner method applied in the usual way to a known weight of a pure hexose sugar gave a recovery of about 85 per cent. It was discovered, however, that pure dextrose and levulose were completely oxidized if a large excess of both potassium dichromate and of sulfuric acid was used. Samples of dextrose and levulose of known purity were separately oxidized; the dextrose gave a recovery of 99.90 per cent and the levulose 99.75 per cent, an average of 99.83 per cent. Hence it may justifiably be said that pure invert sugar, *i. e.*, one-half each of dextrose and levulose, which would result from the acid hydrolysis of sucrose in dilute solution, is, within the limits of experimental error, quantitatively oxidized by potassium dichromate under the proper conditions. Similarly, C. P. glycerol of known purity gave a recovery of 100.06 per cent when oxidized in a solution containing a large excess of dichromate and sulfuric acid.

Pure sucrose oxidized directly by the new dichromate method gave a recovery of 99.98 per cent, as was to be expected, since it must be inverted rapidly in the hot acid solution.

There is one transparent soap on the market which, by test, contains no sugar. Analyses for glycerol by the writers' method were made on this soap and on a sample of the same soap to which 10 per cent cane sugar was added, with the following results, expressed in per cent:

	(1)	(2)	(Av.)
Glycerol in original sugarless transparent soap.....	3.43	..	..
Glycerol in soap + 10 per cent cane sugar.........	3.34	3.40	3.37

Application of the Method to Transparent Soaps

This preliminary work proved that the method would oxidize quantitatively a mixture of invert sugar and glycerol (or of cane sugar and glycerol since cane sugar would of course rapidly become invert sugar in the strongly acid solution used). The method was accordingly applied to the analysis of transparent soaps containing glycerol.

Five samples of transparent soap were analyzed for cane sugar by the regular Munson and Walker method,[18] and for glycerol by the writers' method, with the following results. Each of the check results represents a complete separate determination.

Soap	Per cent Cane Sugar			Per Cent Glycerol		
	Sample 1	Sample 2	Av.	Sample 1	Sample 2	Av.
I	11.76	11.90	11.83	10.27	10.14	10.21
II	5.15	5.25	5.20	12.80	12.85	12.83
III	11.56	11.61	11.59	8.89	8.91	8.90
IV	...	2.72	...	18.30	18.30	18.30
V	...	17.45	...	8.13	8.13	8.13

The only precaution necessary to secure concordant results on transparent soaps was completely to remove the alcohol, which these soaps invariably contain, by boiling the acid filtrate, obtained by cracking the soap, for 20 to 30 min.; otherwise the alcohol remaining would be oxidized by the dichromate and give high and discordant results.

Other Applications of the Method

In the limited time available the authors were able to try the method on only three other types of products.

FERMENTED PRODUCTS—It is often necessary in food analysis to determine glycerol in fermented products, such as vinegar or alcoholic beverages. The authors believe that their method can be successfully used in such cases instead of the Donath and Mayrhofer method. Alcohol can be removed readily by boiling or repeated evaporation, and acetic acid appears not to be oxidized by potassium dichromate and sulfuric acid. (Blanks on the dichromate method, run with and without the addition of a known weight of sodium acetate, showed that no dichromate was consumed; hence no acetate was oxidized.) In fact, some modified dichromate methods for the determination of glycerol, such as those of Steinfels[19] and Little and Fenner[20] use lead or silver acetate in the preliminary purification of samples.

GRAPE JUICE—The difficulty would lie in the complete removal of organic matter other than sugar or glycerol by clarification. The method was tried out on unfermented Concord grape juice (containing no glycerol) both before and after the addition of a known amount of glycerol. The sample was clarified with basic lead acetate and the excess lead removed with anhydrous sodium sulfate. Analyses for sugars by the Munson and Walker method showed 14.81 per cent reducing sugars (calculated as dextrose) and 0.11 per cent cane sugar, or a total of 14.92 per cent. When total sugars were determined on this sample by dichromate oxidation, according to the authors' method, 14.85 per cent were found, a recovery of 99.5 per cent. Oxidation of the sample containing glycerol gave practically 100 per cent recovery. This shows quite conclusively that clarification was complete and that nothing oxidizable but the sugar remained in the solution. Obviously, the method could be applied to the determination of glycerol in a fermented grape juice, and it should also be applicable to the determination of glycerol in vinegar.

NONALCOHOLIC FLAVORING EXTRACTS—Recently there have come upon the market nonalcoholic flavoring extracts in which glycerol replaces alcohol. An analysis for glycerol was made by the authors' method on a vanilla extract which also contained sugar. The sample was clarified with basic lead acetate, and the excess lead removed with anhydrous sodium sulfate. Sugar determination by the Munson and Walker method showed 1.05 per cent sugars, expressed as invert sugar, and 4.25 per cent sucrose—a total of 5.52 per cent sugars, expressed as invert sugar. Glycerol as deter-

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[18] "Methods of Analyses of the A. O. A. C.," 1920 Ed., 78.

[19] *Seifensieder-Ztg.*, **42** (1915), 721; *C. A.*, **9** (1915), 3371.

[20] *J. Am. Leather Chem. Assoc.*, **11** (1917), 254.

mined by the writers' method was found to be 47.42 per cent. A determination of glycerol by the acetin method on the same sample showed 49.24 per cent, a high value on account of the sugar present. The result of 47.42 per cent was stated by the manufacturer to agree very closely with his manufacturing formula.

COMMERCIAL GLUCOSE—Attempts were made to apply the method to the analysis of a mixture of commercial glucose and glycerol. The glucose had a specific rotation of $\alpha_{D836} = 132.0°$, and contained 85.48 per cent solids. When oxidized by the authors' method it showed an equivalent hexose sugar content of 90.60 per cent and 90.63 per cent in check analyses. Repeated attempts to determine the dextrose equivalent of this glucose by the Munson and Walker method, after supposedly complete hydrolysis of the sample, invariably led to low results. Variations in the conditions of hydrolysis, *i. e.*, concentration of solution, strength of acid, kind of acid, duration of hydrolysis, and temperature, were tried without satisfactory results, the highest dextrose equivalent obtained being 85.4 per cent. Since the solids of the sample were 85.48 per cent, of which an appreciable proportion were dextrins and other intermediate products of the hydrolysis of starch, it was obvious that the dextrose equivalent of the solids must be greater than the solids themselves.

If calculated with aid of the composition-specific rotation diagram worked out by Rolfe and Defren[21] for acid-hydrolyzed starch products, the dextrose equivalent of the solids in a glucose of $\alpha_{D386} = 132°$ and total solids of 85.48 per cent will be found to be 91.3 per cent, a figure which agrees quite closely with those obtained by dichromate oxidation.

Obviously, the authors' method cannot be used to estimate glycerol in the presence of commercial glucose, on account of the fact that no satisfactory method now exists for accurately and quantitatively determining the dextrose equivalent of the solids in commercial glucose. In the unusual event that a sample of the glucose was available which was known to have been mixed with the glycerol, in which admixture it was desired to know the glycerol content, the method could be applied by finding the ratio between the dextrose equivalent of the glucose as determined by oxidation and by copper. In such a case, however, it would be far simpler and probably more accurate to determine the glucose by the polariscope. Experiments in our laboratory have shown that glycerol has no effect, positive or negative, on the optical rotation of commercial glucose.

DIRECTIONS FOR METHODS

AS APPLIED TO GLYCEROL IN TRANSPARENT SOAPS—Dissolve 25 g. of soap, accurately weighed, in 300 cc. of hot water in a 600-cc. beaker, add 50 cc. of 1 : 4 sulfuric acid, boil gently for 20 to 30 min. to volatilize any alcohol present and to invert the cane sugar completely so that it can be estimated by the Munson and Walker method. Cool the beaker, remove the cake of fatty acids, rinse the cake with distilled water, transfer the acid solution and rinsings to a 1000-cc. graduated flask, add about 0.5 g. of silver sulfate to precipitate traces of chlorides and soluble fatty acids, make up to the mark, mix the contents thoroughly, and filter. Determine the invert sugar in 50-cc. aliquot portions of the solution (equivalent to 1.25 g. of sample) by the Munson and Walker method.

For the oxidation of sugar and glycerol transfer a 50-cc. portion of the above solution to a 400-cc. beaker, using an accurately calibrated pipet or buret, add accurately with a buret or standard pipet 75 cc. of strong potassium dichromate (74.552 g. per liter, of which 1 cc. = 0.0100 g. glycerol) and then add 25 cc. 1.84 sulfuric acid. Cover immediately with a watch glass, immerse the beaker in a steam bath, and oxidize for 3 hrs. Run a blank with 100 cc. water, 25 cc. 1.84 sulfuric acid and 25 cc. strong dichromate (accurately measured with a buret or pipet), heating as described above. Make up the cooled solutions to 1000 cc. in graduated flasks, mix thoroughly and determine the excess dichromate in 50-cc. aliquot portions (one-twentieth of the oxidized solutions of blank) by adding 50 cc. of water and 20 cc. of 10 per cent potassium iodide solution and titrating the liberated iodine with 0.1*N* sodium thiosulfate.

Calculate results as in the following example:

50 cc. of oxidized solution (1/20 aliquot part) required 37.26 cc. 0.1 *N* $Na_2S_2O_3$.

50 cc. blank (1.25 cc. strong $K_2Cr_2O_7$) required 19.00 cc. 0.1 *N* $Na_2S_2O_3$.

Cane sugar (Munson and Walker method) = 11.83 per cent.

Invert sugar (cane sugar × 1.053) in 50 cc. taken for oxidation = 0.1183 × 1.053 × 1.25 = 0.1557 g.

∴ Invert sugar in 50 cc. taken for titration = 0.007785 g.

1 cc. $K_2Cr_2O_7$ (74.552 g. per 1.) = 0.01142 g. invert sugar.

∴ 0.007785 g. invert sugar required 0.682 cc. $K_2Cr_2O_7$.

Excess $K_2Cr_2O_7$ in 50-cc. portion titrated =

$$\frac{37.26}{19.00} \times 1.25 = 2.451 \text{ cc.}$$

$K_2Cr_2O_7$ used to oxidize glycerol in 1/20 aliquot titrated =

$$\frac{75}{20} - (0.682 + 2.451) = 0.617 \text{ cc.}$$

$$\text{Per cent glycerol} = \frac{0.617 \times 0.0100 \times 20 \times 100}{1.25} = 9.87$$

The above calculation can be readily simplified to four equations as follows:

Let a = per cent cane sugar in the sample.

b = cc. 0.1 *N* $Na_2S_2O_3$ required to titrate 1/20 aliquot portion of the oxidized portion of the sample.

c = cc. 0.1 *N* $Na_2S_2O_3$ required to titrate 1/20 aliquot portion of the blank.

A = cc. strong $K_2Cr_2O_7$ used by the sugar in 1/20 aliquot of the portion oxidized.

B = cc. strong $K_2Cr_2O_7$ in excess in 1/20 aliquot of the portion oxidized.

C = cc. strong $K_2Cr_2O_7$ required to oxidize the glycerol in 1/20 aliquot of the portion oxidized.

D = per cent glycerol in sample.

$$\text{Then } A = a \times 0.05761 \quad (1)$$

$$B = \frac{b}{c} \times 1.25 \quad (2)$$

$$C = 3.75 - (A + B) \quad (3)$$

$$D = C \times 0.01 \times 20 \times 100 = 16\,C \quad (4)$$

Special attention is called to the fact that in the calculations the values A, B, and C are carried out to 0.001 cc. This accuracy is warranted because the titrations are all made with 0.1*N* $Na_2S_2O_3$ and referred back to the strong dichromate whose normality is 1.5204.

FOR SAMPLES OTHER THAN TRANSPARENT SOAPS—Use a sample of such size that the aliquot part finally used for oxidation does not contain over 0.3 g. of sugars plus glycerol. Different samples may require different treatment to purify them from interfering substances, but the writers' results have shown that alcohol and albuminous materials can be readily removed and do not interfere.

SUMMARY

1—The writers have evolved a modified dichromate oxidation method which will determine glycerol quantitatively in the presence of cane sugar, or of reducing sugars of such a nature that they can be quantitatively estimated by some copper reduction process.

2—The method is simple, requires no elaborate preparation of the sample, no special apparatus, and can be carried out in practically the same time as the usual glycerol analysis by the dichromate method.

3—The method has been shown to give very consistent and accurate results for the determination of glycerol in transparent soaps containing sugar, and glycerol in nonalcoholic vanilla extract containing sugar.

4—It is believed that the method can be applied also to the determination of glycerol in fermented products.

5—The method cannot, however, be applied to the determination of glycerol in the presence of commercial glucose, owing to the lack of a method which will determine accurately the dextrose equivalent of total saccharine matter in commercial glucose.

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[21] *J. Am. Chem. Soc.*, 18 (1896), 869.

The Determination of Acid Number of Tung and Other Vegetable Oils[1,2]

By L. L. Steele and G. G. Sward

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Recently Jameson[3] has shown that the heat test for the purity of tung oil (the length of time in minutes necessary to cause polymerization or jellying of the oil at an arbitrary temperature) is influenced greatly by the free fatty acid content of the oil. Gardner[4] has shown that the length of time necessary for the jellying of tung oil in the heat test is increased in direct proportion to the amount of free fatty acid of tung oil added.

As Jameson points out, the free fatty acid content of tung oil is important and he recommends that the present maximum allowable percentage of free acid be reduced to 1 per cent. (Standard specifications of the American Society for Testing Materials allow not over 3 per cent.)

It was noticed at the Bureau of Standards that different acid values were obtained upon a given sample of tung oil when alcohol and alcohol-benzene, respectively, were used as solvents. Gardner and Coleman[5] showed that the acid value of a varnish appears to be higher when alcohol-benzene mixture is used as a solvent than when alcohol alone is employed. Jameson made use of a mixture of alcohol and benzene as a solvent in the titration of the free fatty acid of tung-oil samples.

It seemed desirable to find out whether the higher acid values of tung oil in alcohol-benzene mixture were abnormal or whether the present standard use of alcohol[6] as a solvent leads to low values. In this connection it seemed desirable also to investigate the use of alcohol-benzene mixture as the solvent for other oils in the acid number determination. A third point included was the investigation of two other factors affecting the method of determining acid numbers of vegetable oils, namely, the possible influence of caustic soda, now commonly substituted for caustic potash, and the difference, if any, between the use of aqueous and alcoholic alkali in the titration of free fatty acid.

Method of Procedure

The acid number of a sample of commercial tung oil was determined by the standard method as follows: Four portions of 5 to 10 g. each were weighed into flasks and heated on a hot plate under a reflux condenser for 30 min. with 50 cc. of ethyl alcohol, previously made neutral to phenolphthalein. After cooling, the four samples were titrated with 0.1 *N* aqueous sodium hydroxide, 0.1 *N* alcoholic sodium hydroxide, 0.1 *N* aqueous potassium hydroxide, and 0.1 *N* alcoholic potassium hydroxide, respectively. Commercial samples of cottonseed and linseed oils were titrated in the same manner with the four standard alkali solutions.

The titrations on the oils were repeated, substituting for the alcohol 50 cc. of a neutral mixture of equal parts by volume of ethyl alcohol and C. P. benzene. In this case the oils dissolved in the alcohol-benzene mixture without heating, and titrations were made at once (omitting the half-hour heating period).

The fatty acids of each of the three oils were prepared by the usual method and each sample of fatty acid was titrated in both alcohol and alcohol-benzene as solvent, using the four standard alkali solutions. Weighed amounts of the fatty acids were added to weighed amounts of the corresponding oil, so as to form a series of oils of ascending acid numbers. These samples of oil of known acid content were titrated with both alcohol and alcohol-benzene mixture for solvent and with the four different standard alkali solutions already described.

By a comparison of the actual acid value obtained in each case with the known acid content of the oil, conclusions could be drawn as to the three points in question.

Experimental

OILS EXAMINED—Data were obtained upon the acid number of tung, linseed, and cottonseed oils, and of several mixtures of tung oil and rosin.

REAGENTS: *Sodium and potassium hydroxide*—C. P. sodium and potassium hydroxide sticks were used.

Alcohol and benzene—Ninety-five per cent by volume ethyl alcohol which had been recently redistilled was used. The benzene was C. P., free from thiophene. Both materials were neutralized immediately before use by titrating with alkali to a very faint pink color, using phenolphthalein as an indicator.

Standard solutions—The standard alkali solutions were prepared as for testing linseed oil,[7] except that 0.1 *N* solutions were prepared instead of 0.25 *N* solutions.

The weight of sample taken was so regulated in each case that approximately 15 cc. of the standard alkali solution were necessary for neutralization.

Results Obtained

Table I includes values obtained upon the various oils and fatty acids.

Table I—Acid Values of Oils and Fatty Acids

	Value Found in Alcohol				Value Found in Alcohol-Benzene			
	with Aqueous		with Alcoholic		with Aqueous		with Alcoholic	
Material	KOH	NaOH	KOH	NaOH	KOH	NaOH	KOH	NaOH
Tung oil	6.60	6.76	6.52	6.32	7.05	7.15	7.22	7.15
Fatty acid of tung oil	192.7	192.4	192.6	192.4	190.3	190.1	192.9	192.1
Linseed oil	4.46	4.39	4.52	4.52	4.66	4.62	4.64	4.69
Fatty acid of linseed oil	196.9	196.6	196.0	196.8	195.9	194.9	197.1	197.2
Cottonseed oil	0.68	0.70	0.72	0.72	0.75	0.74	0.71	0.76
Fatty acid of cottonseed oil	184.1	184.7	183.1	184.2	182.1	182.7	183.6	184.4
W. W. rosin	161.8	162.1	160.7	160.1	161.2	161.4	161.2	160.6

The determinations of the acid numbers of the fatty acids of tung, linseed, and cottonseed oils were in good agreement, except in the case where aqueous alkali was used for titration with alcohol-benzene as solvent. It is probable that here there was enough dilution by the water of the alkali solution to cause some hydrolysis, giving slightly low values for the acid numbers. For this reason the two low values in the case of each sample of fatty acid were omitted and the average of the six other values was taken as the true acid number of the sample.

The acid numbers of a series of mixtures of the different oils with their fatty acids were calculated from the weights of oil and fatty acid mixed and the average acid value of the oil and its fatty acid, respectively. In the case of tung oil the average acid value found in alcohol-benzene was assumed to be the true acid number.

Summary

1—The use of alcohol alone as a solvent in the determination of the acid number of tung oil leads to low values,

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[1] Received August 9, 1921.

[2] Published by permission of the Director, Bureau of Standards.

[3] *Analyst*, **45** (1920), 328.

[4] *Paint Mfrs.' Assoc. U. S., Circ.* **119**.

[5] *Paint Mfrs.' Assoc. U. S., Circ.* **87**.

[6] *Am. Soc. Testing Materials Standards*, **1918**, 577.

[7] "Recommended Specifications for Linseed Oil," Bureau of Standards, *Circ.* **82**.

especially in the case of oils with a low acid content. Alcohol-benzene mixture gives values which are correct within the limits of experimental accuracy of the determination. With rosin-tung oil mixtures, alcohol-benzene gives results nearer the theoretical than does alcohol alone.

2—Alcohol as a solvent in the determination of the acid number of linseed and cottonseed oils yields values which average slightly lower than the theoretical acid content. In most of the determinations the average of the values obtained with alcohol-benzene mixture were closer to the theoretical acid content than when alcohol was used as solvent.

3—Alcohol-benzene mixture is preferable to alcohol as a solvent because the end-point in the titration is much sharper.

4—As was to be expected, no difference was noted in any case between the use of sodium and potassium hydroxide, within the limits of experimental accuracy of the titrations.

5—If the weight of sample is so regulated that approximately 15 cc. of alkali solution are required for neutralization, aqueous alkali can be used interchangeably with alcoholic alkali, with no appreciable difference in results within the limits of experimental accuracy.

6—In the case of a material with a very high acid number (above 100), such as a fatty acid, there is evidence of some hydrolysis when aqueous alkali is used with alcohol-benzene as a solvent, and alcoholic alkali should be used for titration.

TABLE II—ACID VALUES OF MIXTURES OF OIL AND FATTY ACID

Sample No.	Calculated Acid No.	Value Found in Alcohol				Value Found in Alcohol Benzene			
		with Aqueous		with Alcoholic		with Aqueous		with Alcoholic	
		KOH	NaOH	KOH	NaOH	KOH	NaOH	KOH	NaOH
TUNG-OIL MIXTURES									
1	15.33	14.40	14.37	14.72	14.20	15.22	15.33	15.38	15.41
2	29.25	28.3	28.3	28.7	28.6	29.3	29.1	29.4	29.3
3	59.1	58.8	58.5	58.9	58.3	59.2	59.2	59.3	59.2
4	99.3	99.2	98.9	99.0	98.7	99.3	98.7	99.4	99.2
LINSEED-OIL MIXTURES									
1	10.61	10.45	10.41	10.55	10.42	10.54	10.52	10.51	10.60
2	24.22	23.76	24.01	24.10	23.85	24.13	24.25	24.32	24.20
3	53.2	52.86	52.88	52.97	52.85	53.15	53.13	53.05	53.18
4	100.4	100.2	99.6	99.9	100.0	100.6	100.2	100.6	100.5
COTTONSEED-OIL MIXTURES									
1	11.29	11.07	11.05	11.25	11.22	11.39	11.33	11.65	11.34
2	25.4	25.07	24.79	25.00	25.03	25.40	25.32	25.21	25.26
3	50.7	50.4	50.5	50.4	50.6	50.6	50.6	50.8	50.8
4	101.5	101.7	101.4	100.9	101.6	100.7	101.3	100.6	101.4
TUNG OIL-ROSIN MIXTURES									
1	15.93	15.36	14.81	15.33	15.53	15.75	15.87	15.75	15.98
2	29.7	28.42	28.33	28.25	28.75	29.32	29.13	29.25	29.50
3	60.7	60.2	59.8	59.7	60.3	60.4	60.3	60.4	60.6
4	102.8	102.0	102.2	102.0	103.0	101.8	102.2	102.8	103.2

Vapor Pressure Determinations on Naphthalene, Anthracene, Phenanthrene, and Anthraquinone between Their Melting and Boiling Points[1,2]

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A search of the literature on vapor pressures reveals the fact that very few determinations have been made on most of the solid hydrocarbons between the temperatures of their melting and boiling points, or above. In view of this fact and also in response to the increased demand for more reliable physical constants, arising from recent researches into different types of reactions both in the liquid and vapor phase, the problem of determining the vapor pressures of some of the more common compounds was undertaken.

In this paper the method employed will be discussed, and some of the results obtained in naphthalene, anthracene, phenanthrene, and anthraquinone will be tabulated. In subsequent publications the results on other compounds, or mixtures of compounds, which are now under investigation will be given.

Up to the present time vapor pressure determinations of compounds of the type in which we are interested seem to have been limited to comparatively low temperatures. Ramsey and Young[3] determined the vapor pressures of camphor between 0° and 180° C.; Vanstone,[4] that of a mixture of camphor and borneol between 78° and 185° C., while Allen[5] worked with naphthalene between 0° and 130° C. Perman and Davis[6] determined the vapor pressure of naphthalene, and of mixtures of naphthalene and β-naphthol at 70° C., and Barker[7] determined the pressures of naphthalene at 20°, 30°, and 40° C. From the vapor pressure curves obtained by Stelzner,[8] it appears that this investigator determined the vapor pressure of naphthalene between 75° and 170° and extrapolated the curve to 218° (b. p.) while in the case of anthracene observations were made for every 10° between 160° and 260° C., and on anthraquinone between 224° and 320°. It appears, therefore, that in no case did the temperatures of the experiments even approximate the boiling point of the compounds or mixtures under investigation.

METHODS OF MAKING VAPOR PRESSURE DETERMINATIONS

The static method of vapor pressure measurement and the dynamic, or air current method, have been used with different modifications so long and with so much success as to become almost standard. Other methods have been proposed, such as the optical method devised by C. and M. Cuthbertson,[9] based on the assumption that the refractivity of a vapor was proportional to the vapor pressure; or the hygrometric method devised by Forbes.[10]

The dynamic method is most suitable for low pressures and low temperature work, and has been used with varying degrees of success by Regnault,[11] Linbarger,[12] Perman,[13] Derby, Daniels and Gutsche,[14] and others. The method consists essentially in passing a known volume of air or indifferent gas over the substance whose vapor pressure is to be determined, and by determining the amount of substance carried over, the vapor pressure is readily calculated from Dalton's law of partial pressures. The air drawn through the apparatus must necessarily be saturated with the vapors, and herein lies one of the chief difficulties. The temperature of the saturator must be kept very constant for considerable periods in cases where the substance under investigation has a low vapor pressure, and this alone is not easy to accomplish especially if the required temperature is comparatively high. Even if constant vapor baths are used, a change of 5 or 10 mm. in the atmospheric pressure

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[1] Presented before the Division of Dye Chemistry at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

[2] Published as Contribution No. 53 from the Color Investigation Laboratory, Bureau of Chemistry, Washington, D. C.

[3] *Phil. Trans.*, **1884**, I, 34.

[4] *J. Chem. Soc.*, **97** (1910), 429.

[5] *Ibid.*, **77** (1900), 412.

[6] *Ibid.*, **91** (1907), 1114.

[7] *Z. physik. Chem.*, **71** (1910), 235.

[8] Dissertation, Erlanger, **1901**, "Über den Dampfdruck fester Körper" (original article not available).

[9] *Proc. Roy. Soc. London, A*, **85** (1911), 305.

[10] *Chem. News*, **106** (1912), 88.

[11] *Ann. chim. phys.*, [3] **15** (1845), 129.

[12] *J. Am. Chem. Soc.*, **17** (1895), 615.

[13] *Proc. Roy. Soc. London*, **72** (1903), 72.

[14] *J. Am. Chem. Soc.*, **36** (1914), 793.

is sufficient to cause an appreciable change in the boiling point of the liquid, and hence in the temperature of the vapor baths.

The old static method offers some advantage over the dynamic, but is by no means without objectionable features. Here again the question of maintaining at a constant temperature a long mercury-filled tube (750 mm. or more) presents itself, and also that of expelling the last traces of air or other impurities that may be dissolved in the mercury or absorbed on the inner surface of the glass tubing. For a more detailed and critical discussion of the merits and demerits of the dynamic and static methods of vapor pressure determination, the reader is referred to the work of Smith and Menzies.[15] The other methods mentioned above, as well as the dew-point and tensimetric methods, have rather limited applicability and need not be discussed in this connection.

Apparatus

The apparatus used throughout this work was a submerged-bulblet, vapor pressure apparatus, as developed by Smith and Menzies. This method seemed to offer a number of advantages not found in any of the others: the temperature could easily be controlled and the pressure could be read off directly on the manometer, thus eliminating errors due to temperature variations, insufficient stirring of the thermostat, or in condensing or absorbing and analyzing vapors, as in the air current methods. The method is also comparatively rapid, since a series of determinations may be completed in one day. The apparatus is shown diagrammatically in Fig. 1.

Instead of using an open-end pressure gage, a manometer a trifle over 1 meter in length was made from Pyrex glass tubing of 8 mm. inside diameter. The mercury used in the manometer was carefully purified by shaking with nitric acid and further by distilling three times under vacuum. Before the manometer tube was sealed off, it was very thoroughly cleaned with hot chromic acid cleaning solution, rinsed with distilled water, and dried by heating while a current of dry air was drawing through. After being filled with the mercury the manometer was carefully boiled out in order to expel all foreign materials which might be dissolved in the mercury or absorbed on the inner surface of the glass. The boiling out process lasted over 2 hrs., under pressure of approximately 3 mm. Not the slightest indication of air bubbles could be detected anywhere along the tube.

The difference in levels of the mercury in the manometer arms was measured by means of a meter stick graduated in millimeters. The accuracy of the calibrations was checked against a standard steel tape, and found to differ by about 0.5 mm. in 1000. The temperature of the manometer was observed and the readings were corrected accordingly, taking the value of the cubical coefficient of expansion of mercury given in the Smithsonian tables (0.0001818). The manometer readings were made with the naked eye and were correct to ± 0.2 mm.

The apparatus, not including the heating device and thermostat, was fastened to a board 24 in. × 13 in. and consisted essentially of three parts: manometer, A; glass connections all in one piece, and isoteniscope, H. The bottle, G, was evacuated to about 2 mm. before each run was made and was used for lowering the pressure in the system by opening stopcock E. A pressure bottle (not shown) was used for raising the pressure in the apparatus by opening the 3-way cock, D, which was also connected with the atmosphere. In cases of pressures below atmospheric the pressure bottle was not used, but D was turned so as to admit air directly from the atmosphere. A small hand pump was used to produce the necessary pressure in the bottle or in the apparatus.

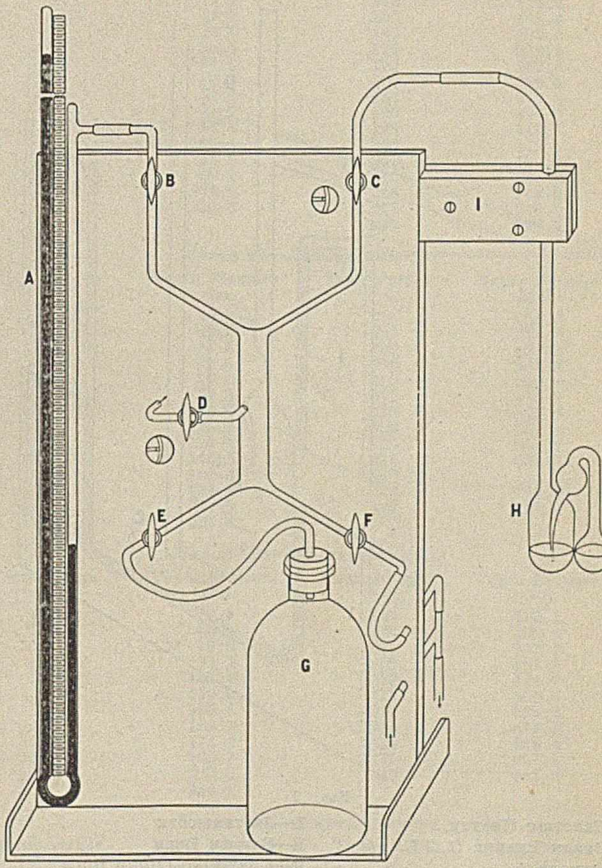

Fig. 1

The isoteniscope, or rather "dynamic isoteniscope,"[16] was made of heavy Pyrex glass and was about 45 cm. in length. The bulb containing the confining liquid[17] was 50 mm. long and 30 mm. in diameter. The side bulb containing the substance was also made of Pyrex glass, but with much thinner walls, and had a diameter of about 20 mm. This part of the apparatus could readily be detached from the rest by removing clamp I which held it in position; and since it was connected to the main part of the apparatus by a piece of rubber tubing it could easily be removed for refilling. All rubber connections were short and held a high vacuum for considerable periods. To test the different connections, as well as the stopcocks, the apparatus was evacuated to about 2 or 3 mm. and left until the following day, when an increase to only about 10 mm. was observed.

The thermostat and method for observation of equal pressure in the side bulb containing the substance under investigation and the manometer are shown in Fig. 2. A beaker of one and one-third liters capacity was used to hold the liquid bath (glycerol for naphthalene and the eutectic mixture of sodium and potassium nitrates for the higher boiling compounds) and was heated by means of an electric heater. This heater was made by winding No. 22 asbestos-covered nichrome wire on a glass beaker with a diameter a trifle larger than the one to be used throughout the observations. This wire was covered with a layer of alundum cement and dried in an electric oven. When perfectly dry it was placed in a cubical wooden box 9.5 in. on a side and insulated with packed asbestos shreds. With this amount

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[15] *J. Am. Chem. Soc.*, **32** (1910), 32.

[16] Smith and Menzies, *Loc. cit.*, 1448.

[17] In each determination the material constituting the confining liquid was the same as that the vapor pressure of which was being measured.

of insulation it became an easy matter to maintain constant temperature of the liquid bath long enough to bring the pressures to equilibrium. By means of a 2-way switch, connections were made with both 110- and 220-volt circuits, the latter being used to boost the temperature to save time.

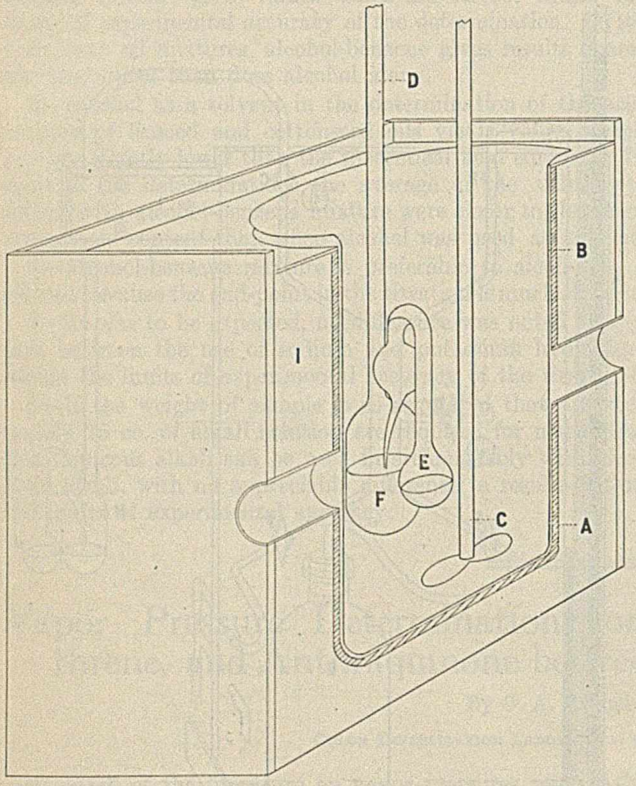

Fig. 2

A—Electric Heater
B—Pyrex Beaker (1, 3 L.)
C—Stirrer
D—Isoteniscope
E—Sample Bulb
F—Confining-Liquid Bulb
I—Insulation: Asbestos Shreds

In order to enable the worker to observe when the levels of the liquid in the tube leading from the side bulb of the isoteniscope and that of the confining liquid were the same, two holes about 1 in. in diameter were made, directly opposite, through the sides of the electric heater and the surrounding insulation. By adjusting the position of the isoteniscope in such a way that the bulb containing the confining liquid was directly in line with these holes, and by placing an electric light at the opening of one of them, observations could very easily be made through the other.

The bath liquid was kept in violent motion by a stirrer revolving at high speed.

Temperature Measurement

It is well known that for temperatures between 250° and 350° or 375° ordinary mercury thermometers cannot be relied upon. From calibrations made by the Bureau of Standards one often observes a correction of from ±1° to ±2° over a range of 50° C. Such errors are not often of much consequence in ordinary work, but in work similar to this an error of 0.1° C., near the boiling point of naphthalene, for example, would produce an error of 1.7 mm. in the vapor pressure.

Smith and Menzies used a platinum resistance thermometer, and were able to observe temperature variations of from 0.1 to 0.01° C. Inasmuch as such an instrument was not available for the present investigation, a multiple junction copper-constantan thermoelement was made, and the temperature calculated from the e. m. f. developed. From the work of Adams of the Geophysical Laboratory[18] this method of temperature measurement is shown to be perhaps the most reliable, as well as the most accurate, so far developed. Adams observed that with a single copper-constantan couple a temperature variation of approximately 0.02° C. would cause a change of 1 microvolt in the e. m. f. produced, or with a sensitive potentiometer a temperature change of 0.01° could readily be observed. Not having available a galvanometer sensitive enough to register such minute changes in e. m. f., instead of using a single couple, the writers employed a multiple element, consisting of five couples connected in series. The e. m. f. with such an arrangement, using 0° for the cold junction temperature, varied from 0 microvolts at 0° to about 94,000 microvolts at about 380°, or a change in e. m. f. of nearly 250 microvolts for a change of temperature of 1° C. The constant boiling liquids used in calibrating the thermoelement were water for 100° C., naphthalene for 217.95°, and benzophenone for 305.9°. Corrections in the boiling points of these compounds were made for changes in atmospheric pressures. To make certain that our calibrations were correct the results obtained in our laboratory at the temperature of the boiling points of water and naphthalene were checked against observations made on our thermocouple at the Geophysical Laboratory, under the supervision of Mr. Adams.

Purification of Materials

The naphthalene was obtained pure from the stock rooms and showed a boiling point of 217.95° at 760 mm. The anthracene was obtained from the commercial product (about 85 per cent) by repeated sublimations and two crystallizations from solvent naphtha, two from benzene, and one from 95 per cent alcohol. The carbazol was removed by fusing with sodium hydroxide and potassium hydroxide before the first sublimation. The final product showed a beautiful purplish fluorescence and had the same melting point as the Kahlbaum product used in one of the runs. Phenanthrene was purified in the same way as the anthracene, and had a melting point of 100° C. The anthraquinone was crystallized twice from benzene and dried for 5 hrs. at 120° C. before using.

Table I—Naphthalene

Temperature ° C.	Vapor Pressure Mm.	Temperature ° C.	Vapor Pressure Mm.
		181.20	310.6
87.47	11.9	185.34	347.6
95.00[1]	15.5	188.30	376.5
100.00	18.5	196.96	464.1
104.39	22.9	198.53	482.1
109.65	28.7	200.50	505.7
114.70	35.9	205.78	576.2
117.15	38.3	206.00	581.9
128.06	58.7	212.17	667.8
133.72	71.2	213.30	682.7
144.45	103.5	217.34	755.8
158.95	165.1	217.87	759.2
163.13	187.1	221.45	825.2
175.10	260.8		
178.44	290.0		

[1] Allen, *Loc. cit.*, 412.

Table II—Anthracene

Temperature ° C.	Vapor Pressure Mm.	Temperature ° C.	Vapor Pressure Mm.
226.53	52.7	297.38	317.7
227.77	52.7	298.22	319.1
231.94	60.2	304.35	363.9
232.12	62.1	310.31	415.6
236.64	69.6	318.20	488.1
244.59	86.5	321.29	515.0
254.86	113.4	325.47	555.5
259.50	129.5	329.47	612.2
261.76	135.5	335.52	674.4
263.74	142.5	337.14	692.7
270.70	169.3	337.70	697.6
271.75	175.0	340.58	738.9
277.50	203.2	341.57	756.4
277.66	198.2	341.70	757.3
286.66	247.7	342.05	761.2
292.15	279.0	343.25	778.2
295.37	303.0		

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[18] *Am. Inst. Mining Met. Eng., Bulletin* **153** (1919).

TABLE III—PHENANTHRENE

Temperature ° C.	Vapor Pressure Mm.	Temperature ° C.	Vapor Pressure Mm.
232.34	62.2	300.91	350.9
233.54	65.4	309.44	420.3
246.59	94.5	308.64	4414.8
249.14	101.5	312.62	446.0
264.73	151.4	319.27	510.7
269.89	172.4	321.24	531.5
281.33	226.1	332.11	654.4
282.73	234.1	333.08	664.6
294.57	307.4	339.91	754.3
295.37	311.4	340.41	762.3
299.88	340.2	340.59	764.2

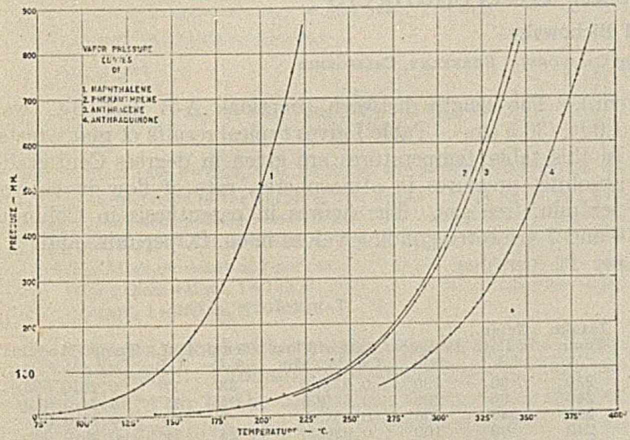

FIG. 3

TABLE IV—ANTHRAQUINONE

Temperature ° C.	Vapor Pressure Mm.	Temperature ° C.	Vapor Pressure Mm.
285.58	104.0	346.11	402.0
286.71	108.0	349.03	428.0
292.74	122.2	351.14	448.2
295.30	133.5	357.00	500.0
302.80	156.0	361.18	546.6
306.74	172.6	362.82	562.3
311.43	189.8	364.54	579.2
315.38	209.5	367.33	615.8
319.83	230.6	370.66	656.0
321.70	241.5	373.71	685.4
325.01	259.4	377.53	733.1
329.22	282.7	378.71	746.4
330.96	296.4	379.73	759.0
334.34	317.5	381.21	779.4
335.35	323.4	382.14	791.6
339.80	352.6	383.18	804.7
344.30	388.0		

RESULTS OBTAINED

The results obtained in the vapor pressure determination on naphthalene, anthracene, phenanthrene, and anthraquinone are given in Tables I, II, III, and IV, respectively. Fig. 3 shows the vapor pressure curves of these compounds using the above values.

The above observations were plotted on 80 cm. × 100 cm. coördinate paper, and the pressures for intervals of 5° were read from these curves. These observations are tabulated in Tables V to VIII, inclusive, and are intended to show the mean values of all our observations on the compounds worked on thus far.

It should be pointed out that since it is hardly possible to read a manometer closer than to within ±0.1 or 0.2 mm. without the aid of a cathetometer or a vernier arrangement, the per cent error is necessarily much greater where the pressures are low; while at higher pressures the large variation due to small changes in temperatures makes observations difficult at these points. It was, however, much easier to obtain good checks at the higher pressures than at the lower, for, as pointed out in the first part of this paper, the temperature was controlled without much difficulty.

As may be seen from the above tables and curves, the boiling points of these compounds are as follows: Naphthalene 217.95° (taken from literature and used in calibrating thermocouple), anthracene 342°, phenanthrene 340.2°, and anthraquinone 379.8°. The results obtained on phenanthrene and anthraquinone agree very well with those given in the literature, namely, 340° and 380° C., respectively. For the boiling point of anthracene the literature gives 350° and 351° C.[19] but in no case was this temperature reached before the pressure reached points much above 760 mm. Further to verify the observations on anthracene at this temperature, the writers made three sets of duplicate determinations on three different samples of anthracene: two, on a sample prepared by Dr. K. P. Monroe, formerly of the Bureau of Chemistry, two, on the product purified from commercial anthracene as outlined above, and two, from a sample of Kahlbaum's. A large number of observations were made on each of these samples at about the boiling point, with an agreement well within the limits of experimental error.[20] Boiling point determinations were also made according to the method described by Mulliken, using an Anschutz thermometer, with results that again agreed with those given above, as obtained by vapor pressure determinations.

TABLE V—NAPHTHALENE

Temperature ° C.	Vapor Pressure Mm.	Temperature ° C.	Vapor Pressure Mm.
85	9.9	155	144.4
90	12.0	160	168.4
95	14.9	165	195.5
100	18.5	170	226.1
105	23.0	175	260.6
110	28.5	180	299.1
115	35.0	185	342.3
120	42.7	190	390.2
125	51.8	195	443.3
130	62.4	200	502.1
135	74.6	205	566.6
140	88.7	210	637.2
145	104.8	215	714.2
150	123.3	218	760.0
		220	797.9

TABLE VI—ANTHRACENE

Temperature ° C.	Vapor Pressure Mm.	Temperature ° C.	Vapor Pressure Mm.
220	42.6	290	265.9
225	49.5	295	297.5
230	57.3	300	332.0
235	66.1	305	269.5
240	76.0	310	410.5
245	87.1	315	454.9
250	99.6	320	502.9
255	113.5	325	554.7
260	129.1	330	610.4
265	146.5	335	669.8
270	165.8	340	732.9
275	187.3	342	760.0
280	211.0	345	799.5
285	237.2		

TABLE VII—PHENANTHRENE

Temperature ° C.	Vapor Pressure Mm.	Temperature ° C.	Vapor Pressure Mm.
230	58.3	290	276.1
235	68.1	295	308.3
240	79.0	300	343.7
245	91.1	305	382.1
250	104.4	310	424.0
255	119.2	315	469.5
260	135.5	320	518.8
265	153.7	325	572.0
270	173.6	330	629.4
275	195.7	335	691.1
280	220.0	340	757.0
285	246.7		

TABLE VIII—ANTHRAQUINONE

Temperature ° C.	Vapor Pressure Mm.	Temperature ° C.	Vapor Pressure Mm.
285	103.0	340	354.5
290	116.2	345	392.9
295	131.3	350	435.5
300	147.8	355	481.9
305	166.0	360	531.7
310	186.0	365	585.4
315	207.9	370	643.4
320	232.0	375	703.0
325	258.5	379.8	760
330	287.5	380	763.4
335	319.4		

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[19] Landolt-Börnstein, "Physikalisch-chemische Tabellen;" Mulliken, "Identification of Pure Organic Compounds."

[20] The experimental error referred to here is the error introduced in reading the manometer, as pointed out above, and a slight error due to inability to observe variations in e. m. f. to less than 2 microvolts corresponding to approximately 0.008° C. It should be noted, however, that the change in pressure corresponding to a change of 0.008° C. in the temperature at about the boiling point of anthracene is of the order of 0.10 mm. so the error in temperature reading becomes negligible.

SUMMARY

A brief resumé of previous vapor pressure determinations has been made.

A detailed description has been given of the method employed in obtaining vapor pressure values for naphthalene, anthracene, phenanthrene, and anthraquinone, and tables and curves of observed vapor pressures of these compounds have been recorded.

Boiling point determinations have been made on anthracene, phenanthrene, and anthraquinone with the following results: Anthracene, 342° C.; phenanthrene, 340.2° C.; anthraquinone, 379.8° C.

Experiments with Heat Interchangers[1]

By F. Russell Bichowsky

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA

In liquid air machines and other refrigerators which depend on the Joule-Thomson effect for cooling, the efficiency depends, for a given intake pressure, temperature, and rate of flow of the gas, on the character of the heat insulation, and especially on the efficiency of the heat interchange between the comparatively hot incoming and comparatively cold outgoing gas. In a perfect heat interchanger, the gas entering the interchanger and the gas leaving the interchanger will have the same temperature. Assuming the intake temperature of the gas (in this case O_2) to be 298° A., and the intake pressure to be 200 atm., and assuming perfect heat interchange and perfect heat insulation, and taking for the value of the Joule-Thomson effect under these conditions $-50°$, for the molal heat capacity of the gas at 1 atm. 6.7, and for the heat of vaporization per mole 1600 cal., it can be shown that 11 per cent of the gas will be liquefied.[2] If the outgoing gas leaves the interchanger at temperatures less than that of the incoming gas, a similar calculation will show that the yield of liquid O_2 (and the same values hold approximately for liquid air and liquid N_2) will be decreased 20 per cent for each 10° difference of temperature between outgoing and incoming gas. Ordinarily, even for the comparatively poorly insulated, small-size liquefiers found in many laboratories, the loss of efficiency due to poor thermal insulation is small, compared with that due to poor interchange.

The heat interchanger commonly used on liquid air machines consists of a coil of one or more copper tubes either wound one tube inside the other, as in the original Linde design, or, as is more common in laboratory interchangers, of the Hampton type, in the form of flat coils, the first coil being wound from the center out and the next from the outside in, either one tube being used or several tubes wound in parallel. In the Linde design the compressed gas, after expansion at the lower end of the coil, passes back the entire length of the coil through the annular space between the inner and outer tubes. In the Hampton type, the gas, after expansion, passes back over the tightly wound coil through the interstices between layers left during winding. One-eighth inch o. d. drawn soft copper tubing is about as small as is practical to use, and one-fourth inch o. d. copper tubing is a convenient size.

To study the efficiency of heat interchange in such small tubes between the walls and the rapidly moving high pressure gas, the apparatus shown in Fig. 1 was constructed. The wire AC was of tested No. 40 constantan which was carefully stretched so as to be exactly central in the tube. The small leads were No. 40 copper, the whole forming a differential thermoelement giving the difference of temperature of the gas between A, B, and C. The initial temperature was given by a thermoelement not shown. The mean inside diameter of the tube was 0.124 in. (0.315 cm.), the outside 0.251 in. (0.638 cm.). The length between junctions A-B and B-C was 1.0 ft. (30.5 cm.). Table I gives typical results of many tests. In this table, temperatures are given in degrees Centigrade absolute, pressures in atmospheres, rate of flow in cu. m. per min. free gas. The figures in parenthesis in Columns 4 and 7 are corresponding values in cu. ft. per min. and ° F. per ft. per deg.

TABLE I

Intake Temp. ° A.	Temp. of Bath ° A.	Pressure Atm.	Rate of Flow Cu. M./Min.	Temp. A-C	Diff. A-B	Temp. Modulus Deg./M./Deg.
290	90	200	0.93(33)	33	17	0.26(0.085)
240	90	200	0.93(33)	25	11	0.24(0.073)
290	240	200	0.93(33)	8	4	0.26(0.08)
240	90	100	0.93(33)	24	12	0.26(0.08)
290	240	100	0.93(33)	8	4	0.26(0.08)
290	90	200	0.47(16.5)	68	35	0.55(0.17)
240	90	200	0.47(16.5)	42	20	0.42(0.13)
290	240	200	0.47(16.5)	15	8	0.52(0.16)

The first six columns are self-explanatory; the last column gives the temperature modulus, *i. e.*, the fall of temperature per meter of tube per Centigrade degree difference of temperature between the temperature of the bath and the temperature of the incoming gas, found by dividing the values in Column 6 by the temperature head, *i. e.*, by the temperature of the bath minus the intake temperature. These results, which are only approximate, show that the temperature drop per meter of tube is independent of the pressure, inversely proportional to the rate of flow, and proportional to the temperature head from bath to incoming gas.

Knowing the modulus as defined above for a given sized tubing and given rate of flow, it is possible to calculate the length of that tubing which will be necessary to construct an ideal interchanger of given thermal efficiency.

Let T_1 = temperature of incoming gas
T_2 = temperature of gas just before expansion
T_3 = temperature after expansion (for liquid air machines this will be temperature of liquid air)
T_4 = temperature of gas leaving exchanger
C_{p_i} = molal heat capacity of incoming gas, under pressure P_i at any point along interchanger
C_{p_o} = molal heat capacity of outgoing gas, under pressure P_o at same point along interchanger
t_i and t_o = temperatures of incoming and outgoing gas at same point
M_i = mass of gas, in moles, entering interchanger in any interval of time
M_o = mass of gas leaving interchanger in same interval

Then for a liquid air machine $M_i - M_o = A$, the mass of air liquefied in that interval; or, choosing the interval so that $M_i = 1$, and assuming that the liquefier has been running long enough so that conditions do not change with the time, $1 - M_o$ equals the efficiency of the liquid air machine. Now C_{p_i} and C_{p_o} will in general be functions of the temperature, *i. e.*, $C_{p_i} = f_{p_i}(T)$ and $C_{p_o} = f_{p_o}(T)$. The function will depend on kind of gas and pressure. This may be determined by experiment.

Let 1 be the length of the interchanger, and let μ be the temperature modulus as defined above, *i. e.*, the drop of temperature per unit length per degree temperature head. Now the heat transferred from the incoming to outgoing gas for any small segment of the interchanger is

$$(t_i - t_o)\mu dl$$

where dl is length of segment. This equals $MC_{p_o}\,dt$ and $+\,C_{p_i}\,dt$, where dt is change of temperature of the gas in length dl. Integrating gives:

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[1] Received March 7, 1921.

[2] This is based on the equation O_2 (g. 298-50° A.) $= xO_2$(1, 90° A.) $+ (1-x)O_2$ (g. 298° A.); $4H = O$. Here x is per cent of gas liquefied and H is heat content. Details will be given by Lewis and Randall, "Treatise on Thermodynamics."

$$1 = \frac{M_o}{\mu}\int_{T_3}^{T_4} \frac{Cp_o dt_o}{ti - to} = \frac{1}{\mu}\int_{T_1}^{T_2} \frac{Cp_i dt_i}{ti - to} \qquad (1)$$

$$\text{and } H = \int_{T_2}^{T_1} Cp_i dt_i = M_o \int_{T_3}^{T_4} Cp_o dt_i \qquad (2)$$

If for any gas Cp is known as a function of T and P, these equations can be solved by usual methods. For a first approximation the value of Cp at the geometrical mean temperature may be assumed. Treating Cp as constant, and integrating, the equation becomes

$$1 = \frac{M_o Cp_o 2.3}{\mu\left(\frac{M_o Cp_o}{Cp_i} - 1\right)}\left[\log(T_1 - T_4) - \log\left(\left(\frac{M_o Cp_o}{Cp_i}\right)(T_3 - T_4) + T_1 - T_3\right)\right] \qquad (3)$$

For the present case $\mu = 0.26$, Cp_o for air at one atmosphere and 160° K. (the mean temperature of the outgoing gas) equals 7.1; fpr air at 200 atm. (the most convenient pressure) and 240° K. (the mean temperature of the incoming gas) $Cp_i = 8.5$.[3] Assuming 60 per cent theoretical yield of liquid air, *i. e.*, liquid air efficiency of 7 per cent, $M = 93$ and $T_1 - T_4 = 50 \times 0.40 = 20°$ C. Using these values, $1 = 180$ m. (550 ft.). If 80 per cent theoretical yield is assumed, $1 = 250$ m. (770 ft.).

These figures accord with our experience with interchangers of the best design. Ordinarily the interchange from the low pressure return air to the tubes is by no means as efficient as that assumed here, and it is therefore not safe, unless special precautions are taken, to reduce the length of an interchanger of 7 per cent capacity to less than, say, 250 meters.

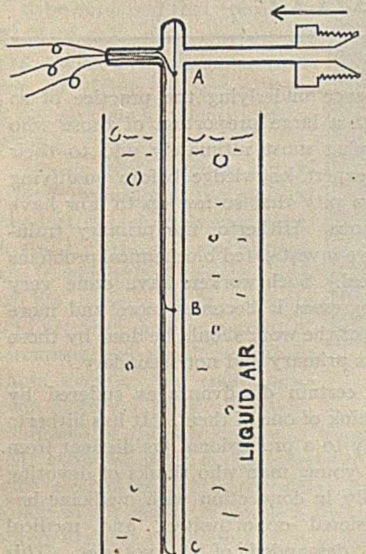

FIG. 1

It was not convenient to repeat the experiments above for different sizes of tubes, since the results for larger tubing would have no practical value to us (larger size tubing being unduly difficult to coil), and since it is doubtful that our type of apparatus would give results of much value for smaller sizes of tubing. It is thought, however, that for a given flow in free feet per minute the rate of interchange would be independent of the diameter, at least for sizes of tubing not too greatly different from one-eighth in. i. d. This approximation is based on the assumption that for constant mass velocity the rate of interchange is proportional to circumference, inversely proportional to diameter, and directly proportional to the linear velocity of gas flowing down the tube.

The problem of heat interchange between the low pressure cold gas and the copper tubing carrying the high pressure gas is not so well adapted to simple experimental investigation as the problem of heat interchange between the copper tubing and the compressed gas. In the last case the flow of gas is approximately of stream type. In the first case we have conditions which vary from nearly stream flow in the Linde type interchanger to extremely turbulent flow in the Hampton type. It is obvious that if the flow is turbulent enough so that the temperature at every point in any cross section normal to the axis of flow is the same, no matter what is the shape or length of the coil of the interchanger, provided its heat conductivity longitudinally is negligible, the same length of tubing will give the same efficiency. This makes the problem of effective interchange of heat from tube to outflowing gas entirely a problem of care in construction, particularly care in preventing the formation of stream channels causing local differences of temperature in a given cross section, and in so winding the coils that the outflowing air always has a resultant of velocity opposite to the velocity of the compressed gas.

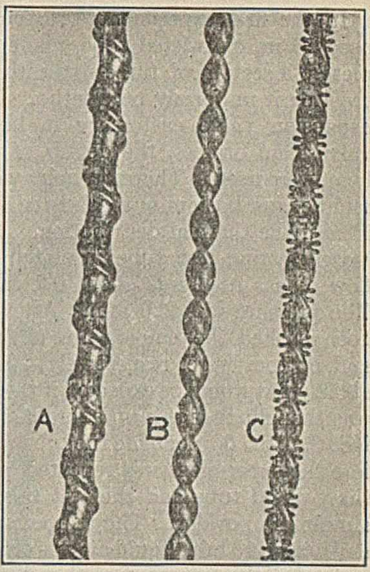

FIG. 2

The necessity for effective heat insulation of the whole interchanger is obvious, but means of providing it are familiar and need not be discussed.

THE NELSON INTERCHANGER

The chief objections to the type of interchanger described above are the length of copper tubing required, making the entire apparatus bulky, and increasing the difficulty of heat insulation, and, more important, the skill and time required to wind the flat coils. Such interchangers are therefore necessarily expensive. To obviate these difficulties Mr. George Nelson suggested on June 11, 1919, the use of short, twisted, flattened tubes in place of long ordinary tubes of the regular interchanger. The advantage of the flat tube over the round is that while the surface area of the tube is constant, the mean distance of heat flow is very much decreased, so that the efficiency of an interchanger, which for conditions of constant flow in grams per minute is proportional to area and roughly inversely proportional to the distance between walls, is greatly in excess for a flat tube than for a round tube of same area. The reason for twisting the tubes, as shown in A or B, Fig. 2, is to allow them to stand the high pressure without bulging.

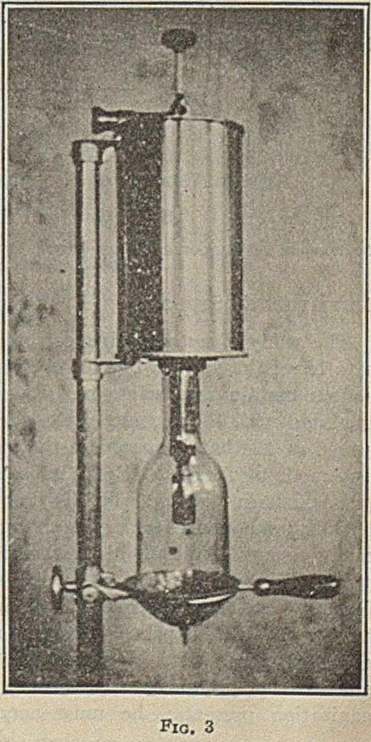

FIG. 3

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[3] Holborn and Jakob, *Z. Ver. deut. Ing.*, **58** (1914), 1429.

In the first experiments (November 8, 1919) there were used 15 in. of twisted tube, made by flattening down completely a section of three-sixteenth in. o. d. copper tube and twisting it uniformly on a lathe. In place of the elaborate expansion valve customary in liquefiers, various sorts of valves and orifices, the details of which are not important here, were used. Thermocouples were soldered on at the top, middle, and bottom of the twisted tube, in order to gain some idea of the thermal distribution. This tube was placed in a loosely fitting test tube insulated with cotton wool. The flow of gas used was about 0.2 cu. m. (6 cu. ft.) per min. The pressure was 220 atm. After thermal equilibrium had been reached, the temperatures of the tube at the top, middle, and bottom were, respectively, +20°, −5°, and −30° C., about what would be expected if there were no interchange. It was thought that this unfavorable result might be due to the fact that the flow outside the tube was not turbulent. Therefore the experiment was repeated, packing the space between the twisted tube and the test tube with coarse copper and aluminium powder. The temperature dropped very rapidly, and within 15 min. liquid air was observed in the bottom of the test tube, the temperature then being at the bottom −180°, at the middle −80°, and at the top +20° C. However, as the temperature of the outgoing gas was −10°, the efficiency of this interchanger was only 40 per cent of theory. In other experiments the aluminium powder was replaced by winding a spring of copper wire, as shown in Fig. 2-C. The efficiency for a 46-cm. (18-in.) interchanger at 0.2 cu. m. (6 cu. ft.) per hr. was 60 per cent. Several twisted tubes in parallel were also tried, and finally Mr. Nelson constructed a complete liquid air machine (Fig. 3), using 2 m. (6 ft.) of twisted tube in the interchanger. This machine had a capacity of 3.5 l. per hr. liquid air, using an intake pressure of 250, an intake temperature of 0°, and a free flow of air of 0.72 cu. m. (24 cu. ft.) per min., or an efficiency of about 70 per cent.

Such liquefiers would seem to have a great use for laboratory purposes. Their cost is but a fraction of the usual liquefier, their size is small (the height of the can in Fig. 3 is 12 in.), and as they use only 2 m. (6 ft.) of copper tubing for the interchanger, the time necessary to run the machine before it begins to form liquid air is much reduced, *i. e.*, 4 min. as compared with 30 min. or so for apparatus of the old type.

Interchangers using the twisted tube were also employed in a successful small-scale liquid hydrogen machine. The first designs of this machine (by Rodebush and Latimer and by the author) have, however, been superseded by a very ingenious design of Dr. Latimer's, which uses also the same twisted tube interchanger, and which will shortly be described by him.

CHANDLER MEDAL AWARD[1]

Introductory Remarks

By George B. Pegram

COLUMBIA UNIVERSITY, NEW YORK, N. Y.

It is our pleasure to be assembled this evening to hear as the Chandler Lecturer for the present year a gentleman who is widely known among chemists as a pioneer in the very remarkable developments of our knowledge that have been brought about through the study of food accessories such as vitamines.

I have the honor of introducing Professor Frederick Gowland Hopkins, of Cambridge University, England.

Medal Address

Newer Aspects of the Nutrition Problem

By F. Gowland Hopkins

PROFESSOR OF BIOLOGICAL CHEMISTRY, UNIVERSITY OF CAMBRIDGE, CAMBRIDGE, ENGLAND

NUTRITIONAL STUDIES AS A BRANCH OF APPLIED CHEMISTRY

The study of nutrition is most productive when it is followed as a branch of applied organic chemistry. As such it doubtless suffers certain disadvantages. It calls for workers fully acquainted with the technic of the chemical laboratory and possessed of all that is special in the chemist's mental equipment and mode of thought. Yet it calls for the application of these possessions in a region which is perhaps more remote from the chemist's experiences during his training than are any other of the many regions in which his science is applied. The successful pursuit of biochemistry, of which science nutritional studies form a part, calls for a second discipline. The young chemist having received his primary training must be content to become next something of a biologist; he must know enough about animals and plants to appraise the problems which their organization presents; he must acquire a biological outlook.

Chemistry is a basal science underlying the practice of so many human activities that a large proportion of those who start with a chemical training must ultimately add to their equipment other kinds of expert knowledge before qualifying for their life's work. It is a pity that so few up to now have chosen biological qualifications. Hitherto, the primary training of most of those who have investigated biochemical problems has been biological or medical. Such workers have done very well, but as knowledge progresses it becomes more and more necessary that at least some of the work should be done by those whose chemical knowledge is primary and not secondary.

But I have referred to certain disadvantages suffered by biochemistry and you will think of one of them. It has hitherto been difficult to point clearly to a professional (as distinct from an academic) career for the young man who thinks of devoting himself to the subject. Only in connection with medicine has it hitherto offered professional opportunities, and medical qualification is often first demanded of its votaries. This state of affairs is rapidly altering. Medical practice can and will in the future be helped by workers whose training has comprised something less than a complete medical course. Biochemical knowledge, moreover, is being sought in many unexpected quarters. The scientific representatives of a firm that manufactures explosives on a great scale asked me some time ago to supply them with a biochemist. At first it seemed difficult to know why; but the explanation was simple enough. There is, or was, some anxiety about the supply of glycerol. Fats which used to be hydrolyzed are now being used intact in all sorts of fresh ways, and there is less glycerol as a by-product. Hence a desire to develop the methods by which it is produced by microörganisms, and the biochemist gets an opportunity. This is but one illustration. I can say with certainty that, in Great Britain at any rate, there is a demand for professional biochemists which is greatly in excess of the present supply. This I find satisfactory, for if a profession opens up we shall find it easier to obtain workers who during one period at least of their career will help advance the science itself.

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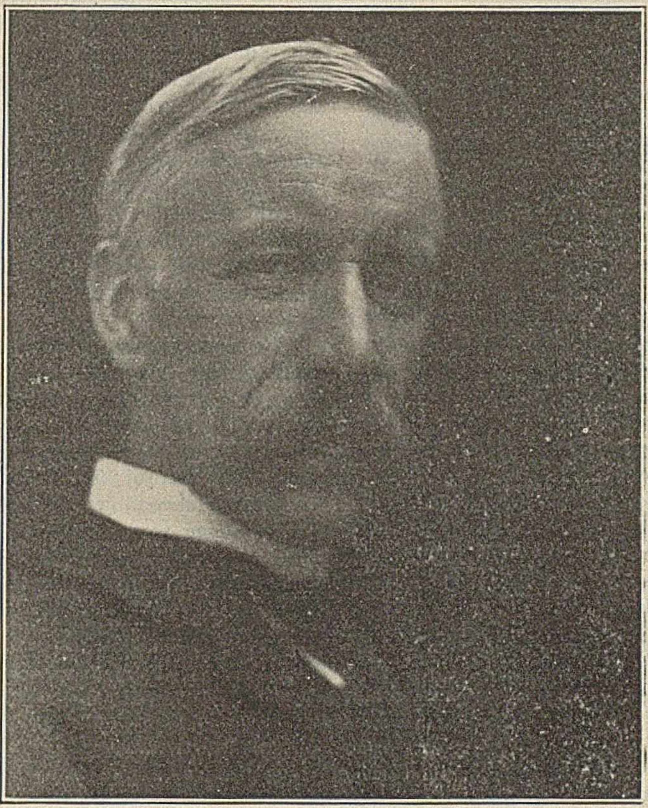
[1] Presented at Columbia University, New York City, April 18, 1921.

Need for Organic Chemists in Biology

I find it difficult, when addressing an audience composed largely of chemists, to avoid a propagandist attitude: because it is so very desirable that a proportion of our young chemists, greater than heretofore, should devote themselves to biological problems. I will confess that I am at the moment thinking in particular of organic chemistry. For it seems to me that on the whole the tendency has been for those who have especially qualified as physical chemists to devote themselves to biology rather than their colleagues who are more particularly accustomed to think in terms of molecular structure. Now no student of the plant or the animal can do otherwise than offer a hearty welcome to the physical chemist. He is now providing knowledge for which a whole generation of biological workers has been waiting. But if it be supposed that the application of the methods of physical chemistry, elegant and precise as they are, or the physical chemist's particular way of looking at things, is going to take us more directly and quickly into the secret habitation of life than other forms of chemical study; in particular if it be supposed that considerations of molecular structure are not essential to an understanding of living processes—then, I am sure, such suppositions are wrong.

In the main, though not of course exclusively, the physical chemist in biology is engaged in a study of the colloidal apparatus in which the dynamic events of life occur and in carefully and precisely defining a group of circumstances which conditions those events. We could, however, picture a physical system, composed of colloids similar to those which exist in the living cell, endowed with a characteristic structure, and in contact with electrolytes at a particular hydrogen-ion concentration, which would closely resemble a living unit when viewed from a purely statical standpoint; but unless what is ordinarily called metabolism occurs in such a system it is dead. Now metabolism consists in the continuous process of a set of organic chemical reactions in dynamic adjustment. Until our knowledge of these reactions and of their mutual relations is complete, our knowledge of living tissues will remain incomplete. This knowledge cannot come without continued thought and experiment on the lines of what we are accustomed to call organic chemistry. This applies to biochemistry as a whole, and not least to that branch of it which comprises the study of nutrition.

There is of course one method of estimating the nutritional needs of the body which avoids consideration of chemical details. They may be dealt with from the standpoint of energetics. Indeed, as the last century closed, the facts of nutrition were coming to be viewed more and more exclusively from this standpoint. The criterion of an efficient dietary was apparently destined to be its caloric value, and, with one qualification, which seemed then to be lessening in significance, its caloric value alone. The chemical standpoint, in so far as it envisaged details, seemed to be losing its practical importance.


Professor Frederick Gowland Hopkins

Successes and Limitations of Calorimetry

Those years saw a remarkable development in the technic of human calorimetry. The accuracy with which the energy exchanges in the body came to be measured gave rise in the minds of all students of nutrition to a sense of real accomplishment and to a feeling that, in addition to certain theoretical conclusions of great interest, calorimetry was making available, perhaps for the first time, information of a really quantitative kind to serve in practical guidance. The vague standards based upon statistical studies of the habits of the communities could at last, it was felt, be checked, and if need be corrected, by data which were in the truest sense scientific. What, in terms of energy, are the basal requirements of the body? What the caloric equivalent of various forms of mechanical work? What the efficiency of the human body as a machine? What the relative value of foodstuffs as sources of muscular energy? All these and kindred questions were being answered or the methods for their future solution made clear as the last century closed. They are, indeed, still being investigated, and with increasing accuracy, chiefly in the country where they were first seriously dealt with. For American workers, Graham Lusk, Benedict, Dubois and others are continuing the work of Atwater and Rosa, and are obtaining quantitative data which can be so controlled as to carry their own inherent proof of striking and even startling accuracy. The investigations are extending into the domain of pathological metabolism, and there I am convinced will have important bearings. Calorimetry as applied to human beings is an American science, and this country should feel the utmost pride in what it has accomplished. It is, in fact, impossible to overestimate the theoretical and practical importance of the data of human calorimetry. My only contention is that they are, and must always remain, insufficient for complete knowledge. In a limited sense calorimetry applies the methods of thermodynamics to the study of the body and its results share the advantage of conclusions reached by these methods in other branches of science. They involve quantitative statements which will remain true however our view may change with regard to the mechanism underlying those manifestations of change which permit easy measurement. The thermodynamic method is however sometimes like a blind man's stick. It carries us safely along a path which we cannot see, but fails to show us how we may best reach our ultimate goal. When there is complexity of a kind which cannot be reduced to statistics, the method of thermodynamics is apt to fail us. The human body obeys the laws of thermodynamics when, for this or that good reason, it is surely perishing!

Without, therefore, underestimating for one moment the value of thermal studies as applied to nutrition, I think it must be admitted that they in themselves can never constitute a sufficient guide for the progress of knowledge.

Importance of Structural Chemistry

Anyone, at any rate, who will trouble himself to appraise the nature of the progress which the detailed studies of the last twenty years have contributed to our views concerning animal and human nutrition will not doubt what I have said earlier as to the importance of thinking in terms of organic chemistry. Up to the end of the last century, thought about the chemistry of living beings scarcely employed considerations of molecular structure, or employed them, at any rate, in a very limited sense. Now, as the result of twenty years' progress, all concerned are doing their best to think in terms of structural chemistry; with the result that vague views about metabolism are giving place to clearer conceptions from which must follow a better understanding of the nutritive needs of the body.

Perhaps only those, who, like myself, have had to talk to students about such matters for five-and-twenty years, can fully realize how much the clarification of thought has progressed.

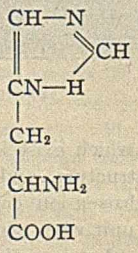
Modern Conceptions of Protein Metabolism

Especially, of course, is all this true in connection with the nutritive functions of protein. So long as we had to fit into our mental picture of what occurs in living tissues the hypothetical behavior of a complex molecule of which we knew little, and conceived of it as being oxidized, or otherwise utilized as a complex whole; oppressed therefore by the feeling that its very complexity would remove the processes involved from the domain of clear chemical presentation; so long as all this was the case we had to think in intellectual blinkers about the functions of protein. But simultaneously with the beginning of the present century, progressive work began which has changed the outlook. We have come to know that the complex molecule is built up of some twenty structural units, each a chemical species, but all belonging to the same chemical genus. We know the structure of each of these amino acids and realize that among them unity of type is combined with great diversity in structural detail, the unity and diversity being equally significant for the student of nutrition. We know, moreover, that the process by which we liberate these constituents from the protein complex in the laboratory—the process of hydrolysis—is identical with that which occurs in digestion. We know finally that in the alimentary canal this process is very completely carried out before adsorption of material occurs; so that the immediate phenomena of nutrition begin not with a supply of protein as such, but with a supply of amino acids. When we eat protein we consume, in effect, not one substance but twenty, and each of these may have quite special functions in nutrition. All-important to present and future progress is the fact that they are substances of known molecular structure. It is impossible, of course, for me to deal historically with this advance in knowledge. I have been instructed to narrate personal experiences, and though it may be unfair to others I will confine myself to illustrations drawn from such experiences.

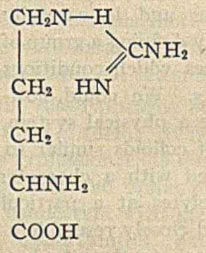
I can claim that some eighteen years ago my imagination (doubtless like that of many others) was greatly stirred by the facts then becoming available. It seemed to me essential for the understanding of protein nutrition, and for the analysis of the factors concerned in the maintenance of nitrogenous equilibrium, that the relative nutritive importance and ultimately the precise fate of each individual amino acid should be determined separately. In 1906, in conjunction with Miss Edith Willcox (now Mrs. Stanley Gardiner), I published results of some experiments which illustrated the special nutritive importance of the indole nucleus contained in tryptophan, an amino acid first separated from protein a few years earlier by S. W. Cole and myself. Incidentally these experiments indicated that an amino acid may be used, not alone for the building up of tissue proteins, but also immediately and directly for more specific purposes. It is important when approaching studies of metabolism and nutrition to realize in advance that more than one path of change may lie before any particular unit in the food eaten. The results of the unambitious pioneer research just mentioned, in so far as it bore upon the importance of the indole nucleus, have since been confirmed by myself, and abundantly by others, on more conclusive lines. The fact recently demonstrated by Kendall, at Rochester, Minnesota, that the all-important active principle of the thyroid gland is an iodine derivative of indole has shown us one probable reason for the importance of a supply of tryptophan in the diet. This is only an illustrative instance of the special functions which may be subserved by individual parts of the protein molecule.

The circumstance that an animal can be normally nourished when, instead of intact protein, it receives a complete mixture of amino acids has greatly assisted studies meant to determine the relative nutritive importance of the different molecular groups in the protein molecule. The original amino acid mixture obtained by digesting any normal protein may be fractionated, and this or that constituent may be withdrawn from the mixture before it is supplied to the animal. Ultimately, by so withdrawing a particular unit and observing the effects of its withdrawal, we may not only measure its importance but also obtain information as to any special functions it may subserve.

I have myself tried the effects of withdrawing certain amino acids besides trytophan. If for instance an animal be given as its sole nitrogenous nutriment, the amino acid mixture deprived of hystidine and arginine, nutrition fails. It promptly becomes normal again when these two units are restored to the food. The first of these substances contains the iminazole ring, and the second gets its special stamp from the existence of the guanidine group in its molecule. Now it is remarkable that, though the absence of both these amino acids from the food supply is fatal, the absence of either alone is well borne by the animal, and experiment shows that one can take the place of the other in metabolism. Considerations of molecular structure make it easy to understand why this may well be the case and the body in this case clearly takes advantage of certain possibilities which are obvious to the chemist.



Histidine



Arginine

Similarly a deficiency of tyrosine may be compensated by a larger supply of the closely related phenylalanine; and there are probably similar cases. Such facts help to throw light upon the equipment of the tissues as laboratories: they must also be borne in mind when we are estimating the nutritive value of any particular form of protein.

Considerations of molecular structure made it probable that arginine and histidine might well be the precursors of the purine bases which are characteristic constituents of the nucleic acids found in all tissue cells. Led by the structional suggestions, Ackroyd and the writer some years ago tested this matter by feeding experiments, and obtained evidence to show that the suggestions were fulfilled. Arginine and histidine seem to be the special raw material for the synthesis of purines in the body.

On the other hand, there are constituent groups in protein which are certainly of much less nutritive importance than those discussed. Especially would this seem to be true of those amino acids which have a relatively simple constitution—the aliphatic substances, for instance, with a normal chain of carbon atoms. I have myself found, for instance, that if glutamic acid, aspartic acids, and hydroxyglutamic acid recently identified by Dakin be all removed from the amino-acid mixture, animals can maintain themselves quite well upon the residual amino acids. The contrast between the fatal effects of removing tryptophan, which constitutes some two per cent only of a normal protein, with the almost negligible effects of removing the amino acids just mentioned, which may represent perhaps thirty per cent of the protein, is sufficiently striking. There is little doubt that the difference is due, not to the fact that the tissues can dispense with any protein constituent necessary to their normal chemical make-up, but rather to the range of synthetic possibilities within the body. When deprived of a supply of certain amino acids, it can synthesize them for itself; the synthesis of others is not within its powers.

Very interesting is the knowledge, incomplete as yet, which we possess concerning the chemical changes which individual amino acids actually undergo in the body. The fate of each is individual because its molecular structure is individual. I could indeed better illustrate the truth of my opening contention concerning the importance of structural considerations in biological chemistry if we were considering intermediary metabolism rather than nutrition in the more limited sense. The few facts I have put before you will, however, illustrate it sufficiently.

The outcome of the recent advances in knowledge concerning the chemistry and metabolism of protein when viewed from the standpoint of practical dietetics is in the main this: We cannot any longer be content to speak of the body's demands for "protein" in unqualified terms. The balance of individual amino acids, the relative amount of this or that acid, may be, we know, very different in different proteins, and this difference may markedly affect the relative nutritive value. For the future we must in this connection think of quality as well as quantity.

What we know about the functions and fate of the other basal foodstuffs, the carbohydrates and fats, illustrates equally well the importance of structural considerations in biochemistry. But with these I cannot deal.

VITAMINES

I will rather pass at once to a newer aspect of our knowledge concerning the nutritional demands of the body, and remind you of facts which more than any others illustrate the necessity, when we are seeking to define an efficient dietary, of considering the nature of the material, as well as the energy supply. I mean, of course, the facts concerning the accessory food substances, as I once ventured to name them, or (to use the more familiar name conferred on them by Casimir Funk) vitamines. As you are doubtless aware, the chemical nature of these substances is as yet unknown. Their properties cannot therefore at the moment be used to illustrate further my theme concerning the importance of molecular structure in nutritional phenomena, though I doubt not that once they are isolated the biochemist will have an interesting task in relating their action to their structure. But there are other reasons why I should speak to you concerning them. I have received credit—perhaps too much credit—as pioneer in their discovery. Ten years ago the time was ripe for the emergence of certain facts. They were in the air; and when, in the progress of science, this is the case, questions of priority lose their importance. I will however relate my own experiences.

During 1906 I was engaged in feeding animals upon mixtures of different amino acids, and of necessity had to employ synthetic foods. Starch, fats, and salts were added to the amino acids to complete the dietary. The first circumstance which set me thinking was the observation that animals prospered better when they were fed upon amino acids obtained by fully digesting *tissues* than when the source of amino acids was a separated and purified protein digested in the same way. Lean beef, for instance, gave better results than casein. At first one was inclined to attribute the differences either to the fact that the amino acid balance was better in the former, or to the presence in the tissues of familiar substances, such as lecithin, but I could not get confirmatory evidence for this supposition. The first strong suggestion that something special had to be looked for came not from my main experiments, but from their controls. In the latter the animals were, for the sake of comparison, given intact casein instead of the amino-acid mixture, the rest of the diet being the same. Now, for a long time these control animals grew very well and kept in good health. If growth was slow I put it down to the fact that a synthetic diet might in any case be somewhat unsuitable for an animal. From a certain date onward, however, all the animals on casein began to do badly. They showed no growth at all and their health failed. After some time the reason occurred to me. For the preparation of amino acids I used pure casein, but for the food of the control animals a commercial article was used. On the date referred to I had begun to feed these animals on a casein preparation different from that which for a long time previous had served as the protein supply of my laboratory. The new preparation had just come on the market and in appearance seemed a much better article; but there was soon no doubt that its use was the cause of the failures. When put upon the old casein supply all the animals grew again!

At first I was naturally inclined to think that the new protein had suffered some sort of denaturation during the course of its manufacture, but that supposition suffered easy disproof. When, earlier, I began experiments with synthetic diets I added small quantities of meat extracts and extracts from yeast to give flavor to the tasteless food. I was thinking then of the animal's "appetite," as was natural, and as most people do when they start such experiments. I quickly found, however, that rats ate synthetic diets very well without such additions, and at the time of the experience with casein just mentioned I had ceased to use them. Nevertheless my memory at this time, if not my notebooks, carried suggestions concerning the influence of the extracts which led me to try adding them to diets containing the new casein, with striking results. Growth was now as good, and sometimes better than with the old casein, and growth occurred, too, in animals which were eating no more, or even less, than other individuals living on the pure casein diet without addition and showing continuous loss of weight as a result. The extracts powerfully affected nutrition. I now extracted the old casein with various solvents and finally got a product which behaved exactly like the new. When the substances dissolved out were returned to the food, growth occurred as before.[2] I wasted next a good deal of time by trying the effect of various familiar substances of determined nature known to be in yeast; always with unsatisfactory results.

By this time I had come to the conclusion that there must be something in normal foods which was not represented in a synthetic diet made up of pure protein, pure carbohydrate, fats, and salts; and something the nature of which was unknown. Yet at first it seemed so unlikely! So much careful scientific work upon nutrition had been carried on for half a century and more—how could fundamentals have been missed? But, after a time, one said to oneself, "Why not?" The results of all the classical experiments had been *expressed* in terms of the known fundamental foodstuffs: but these had never been administered *pure!* If, moreover, the unknown, although clearly of great importance, must be present in very small amounts—again, why not? Almost infinitesimal amounts of material may have a profound effect upon the body, as pharmacology and the facts concerning immunity assure us. Why not then in

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[2] It is remarkable what a considerable proportion of the vitamines present in milk is adsorbed by precipitated casein. A failure to recognize this has often obscured the results of feeding trials.

nutritional phenomena? The animal depends ultimately upon the plant for the synthesis of materials which bulk largely in its food: there is no reason why it should not be adjusted so as to be in equal need of substances which the plant makes in small amount. Only if energy were the sole criterion of an animal's needs would this be impossible; but certainly it is not the sole criterion.

So my faith grew in the existence of a previously unrecognized type of nutrient.

At this period I spent much time in the endeavor to isolate from yeast extracts an active substance with definite chemical properties, but wholly without success.

The experimental period that I have been describing was, for me, in one particular, unfortunate. I experienced periods of continuous success in maintaining growing animals upon purified dietaries after the addition of very small quantities of fractionated yeast preparations, but they were interspersed with occasional failures which shook my confidence. Only when milk, in small amounts, formed the addendum did failure never follow. The explanation is now clear. The protein and carbohydrate used in my experiments were thoroughly purified and standardized, but for fat I used lard. But lard, as many experimentalists now know to their cost, is a variable fat. What I was adding or witholding in my early experiments was vitamine B alone. I taught myself nothing about vitamine A, which is associated with most animal fats. The amount of it in commercial lard varies greatly; and I have no doubt that when my animals did well the lard they consumed contained enough of it; while when they did ill the lard was deficient in this particular.

I was on safer ground in using milk, for though milk is not especially rich in vitamines it always contains both A and B. When, therefore, at last, I ventured on publication it was mainly my experiments with milk that I described in proof of the existence of accessory food factors.

A great step forward was made in 1913 when McCollum and Davis made it clear that there are at least two vitamines—those just mentioned—concerned in nutrition; for we have since learned how great is the nutritive importance of fat-soluble A, of which the existence was then demonstrated. It seems to me fair to say that a recognition of the importance of a factor associated with fats was implicit if not explicit in papers published at this time by Osborne and Mendel, and their experiments in proof of this appeared close on the heels of McCollum's now classic publication. Such fundamental matters could not indeed long escape the organized and intensive work which was being done at the American centers of activity.

I have given you a brief account of my own early experiences in this domain (never having told about them before) because I was assured that you would care to hear it. I fear you may have found it trivial, though the period it deals with contained some thrilling moments for me.

It would have been more useful, I imagine, if I had attempted to give you a critical appraisement of the present position of our knowledge of vitamines. To attempt one now would be unwise, for to be of use it would take much time. Advances have been real during the last year or two, but chiefly in matters of detail. Perhaps no considerable advance can now occur until a vitamine has been isolated in pure form and its constitution determined. I am sure that this will be no very distant accomplishment.

If indeed there be any in this audience who feel skeptical with regard to the whole question of vitamines or at any rate with regard to their practical importance (there are still some skeptics in my own country!), I feel that I am qualified to ask them to reconsider their attitude. Apart from the many hundreds of experiments I have made myself, I have seen the work which is being done upon the subject at some of the chief centers of activity. I can testify to the care and effort which is being put into the study at the Lister Institute and at University College, London. I have recently paid illuminating visits to the departments of Drs. Osborne and Mendel at Yale, and to that of Dr. E. V. McCollum at the Johns Hopkins University. In each and all of these centers one finds thorough organization and a properly critical atmosphere. The technic used in the study of vitamines has now been developed till, in its own special way, it is exact and reliable. All concerned have to talk and write under the disadvantage which arises from the fact that the actual nature of these substances remains unknown, but in spite of this a great amount of real knowledge of practical value is being accumulated.

Between the experiments on animals and actual human experience there are, as you know, links enough. The absence of one particular vitamine from the food is the whole and sufficient reason for the occurrence of human scurvy, the absence of another forms the main factor in the etiology of a second disease, beriberi, the absence of a third plays at least a large part in the induction of rickets. But if extreme deficiency in such factors results in actual disease, who shall say how much vague ill health may follow upon relative deficiency? That is the consideration which gives importance to this newest chapter in the science of nutrition.

While the newer knowledge which has grown up on the lines that I have briefly and incompletely indicated has undoubtedly important practical bearings, those engaged in the work should doubtless use caution in their relations with the public. We should keep a sense of proportion. It would be wrong, for instance, or so it seems to me (I have heard the contrary opinion expressed) so to exaggerate the importance of the fat-soluble vitamine as to teach that vegetable fats which do not contain it should disappear from the market. Fat, as such, is after all a valuable and necessary food of which it is none too easy to maintain a supply. We should rather show how such fats are to be supplemented properly whenever they form a considerable part of the public supply.

Again, although there can be no doubt that the fundamental phenomena of nutrition are the same in all mammals, there are specific differences which we should not forget in applying our laboratory results. Deficiencies are felt more immediately and directly by the small animals on which so many of our experiments are done than by larger species with slower metabolism. We may consequently tend to exaggerate the general importance of this or that factor. We should not, I fancy, make too much of the "biological value" of proteins in connection with human nutrition until more observations have been made upon human subjects. The most favorable balance of amino acids may be different in different species; though as a matter of fact the weight of evidence is against this possibility. At any rate, we must remember that physiological adjustments may be made during long periods of use and custom which could not occur during the relatively brief duration of an experiment. In connection with the part that food deficiencies may play in the causation of human diseases, we should bear in mind that a clinical condition is usually more complex than conditions observed in the laboratory as the result of varying a single factor.

Nevertheless, as I have already said, there exist many links of evidence to show that laboratory results are fully paralleled in human experience, and evidence of this sort tends to increase. There is at any rate no fear of exaggerating the importance of the newer outlook when the rearing of children is in question. If one had to sum up in a sentence what constitutes that newer outlook, I would say that it is a fuller recognition of the fact that quality is as important as quantity in all that concerns nutrition. But "quality" must be read in a new sense, a sense sufficiently defined by the facts I have been discussing.

I referred earlier to the literal fact that human calorimetry is an American science. It seems to me as I think of those who are engaged in the study of nutrition on the fresh and extended lines that, unless we who work elsewhere work very hard, the new science which is developing will come into the same category.

Presentation of Chandler Medal

By George B. Pegram
Columbia University, New York, N. Y.

There are certain names that stand for whole periods in the existence of institutions, epitomize epochs of development and accomplishment. No such name at Columbia stands for more than Chandler. Reaching from the foundation of the School of Mines in 1864 to the present and covering nearly half a century of labor and responsibility in active connection with the development and progress of scientific work at Columbia, his great personality has built itself into the structure of this University in so intimate a fashion that the keenest analysis could not separate it out. It was, therefore, a most appropriate action for a group of his friends to present to the Trustees of Columbia University a sum of money constituting the Charles Frederick Chandler Foundation, the income from which is to be used to provide each year a lecture by an eminent chemist and to provide a medal to be presented to the lecturer in public recognition of his achievements in science. The previous lecturers on this Foundation have been L. H. Baekeland, Sc.D., W. F. Hillebrand, Ph.D., and W. R. Whitney, Ph.D.

On the recommendation of a University committee, the Trustees of Columbia University have awarded the Chandler Medal for this year to Frederick Gowland Hopkins, F.R.C.P., F.R.S., F.I.C., F.C.S., Fellow of Trinity College, Honorary Fellow of Emanuel College, Cambridge, Member of the Medical Research Council, and of the Consultative Council to the Minister of Health, Professor of Biological Chemistry, Cambridge University.

Professor Hopkins, this medal is presented to you in public recognition of your pioneer and valuable researches in biochemistry, particularly in connection with food accessories, such as vitamines, and your public service on the Medical Research Council and the Consultative Council to the Minister of Health.

ADDRESSES AND CONTRIBUTED ARTICLES

Contribution to the Theory of the Water-Gas Process[1]

By S. Kohn
Rohm & Haas Co., Inc., 40 N. Front St., Philadelphia, Pennsylvania

The usual explanation of the interaction between steam and carbon is that at about 600° C. carbon dioxide and hydrogen are the chief products formed, according to the equation

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

and that, as the temperature rises, more and more carbon monoxide appears in the resulting gases. Finally, at about 1000° C. and above, carbon monoxide and hydrogen are practically the sole constituents of the gases, which may conceivably be formed according to the equation

$$C + H_2O = CO + H_2. \qquad (B)$$

At temperatures between 600° and 1000° C., both reactions may be considered as taking place simultaneously.

The standing of Equations A and B, as an explanation of the chemistry of the water-gas process, is that of a fairly useful hypothesis. We have no proof that the reactions actually proceed in the manner indicated. Furthermore, while these equations do explain satisfactorily some of the phenomena, they are not sufficient to explain all. Haber,[2] after introducing and discussing Equations A and B, adds: "Now one can consider that A and B are also connected by the equation

$$C + CO_2 \rightleftarrows 2CO,"$$

and he uses this third equation for further elucidating the peculiar relations between the volume concentrations of the resulting gases in the water-gas process. Rideal[3] thinks that the following combination of three equations represents the chemistry of the water-gas process:

$$\begin{aligned} C + H_2O &= CO + H_2 \\ CO + H_2O &\rightleftarrows CO_2 + H_2 \\ C + CO_2 &\rightleftarrows 2CO \end{aligned}$$

These instances will suffice to prove that our present conception of the chemistry of the process is open for discussion, and that each investigator is wont to call upon such a set of two or three equations as may seem to him necessary and sufficient to depict the reactions and explain the results obtained.

As will be shown below, ten sets of equations are theoretically possible. This number will be reduced to three by making a certain assumption, and it will also be demonstrated that the analysis of the resulting gases, in the cases under observation, not only supports the assumption made but also contains a definite clue as to which of the three sets of equations represents the actual procedure of the reactions.

Possible Reactions of Steam and Carbon

When steam reacts on carbon, carbon dioxide, carbon monoxide, and hydrogen are formed (we shall ignore here the formation of small amounts of methane and other hydrocarbons), and all possible interactions between the steam and carbon and the resulting three gases are represented by four reversible equations:

$$\begin{aligned} C + 2H_2O &= CO_2 + 2H_2 && (A) \\ C + H_2O &= CO + H_2 && (B) \\ CO_2 + H_2 &= CO + H_2O && (C) \\ CO_2 + C &= 2CO && (D) \end{aligned}$$

It may happen that reactions according to all four equations occur simultaneously (A, B, C, and D) or that under certain conditions only the four possible combinations of three will assert themselves, and finally we can think of the possibility of either one of five possible pairs of equations representing the actual procedure, that is, A and B, A and C, A and D, B and C, and B and D.

If we consider, however, that there are indications that carbon monoxide is not formed by the direct oxidation of carbon[4] but that carbon dioxide is formed primarily and the occurrence of carbon monoxide in the gases is to be ascribed to a secondary reduction of CO_2 to CO by means of hydrogen or carbon, the ten combinations enumerated above dwindle to three, namely, A and C, A and D, or A, C, and D. That is to say, the chemistry of the water-gas process most probably consists of two consecu-

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[1] Received August 3, 1921.

[2] "Thermodynamik technischer Gasreaktionen," 293.

[3] *J. Soc. Chem. Ind.*, **40** (1921), 13*t*.

[4] Haber, *Loc. cit.*, 238.

tive steps: first, carbon dioxide and hydrogen are formed from steam and carbon, and, second, the dioxide is reduced to monoxide either by hydrogen or by carbon or by both hydrogen and carbon simultaneously.

The main object of this paper is to answer the following questions:

> Do the differences in the manner of working of Schemes A and C, A and D, and A, C, and D make themselves felt in the composition of the resulting gases?
>
> If so, how can we use these differences to determine whether a gas of given composition has been the result of the first, second, or third combination?

Relations between Volumes of Gases

Before going into this matter, the relationship between the volumes of H_2, CO, and CO_2 will be shown by utilizing one of the pairs of equations which have been dropped as practically improbable but which remain, of course, theoretically correct and useful. The pair chiefly used in textbooks is A and B. It probably does not represent actual working conditions for several reasons, but its merit lies in its clearness and in the fact that the two reactions proceed parallel and not in series. However the water-gas process actually proceeds, it is theoretically correct to say that the resulting gases could have been formed according to these two reactions. Certain general characteristics of the process can be deduced from them more easily than from any other. One of these characteristics of which we shall make repeated use in the following calculations lies in the fact that the volume of hydrogen is always equal to the sum of the volume of carbon monoxide plus double the volume of carbon dioxide. If we call X, Y, and Z the respective concentrations by volume in the end gases of CO_2, CO, and H_2 we can say that

$$Z = Y + 2X. \qquad \text{(E)}$$

Equation E also indicates that, for a given value of any one of the three gases after removal of the excess of steam, only one set of values for the other two gases is possible. For instance, if X is given or determined, Y and Z can be calculated as follows:

$$Y = \frac{100-3X}{2} \text{ and } Z = \frac{100+X}{2} \qquad \text{(F)}$$

Equilibrium relations—Returning now to the problem of determining the direction which the reaction has taken by the analysis of the resulting gases, the first advance in attacking this problem has been made by recognizing the apparent impossibility of utilizing the law of reaction equilibrium for this purpose. The equilibrium of the resulting gases with each other and with the carbon, that is, the equilibrium represented by the two following equations, is in the first instance only exceptionally obtainable; in the second, as a rule, not even approximately reached.

$$\frac{U\ Y}{X\ Z} = K$$

$$\frac{Y^2}{X} = K_1$$

X, Y, and Z are again the volume concentrations of CO_2, CO, and H_2, and U is the volume concentration of the unconsumed steam.

The explanation of the failure of these equilibria to establish themselves under ordinary working conditions lies in the fact, proved by experiment, that even if the observations are started with definite amounts of, say, CO_2 and H_2, which are not changed from the outside, it takes a longer or shorter time, depending on conditions, for the equilibrium to assert itself. If then, as is the case in the water-gas process, one of the gases is continually introduced in new quantities, we can hardly be surprised that the equilibrium can never be reached.

Evidently if the two reactions under observation are not working in parallel, and if the second is dependent upon the reaction products of the first, we must look for other means to detect the law of interdependence. Considering the fact that the first step produces CO_2 which the second uses for the production of CO, it is to the point to endeavor to find the relationship between the rate of production of CO_2 by the first step and the rate of destruction of CO_2 by the second step; or, what amounts to the same thing, between the rate of decomposition of water by the first step and the rate of decomposition of CO_2 by the second step. Further, if the combination A and C works differently from A and D, these differences will show themselves in the end gases and permit answering the problem.

Equations A and D—Let us consider first pair A and D, as the simpler one, taking as a basis one volume of steam before it is decomposed. Assuming that under given conditions of temperature, etc., fraction p of the steam used has been actually decomposed by interaction with carbon according to A, and that fraction q of the formed CO_2 has been reduced to CO according to D, the volumes of the four resulting gases will be proportionate to the following values:

Undecomposed steam $= 1-p$
Hydrogen $= p$
Carbon monoxide $= pq$
Carbon dioxide $= \dfrac{p(1-q)}{2}$

While it is evident enough that p is equal to $\frac{Z}{U+Z}$ we cannot call q equal to $\frac{Y}{X+Y}$, because, as Equation D shows, the volume of the CO_2 doubles by the change to CO. As the rate of reaction will depend on the volume concentration of the CO_2 during the reaction and not after the reaction, we must make

$$q = \frac{\frac{Y}{2}}{X + \frac{Y}{2}} \quad \text{or} = \frac{Y}{2X+Y}$$

Equations A and C—Conditions are slightly more complicated with pair A and C. This combination differs in two respects from A and D:

(1) One volume of CO_2 produces only one volume of CO and we can therefore put $q = \frac{Y}{X+Y}$.

(2) Equation C reproduces one volume of steam for each volume of CO_2 used up.

In order to finish our observations again with p volumes of water decomposed and $1-p$ undecomposed, we must start our observations with a large volume of steam initially decomposed by Reaction A, which we shall call P. P can be determined by the following equations:

$$1 - P + \frac{P.q}{2} = 1 - p \qquad \text{(G)}$$

$$P = \frac{2p}{2-q}$$

If then $\frac{2p}{2-q} = P$ water is decomposed according to Equation A, $\frac{P\,q}{2} = \frac{p.q}{2-q}$ water is reproduced according to Equation C. This is the same as if only p water had been decomposed and $1-p$ had been left undecomposed, and the four gases after the reaction are again represented in the following proportions:

Undecomposed steam $= 1-p$
Hydrogen $= p$
Carbon monoxide $= \dfrac{pq}{2-q}$
Carbon dioxide $= \dfrac{p\,(1-q)}{2-q}$

If the second step depends on the formation of CO_2 by the first step (and on the other hand, the rate of formation of the CO_2 will be dependent on the rate at which it is removed by the

OBSERVATION	(1) T ° C.	(2) H_2 (Z)	(3) CO Y	(4) CO_2 X	(5) H_2O U	(6) Flow Liters Sec.	(7) K Observed	(8) K Calculated Luggin	(9) Y + 2X = Z	(10) p	(11) q_d	(12) q_c	(13) $\frac{Y}{X}$	(14) $\frac{Z}{U}$
I	674	8.41	0.63	3.84	87.12	0.9	1.70	0.49	8.31	8.8	7.53	14.1	0.164	0.0965
II	758	22.28	2.67	9.23	65.82	1.8	0.85	0.70	21.13	25.3	12.6	22.4	0.289	0.339
III	838	28.68	6.08	11.29	54.09	3.65	1.01	0.98	28.62	34.7	21.1	34.8	0.536	0.531
IV	838	32.77	7.96	12.11	47.15	3.28	0.94	0.98	32.18	41.0	24.7	39.8	0.659	0.695
V	861	36.48	11.01	13.33	39.18	5.3	0.89	1.07	37.67	48.2	29.3	45.2	0.835	0.930
VI	954	44.43	32.70	5.66	17.21	6.3	2.25	1.41	44.02	70.2	74.2	85.2	5.77	2.58
VII	1010	47.30	48.20	1.45	3.02	6.15	2.12	1.65	51.01	94.0	94.0	97.0	33.2	15.7
VIII	1060	48.84	46.31	1.25	3.68	9.8	2.78	1.88	48.81	93.0	94.8	97.4	37.0	13.3
IX	1125	50.73	48.34	0.60	0.303	11.3	0.48	2.11	49.54	99.4	99.9	100	80.5	167.0

second step), the equilibrium between these two reactions working in series will be established if q equals p. For, assuming that at the very beginning of the reaction q does not equal p, the higher rate of decomposition of one of the two gases will enhance the rate of decomposition of the other gas by increasing its volume concentration and at the same time reduce its own rate of decomposition by decreasing its own volume concentration. Equilibrium will be quickly established, and the rate of decomposition of steam will become equal to the rate of decomposition of CO_2. The shortest adequate mathematical expression for this fact is

$$q = p.$$

In this case we have the desired criterion as to whether the reaction has proceeded after A and C or A and D in the following simple relations:

$$\frac{Y}{X} = \frac{2p}{1-p} = \frac{2q}{1-q} \text{ for the combination AD}$$

$$\frac{Y}{X} = \frac{p}{1-p} = \frac{q}{1-q} \text{ for the combination AC}$$

$$\text{or } \frac{Y}{X} = 2\frac{Z}{U} \qquad \text{(H)}$$

$$\frac{Y}{X} = \frac{Z}{U} \qquad \text{(I)}$$

U stands here for the volume percentage of undecomposed steam in the resulting gases.

APPLICATION TO BUNTE-HARRIES OBSERVATIONS

The application of these deductions has been tried out on the series of nine observations made by Bunte–Harries. To the table of Harries, which after the recalculations and additions by Luggin[5] amounts to the first eight columns of the accompanying table, we add a Column 9 marked Y + 2X. This indicates the degree of analytical accuracy of the gas determinations. In most cases the values given under Y + 2X check very well with the values for hydrogen. Column 10 contains the quotient of decomposition of the steam in per cent, as given by the original Harries table. Columns 11 and 12 give the q_c and q_d, respectively, meaning the quotient of decomposition of CO_2 by Equations C and D, respectively.

If in this table we consider the fact that the last two or three observations are of minor accuracy on account of the very small value for CO_2 and steam, and the fact that p and q are very near 100 per cent, we are surprised to find that p is always very nearly equal to q_c or q_d and never shows values between the two decomposition factors of CO_2. This can mean only that in the cases observed the equilibrium between the first and second reactions has always been very nearly established, and that if for any reason the Reaction C was favored against the Reaction D, the equilibrium by this reaction was so quickly reached that the D reaction was left far behind, or vice versa.

Columns 13 and 14 show $\frac{Y}{X}$ and $\frac{Z}{U}$, respectively (see Equations H and I). It is surprising to find the indications in Observations II, III, IV, and V for the pair AC, and in I, VI, and probably VII for the pair AD (Observation I should probably not be given too much weight as pointing toward AD, because of the low CO figure). Differences of working conditions may have been responsible (such as different quality of carbon or different size of the charcoal pieces), or it also may be that there is always (even under strictly comparable working conditions) a sudden turn in favor of AD around 900° C. For Reaction C is endothermic and therefore favored by increased temperature, but the enhancing influence of a rise in temperature diminishes, the higher the temperature climbs, and this may be responsible for the sudden turn around 900° C. The table also explains why "K observed" does not check with "K calculated." From Equations H and I, we can calculate that "K observed" will equal 1 or 2, depending upon the course of the reaction. Excepting in Observations II and VII, where a comparison of Columns 2 and 9 shows that the analytical errors were considerable, the fact that Equations H and I are not more perfectly satisfied can be taken as an indication, where the values for $\frac{Y}{X}$ are too high, of a direct formation of some CO, without the intervention of CO_2, in accordance with the proposed existence of a primary complex C_mO_n. As can be seen, however, the part played by this complex would amount to only a small fraction of the total sum of reactions.

Similar calculations as outlined for AC and AD lead to the following equation for BC and BD:

$$\frac{Y}{X} = \frac{U}{Z} \quad \text{for BC}$$

$$\frac{Y}{X} = 2\frac{U}{Z} \quad \text{for BD}$$

This is, in view of the above table, a direct proof that the Reaction B did not occur. As to AB, this pair of equations shows only a different way of writing AD. The resulting gases would only then indicate a possibility of the reactions proceeding according to AB if no such relations as H and I call for were observed. Since A and B are working independently of each other, only the more general interrelations given by Equation G would have to be satisfied.

APPLICATION TO SELECTIVE ACTION OF CATALYSTS

It is interesting to note what light these observations throw on the assumed selective influence of certain catalysts. As can be seen, a catalyst which increases the velocity of C or D will most probably also automatically increase A. But there may be some catalyst which will increase C without being effective on D. Such an instance is cited by Rideal[6] as a suggestion of Haber, but the figures of Gwosdyz cited later are not in keeping with such an assumption. Rideal gives only the CO_2 percentages of two experiments by Gwosdyz[7] and says: "A coke containing 8.5 per cent ash yielded 29 per cent CO_2, while pure carbon (lampblack, 0.1 per cent ash) yielded only 8.6 per cent CO_2 at 560° C." If this means percentages in the dry gases, we can figure out with the aid of Equation F that in the case of coke the gas analyzed 29 per cent CO_2, 6.5 per cent CO, and 64.5 per cent H_2, and in the case of lampblack 8.6 per cent CO_2, 37.1 per

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[5] Haber, *Loc. cit.*, 121.

[6] *J. Soc. Chem. Ind.*, **40** (1921), 141.

[7] *Z. angew. Chem.*, **1918**, 137.

cent CO, and 54.3 per cent H_2; from this, one would conclude that the greatly enlarged surface of the lampblack greatly expedited Reaction D, as otherwise the high percentage of CO would be unexplainable at this temperature. On the other hand, the composition of the gas in the other instance is about what would normally be expected at 560° C., and explanation on a basis of the ash content of the coke seems superfluous.

If the amount of undecomposed water had been given, we could draw more definite conclusions about just what happened in those two cases, although a high carbon monoxide content at low temperature is always pointing toward combination AD.

SUMMARY

1—The ten possible and three probable combinations of reactions which can be called upon to explain the water-gas process are discussed.

2—Demonstration is made of a possibility of drawing conclusions from the composition of the resulting gases to the actual procedure of the reactions.

3—The applicability of the principles outlined is tested on a series of nine observations published by Bunte and Harries.

4—The application of these considerations to catalytic observations is discussed.

The Latent Heat of Vaporization of Coal-Tar Oils[1]

By John Morris Weiss

THE BARRETT CO., 40 RECTOR ST., NEW YORK, N. Y.

Some time ago W. J. Huff[2] published the results of work carried on in our laboratories on the vapor densities of coal-tar fractions. It has since proved desirable to have some knowledge of the latent heats of vaporization of these fractions, and we have found that the latent heats can be calculated from the vapor densities with a fair degree of accuracy.

According to the principles of physical chemistry, the quotient obtained by dividing the molecular heat of vaporization by the boiling point (expressed as absolute temperature) is an approximate constant for normal substances. This is known as "Trouton's Rule." This relation was later critically examined by Nernst and the formula changed so as to make it of more rigid application.

Let T = absolute boiling point and
M = the molecular heat of vaporization

Then Nernst's revised rule of Trouton is

$$\frac{M}{T} = 9.5 \log T - 0.007\,T.$$

In this expression M is defined as the "amount of heat in gram calories required to vaporize 1 g. molecule of the substance." From this formula, given the molecular weight of a material and its boiling point, we can readily calculate its heat of vaporization by dividing M by the molecular weight.

Certain substances do not conform entirely to this law. This apparently includes materials which are considerably polymerized in the liquid state but which possess normal densities in the gas state. With coal-tar compounds, however, there is no evidence of any such association in the liquid state and it seems safe to conclude that the latent heat of these materials can be obtained accurately by calculation. It is somewhat interesting to note here a comparison between actually determined latent heats and calculated latent heats according to the revised rule of Trouton. The basic data are taken from Landolt-Börnstein, Section 185.

	Boiling Point °C.	Latent Heat of Vaporization Calories per Gram	
		Determined	Calculated
Pyridine C_6H_5N	115	101–104	107.5
Toluene $C_6H_5CH_3$	110.8	83–87	91.4
m-Xylene $C_6H_4(CH_3)_2$	139.9	78–82	85.5
p-Xylene $C_6H_4(CH_3)_2$	138.5	80–82.5	85.3
Benzene C_6H_6	80	93–95	98.2
Turpentine $C_{10}H_{16}$	159	68–74	69.9
m-Cresol $CH_3C_6H_4OH$	201	100.4	97.1
Cyclo-hexane C_6H_{12}	80	85–87	91.2
Octyl alcohol (normal) $C_8H_{17}OH$	196	79–5	79.7

This shows clearly the difference which might be expected between the calculated latent heat and that obtained by actual experiment, and it is evident that the error in the majority of cases would not be more than 5 per cent. It is in fact probable that the calculated latent heats are more nearly correct than those obtained experimentally because of the technical difficulties of latent heat calorimetry.

We have similarly calculated the latent heats of oil fractions, using as our basis the vapor densities determined by Huff, and in the higher fractions have naturally transposed the boiling points under the reduced pressures to correspond approximately to the lighter fractions which were taken under normal pressures. In addition, we have extrapolated the last fraction so as to obtain some idea of the latent heat of vaporization of materials above 440° C. boiling point.

FRACTION	Temperature Range ° C.	Vapor Density Grams per Cc. at Normal Temperatures and Pressures	Molecular Weight	Heat of Vaporization, Cal. per G.
I	199–249	0.00578	129.5	84.8
II	249–296	0.00667	149.5	81.0
III	296–345	0.00691	154.8	85.1
IV	345–392	0.00867	194.2	73.3
V	392–438	0.01047	234.5	65.1
Assumed	438–488	0.011–12	257.5	63.1

It is to be regretted that the writer has been unable to find authentic data on the latent heats of materials such as naphthalene and anthracene to check the oil fractions further with experimental data of substances which have similar boiling points. It is believed, however, that the results are accurate enough for all practical purposes and that they may be useful as an addition to the known constants of these rather complicated mixtures, the coal-tar distillates.

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[1] Received October 1, 1921.

[2] THIS JOURNAL, 10 (1918), 1016.

Science in Verse

Dr. C. E. Ruby has in preparation an anthology of scientific doggerel, which will probably be entitled "Jingles in Science." In order to make this collection of scientific nonsense in verse as complete as possible, and as entertaining as possible, readers are invited to send any verses or limericks dealing with the sciences to Dr. Ruby, 7 St. Paul St., Cambridge, Mass.

Seventy-one companies with an authorized capital of $50,000 or greater were organized during the month of November 1921 to engage in some branch of the petroleum industry, involving a total indicated investment of $60,129,000. This is an increase in number of companies but a decrease in total capitalization, as compared with October 1921, which showed 55 companies with a capitalization of $83,450,000. In November 1920, the total capitalization was $266,190,000. The average monthly indicated investment and average capitalization for each company formed are given in the following table:

	Monthly	Company
Five months, 1914	$ 7,647,400	$ 497,000
Year, 1915	6,711,100	410,900
Year, 1916	34 978,800	1,748,000
Year, 1917	70,018,283	1,641,053
Year, 1918	35,873,300	524,900
Year, 1919	315,500,500	2,324,128
Year, 1920	232,234,500	1,627,812
Eleven months, 1921	108,185,700	1,355,400

Chemically Speaking, How's Europe?

By Watson Davis

1418 Rhode Island Ave., Washington, D. C.

We Americans have been hearing much about conditions in Europe since the war. Our friends have gone over, and they have brought us back stories of their impressions of places, things and people here and there. We are interested in knowing how science is recuperating after the years of its serfdom to war; whether it is taking hold again and whether it will succeed in making Europe again worth living in.

This account is a composite picture drawn by three or four scientists who are lucky enough to have been over in Europe this past summer on roving commissions. It is written much as they told it to me and as they would tell it to you if you persuaded them to go over what is now to them an old story. The chemistry of this account often will not stand out pure and unapplied. It will blend into science in general, and in many cases even science will fade into the vivid background of hungry faces, depreciated currency, and war wreckage that is as yet only slightly cleared away.

Conditions in Germany

Scientific Germany is somewhat like a broken man, who has been sick and is now living on his stored vitality of past years. It must not be said that the patient will not recover, but just now scientifically he is largely relying on the achievements of better days before and during the war. There is a tendency to capitalize the things that were developed then.

The dearth of equipment, books, supplies and all the things that make up a workshop for scientists is a real one, not only chemically but in all scientific lines. The talk of poor conditions that we have been hearing is more than mere bluff.

Many of the largest universities and research laboratories, whose names were awe-inspiring in chemical circles before the war, have had practically no American scientific literature since the beginning of the war in 1914. And it is a financial impossibility for them to obtain foreign publications without outside help. The mark has lost so much caste among the moneys of the world that when it gets outside of its own country's borders it can hardly demand anything. Not to know what the chemists of other nations have been doing for seven years is a serious handicap to the work of German scientists. It is declared that in all Germany there is but one set of *The Physical Review*, the journal of the American Physical Society, complete to date. The lack of chemical literature is believed to be just as great.

Universities are having a hard time of it financially. University salaries and grants are notoriously hard to increase in this country, and the conditions are similar in Germany. One of the institutes of the University of Bonn on the Rhine has had a superficially generous increase in yearly funds from the pre-war sum of 17,000 marks to 170,000 marks, but this becomes small indeed when it is learned that it costs 50,000 marks to heat the buildings of the institute.

What the German universities lack in funds and equipment they have a tendency to make up for in students. The research laboratories at Leipsig are declared to be very crowded.

Salaries of professors are meager now in German universities. Before the war many of the university men had independent incomes of their own that supplemented their salaries. For the most part these auxiliary incomes have disappeared. Now nearly every professor has to hunt around for something to do on the side. They have been forced to adapt themselves to do more remunerative things in part of their time so that they may continue to teach.

This situation promises to bring about a more intimate interlacing between the universities and the industries. Those who would normally be doing research in pure chemistry are being forced into commercial research for the industries because of the money there is in it for them.

The glass works at Jena seem to be producing, but it is difficult to tell what was made during the war and what is new production. Quite obviously some was made for war use only.

A journey to a little inn on the top of the neighboring hills revealed a fine 15-cm. telescope with multiple high power eyepieces mounted as though on a man-of-war. Such a fine instrument seemed out of place there. Its only use was to provide magnified peeps at the surrounding country; its only reward was the few coins that went into the penny-in-the-slot device that was attached to it.

Food, which is interesting to the chemist both chemically and physically, is plentiful in Germany, although somewhat restricted as to certain kinds. Milk is the only food that people stand in line for now, and dairy products as a class are difficult to obtain and high in price. If you want white bread and butter you have to pay as much for them as you do for the rest of your breakfast. Vegetables are served liberally, and meat is being used in much the same old German way, largely as sausage and similar products.

Another sign of the times in Berlin is that the pushcart book sellers are offering new and modern books instead of old and second-hand books as they did before the war.

German firms are understood to be planning foreign exploitation of some of the new metals developed shortly before or during the war. One of these is the aluminium alloy that was intended for use as material for dirigible frames. It will be pushed as a material for engines, automobiles, and similar machinery.

Austria

The small area that still remains under the name of Austria appears strangely self-contained. There is seemingly a supply of raw material, and though wages are low there is, or at least was last summer, work for all, and an unemployment problem was not acute.

In Vienna the foreigner can get practically anything he wants in the way of food and other necessities. Although the hotels are hardly up to the standard that was set by them during the tourist trade of pre-war days, they are remarkably good. In the shops of Vienna can be seen many articles from Czechoslovakia, and trade and other relations with the Czechs are rapidly coming back to normal, as far as the exchange permits. Knickknacks from Germany, reminiscent of pre-war days, are displayed. These small importations are indicative of future commercial relations. From a business standpoint there is good feeling among Germans, Austrians, and Czechoslovaks, who just after the war were on very different terms.

Educational Vienna is worse off than the universities of Germany. The University of Vienna has only money enough to heat its buildings one month out of the year, and as a consequence does not heat them at all. Practically the same appropriation for its work is received as before the war, and this is now ridiculously small in purchasing power. One of the institutes receives 5600 crowns a year, which at a certain time last summer amounted to $2.15 in real American money—it is probably worth less now. It would take nearly four years' appropriations for that institute to subscribe to This Journal for only a year. And this was all the money that was available for salaries, heating and equipment, as well as publications. Obviously subscription to foreign scientific periodicals is out of the question. Under these conditions university work there is limited to lectures, given in cold rooms. There is little or no research work.

The effect of low foreign exchange in Europe is brought home by the following incident. A Polish chemist published a paper in the *Journal of the American Chemical Society*. He was asked if he wanted the fifty free separates that each author is entitled to. He did. And innocently he asked for them with covers. In due and routine time he was sent a bill for $1.77, the cost of the covers. He wrote back from Poland: "This is a just bill but just now it would take a quarter of my month's salary to pay it. Can payment be deferred a few years until conditions of exchange are better?" He was told to forget it.

Science in Russia

Russia has been a land in the shadow since the Soviet government has been in control. We have heard little about how science has fared in Russia, and that little has been pessimistic.

Now that our relief organizations are penetrating into Russia to ameliorate famine conditions and the Soviet government is sending scientists to the other countries of Europe and to America, we are beginning to get a little information on scientific Russia.

According to a botanist who had been sent into Germany to buy scientific books for the Russian government, the chemists at Moscow are still in their laboratories and, relatively speaking, they have been making out very well. It appears that the Soviets have established a policy of giving the productive academic men, those whose researches can be seen to influence industry directly, the same food and treatment as the children. And the children have been the first concern in Russia, both where the relief missions have and have not reached.

But even with the most liberal treatment in Russia, even though university salaries are paid by the government in part in priceless food rations of the highest grade, the professors have to look around for odd jobs. This is a quotation from a statement made by one of our leading biologists, who has just returned from Russia as a special representative of the American Relief Administration:

> The salaries and food rations of the professors in the University of Kazan had been so meager that not a man was able to live on them, and every professor was meeting his family's needs for food by doing something besides regular university work. The means for keeping himself and family alive were various, but in almost all cases they included the successive sacrificing of personal and household belongings. One professor of biology told me that he made shoes, and that his wife baked cakes and sold them in the city market. He had sold all of his own and his wife's simple jewels and trinkets and one of his two microscopes. Yet this man, who had not been able to see any books or papers published later than 1914, has struggled along with his special researches and has actually achieved two pieces of experimental work on vitamines which seem to me, with my little knowledge of the subject, to contribute certain definite new knowledge concerning these interesting substances.
>
> But beginning in August, there had been a material increase in salary and in food ration. The monthly food ration had been put, in August, on the following basis: dark (mostly rye) flour, 30 lbs.; dried peas, 5 lbs.; cereal grits, 13 lbs.; sweets, (not cane or beet sugar), $2\frac{1}{2}$ lbs.; tobacco, $^3/_4$ lb.; butter, 6 lbs.; meat, 15 lbs.; fish, 5 lbs.; tea, $^1/_4$ lb.; white flour, 5 lbs. The items from dark flour to tobacco, inclusive, had been received, the rest of them promised but not received. About 250 professors and instructors receive this ration. The university buildings are so cold that most of the men do all their work except lecturing in their homes. About 5000 students had registered but only about 10 per cent of them were in actual attendance. The largest departments in point of student enrolment were medicine and science. My friend, the professor of biology, had never before ridden in an automobile until he rode with me in our relief car. About 20 men of the Kazan faculty have died in the last two years.

An impression obtained in Europe is that the Soviet government has been fairly successful in carrying out its program in the territory that it directly controls, that is, within about 300 miles of Moscow. However, as far away from the seat of government as Petrograd, for instance, where control by the central government is difficult, preferential treatment of scientific and academic men has been much more irregular.

Scientific eyes in central Europe are looking longingly toward America. The chemists and other scientists of these states are keen to come to America, where living conditions are ideal in comparison with the situation in their native lands. Many leading American scientists have been flooded with correspondence from those countries and the ultimate object, in most cases, is a place in America. This desire for migration from Europe to America began with the Russian revolution and the exodus of many scientists from Russia.

How an influx of European scientists would affect the conditions of American scientists is problematical. In these times of industrial depression, when many chemists are out of work, it is to be expected that American chemists will be sensitive about the possibility of greater competition for jobs. However, the scientists who wish to come to America because European times are hard will be apt to stay here and in many cases would be valuable additions to science circles in America.

Belgium, Switzerland, and Holland

Belgium is the country that seems to be more nearly back to normal than any other part of Europe. There factories are working nearly in a pre-war fashion and university laboratories are again assuming a peace-time aspect. Belgium, first attacked in the war, has received the first part of Germany's reparations and this has helped to make her the most normal country of Europe.

Switzerland and Holland, the two neutral border states, both face outside competition. They have raised high and stringent tariff barriers to prevent a flood of goods from Germany and Austria and the other low-wage-plane countries from engulfing their own manufacturing establishments. There is a feeling, undoubtedly based on fact, that considerable smuggling is under way and that goods from the outside are appearing for sale in those countries relabeled under native disguise.

The educational situation in Holland is quite similar to that of the rest of Europe. At Leiden the number of students is getting back to normal.

The Condition of France and England

France and England are gradually getting back into their old scientific stride.

Paris has been the center for international gatherings since the war and has had the benefit of contacts with visiting scientists of all nations. Industrially the condition of France is nearly as far along as that of her smaller sister, Belgium. Food in France is practically up to normal in quality, although the bread is still not quite what it was before the war.

The University of Paris is suffering from a scarcity of students due to the high living costs. The French of the better class who send their sons to college now find that they can hardly afford it.

In England the university conditions are quite similar to those here in America. The colleges are a little over-full. Industrial depression has forced the young men whose education was interrupted by the war back into college. Industry now has no strong call for them and those who can are entering the colleges to finish their education.

The meeting of the British Association for the Advancement of Science held in Edinburgh this summer had much the tone and spirit of the meetings before the war.

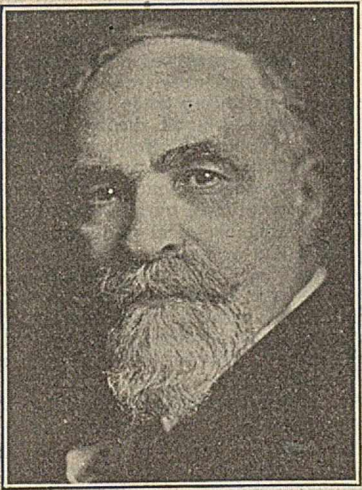
From a food standpoint also, England is getting back to normal. They still have one crude chemical, brown sugar, on their tables, usually along with refined lump sugar, and this seems odd to Americans who find it nearly as hard to buy brown sugar for candy making as they did before the war.

Views of French Chemical Warfare Advisers

Reparations!

That is the answer of Professor Charles Moureu, president of the International Union of Pure and Applied Chemistry, and one of the leading chemists of France, to the question, "What is the most important factor in France's chemical situation?"

"Ten districts devastated. If the Germans cannot pay, well, what can we do?" Uppermost in the minds of Frenchmen is this question of the German indemnity. Germany must pay. Germany by her reparations must reëstablish a large part of France, not alone chemically, but industrially. This is without a doubt one of the all-enveloping thoughts in the minds of the French delegates now in Washington at the Limitation of Armaments Conference. Professor Moureu is attached to the French delegation as official adviser on chemical warfare.



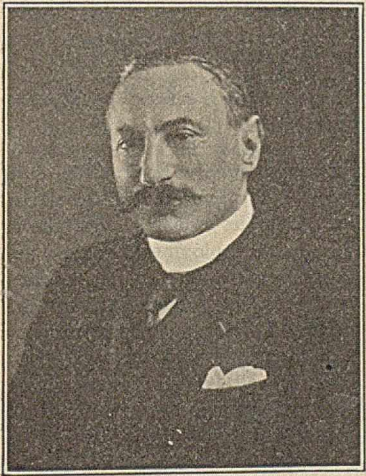
Harris & Ewing

Professor Charles Moureu

Professor Moureu is professor of organic chemistry at the Collège de France and he has been a leading figure in chemical research of that country. Some of his latest work has been on the origin of helium.

Professor Moureu is enthusiastic over the future of the International Union of Pure and Applied Chemistry.

Next year when the meeting is held at Lyons, France, in June, he believes that twenty-five nations will be represented at this gathering of the chemists of all nations. At the Brussels meeting held this summer twenty-one nations sent representatives.



Harris & Ewing

Professor André Mayer

Professor Mayer is now professor at the Université de Strassbourg in repatriated Alsace. He established the tuberculosis laboratory at the Puteaux near Paris which during the war became the laboratory of the American Chemical Warfare Service.

"Will Germany be included?"

Emphatically no. Germany, the country that will not pay the indemnity, Germany, the country that devastated France, that Germany cannot be allowed to join the international organization of chemists. This Professor Moureu strongly believes; this seems to be the opinion of most of France, scientific and nonscientific. They are not ready now to fraternize with recent enemies; they are not even ready to meet them scientifically.

Professor Moureu tells how ten committees of the International Union are at work. "Two are headed by your countrymen," he said. "Prof. F. W. Clarke, of your Geological Survey, is honorary chairman of the committee on chemical elements, which has sub-committees on radioactivity, isotopes, and atomic weights. Your great Professor Richards of Harvard is the chairman of the committee on nomenclature."

But while industrial France, including the chemical industries, is slowed up by German slowness of paying, scientific France is organized.

France's seven chemical societies are affiliated and combined into a federation of chemical societies. Similarly all the biological societies of France are brought together, and also all the physical societies are federated. Those organizations dealing with the law, philosophy and history also come within the category of science, and are all brought together in one federation. These four federations have been fused, and there has emerged the Conféderation de Sociétés Scientifiques, corresponding in a way to our American Association for the Advancement of Science.

Then also there is the National Committee of Research, with four councils of chemistry, physics, biology, and mathematics. This organization is official and is supported by the government. It is similar to our National Research Council and is affiliated with the International Research Council.

The future of chemical warfare is interesting to chemists of America, France, and the rest of the world. Perhaps the Limitation of Armaments Conference will have something to say about it. Professors Moureu and Mayer are here to advise M. Viviani and France's other representatives on the chemical warfare that was inaugurated in their country by the Germans. But no, they are here officially. They cannot talk about chemical warfare. I must hardly mention it. So I have not.

A Lesson from History—Lest We Forget

By Charles E. Munroe

National Research Council, Washington, D. C.

The admirable address by Dr. Haller on the "French Chemical Industry during the War"[1] and "La chimie et la guerre" by Dr. Charles Moureu in Masson et Cie's series of "Les leçons de la guerre" present most vivid pictures of the almost superhuman efforts by which the enormous and varied demands for war supplies were met; the many ingenious devices by which the splendid organizations created increased the speed of production and effected economies in operation; and the resourcefulness shown in adapting such material as could in any way be obtained to the many and various needs. They record the wonderful achievements of a most brilliant epoch in the application of chemistry to supplying the bitter needs of a nation in great distress. But it is repeatedly emphasized throughout these histories that in 1914 France was, as regards the supplying of its needs for chemical products, a very dependent nation.

Yet recalling that the use of picric acid as a fragmentation charge for high explosive shell was developed to complete operativeness by Turpin in France soon after 1885, and that the many other nations which adopted this material as charges for H. E. shell, under the names of Lyddite, shimose and other pseudonyms, patterned their practice on his, it is astonishing to learn that in 1914, notwithstanding that there were then in France a large number of accomplished and most competent chemists and chemical engineers, the supplies of phenol for the manufacture of the picric acid which had been adopted by the French government for its H. E. shell, "came from foreign countries and particularly from Germany."

This is the more remarkable when it is recalled that France had previously passed through severe trials and been succored

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[1] *Bull. Soc. d'encour. l'ind. nat.*, **132** (1920), 761.

by its chemists, as at the time of the French Revolution when it was sorely beset by enemies without and within. So strenuous were conditions that the *Annales de Chimie* was forced to suspend publication, but when in 1797 the tide of struggle turned and victory was wrested from the enemy by the armies of France, publication was resumed with Volume 19, which carries the following preface:[2]

> The *Annales de chimie* has been suspended during three years following the publication of volume eighteen. The necessity for each devoting oneself solely to the defense of the Republic; the events of the revolution; and finally the public occupations and functions of its authors have naturally compelled this suspension. But the time has not been entirely lost to science; chemistry, above all, has been cultivated with an activity and success to which all testify; she has developed for the defense of the country truly unexpected resources and expedients. Her ability to relieve immediately the most urgent needs has rendered her most precious and commendable in the eyes of the lovers of mankind, and of all true citizens. Further the number of those becoming students has increased each day; it has become a fundamental topic in all modern schools, and above all in those which seek the higher planes of human knowledge.
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> Among all the civilized nations, where one works without ceasing for the perfection of reason, the sciences which influence territorial and industrial production, and among which chemistry to-day occupies the first rank, are held in general esteem. The cultivation of the fields, the multiplication of animals, the establishment of manufacturers, the exchange of the industrial creations for the products of other people constitute the true source of the prosperity of nations to which all men are called according to their abilities and where they find, in serving their country, their chief pleasure.
>
> Chemistry clarifies the practice of the arts; without her neither constancy in products, economy in process, nor perfection in operation can be hoped for. Unable to know in advance and to calculate the results, manufacturers have often made errors which have lost them their establishments. Consequently many chemists have in recent years become manufacturers and already France has ceased to be tributary to other nations for a great number of useful products; the preparation of the mineral acids, different salts, metallic oxides, dyes, and glass, multiplied in France during the last five years, are authentic proof of the inestimable advantages of chemistry. Without the light of this science from where would have come the quantities of saltpeter and powder for our armies which was made in the last four years? From where the copper, iron, steel, potash, soda, leather, and all the other precious materials which have enabled us to conquer our enemies and to maintain our existence? Without chemistry we would have been helpless.
>
> At the moment when victory has crowned our efforts, when talent has been recognized and called to the service of the State; at the moment, above all, when new schools have been opened in the Departments which seek to spread knowledge and make known its needs, the authors of the *Annales de chimie* believe it a pressing duty to go on again with the circulation of this journal. Their aim is to carry the torch of science into all workshops; to make known the new processes; to describe the little known or unused arts; to improve bad practices; to correct errors which occur too often in many of our factories; to describe means for the utilization of neglected or wasted by-products; to expose the often misleading trade secrets and the perfidious charlatanism; to establish lucid theories of the most obscure operations; to direct the nearly always unassured or uncertain steps of the manufacturer; to destroy mystery, and to repress fraud. In a word, to serve science in the most exact manner and to increase the varieties of national industry.
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> We believe that, without neglecting chemical philosophy, it is its special applications to the useful arts that will clarify and improve those arts. Brilliant and ingenious theories will not be refused, particularly if they have useful applications. It is for intelligent and reliable artists, manufacturers, workmen, and merchants that this work is especially designed. At the same time savants and philosophers will find records of the progress of physics and the march of human events. It is fine to be able to view the improvement in the arts and also in well doing among a great people.
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> It is hardly necessary to say that all possible effort will be made to join to the discoveries made in France those made by other nations where chemistry and the chemical arts are cultivated with success, and especially Germany, Spain, Holland, Italy, and England.
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> The authors of the *Annales de chimie* having undertaken to continue their work propose to present in the nineteenth and twentieth volumes the principal discoveries and most remarkable achievements in chemistry made in France between September 1795 and January 1797.

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[2] *Ann. chim.*, **19** (1797), 5.

SOCIAL INDUSTRIAL RELATIONS

Waste in Industry

By H. W. Jordan
Syracuse, N. Y.

The report upon the research made this year by the Federated American Engineering Societies, under leadership of Herbert Hoover, is issued as the book "Waste in Industry," published by the Societies.[1] The research marks a new phase of engineering in that the creators of modern industry, the engineers, have applied their methods of investigation by research and mathematical analysis to industrial management and industrial contact with the public.

This research upon six typical branches of industry, building, men's clothing, shoe manufacturing, printing, metal trades and textile manufacturing, disclosed that on the average labor is responsible for 16 per cent of the waste, defective relations with the public for 16 per cent, and management answerable for 68 per cent.

THESE SUMMARY FIGURES ARE BASED ON THE FOUR MAIN CAUSES OF WASTE:

1—Low production caused by faulty management of materials, plant, equipment, and men.

2—Interrupted production, caused by idle men, idle materials, idle plants, idle equipment.

3—Restricted production intentionally caused by owners, management, or labor.

4—Lost production caused by ill health, physical defects, and industrial accidents.

As Mr. Hoover says in the foreword of the book, "We have probably the highest ingenuity and efficiency in the operation of our industries of any nation. Yet our industrial machine is far from perfect. The wastes of unemployment during depressions; from speculation and overproduction in booms; from labor-turnover; from labor conflicts; from intermittent failure of transportation of supplies of fuel and power; from excessive seasonal operation; from lack of standardization; from loss in our processes and materials—all combine to represent a huge deduction from the goods and services that we might all enjoy if we could do a better job of it."

THE SURVEY SHOWS SUCH STRIKING SIMILARITY BETWEEN THE SIX INDUSTRIES that it indicates the existence of universal laws that govern industrial mass action. Although equipment of the several industries varies widely, five of the six showed close approximation to the above average distribution of waste. Textile manufacture, the oldest American industry, showed but 50 per cent of its waste due to management. Its greater losses, 40 per cent, are due to outside contacts.

Interrupted production caused by seasonal conditions, com-

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[1] "Waste in Industry," McGraw-Hill Book Co., Inc., New York, N. Y., 1921. xi + 409 pages. Price, $4.00.

petitive trade practices, and unbalanced operations between departments of manufacturing plants were a large cause of waste. Interruption due to labor strikes was found less serious than is popularly supposed, because so many strikes are in seasonal trades, like manufacture of clothing or the building trade, where the loss is not absolute because it is made up by energetic work at a later date.

Destructive competition, absence of coöperation, lack of comparative statistics of industry coöperatively collected and intelligently used are among principal causes of waste. Lack of standardization of machines and of methods, maintenance of an excessive number of patterns, sizes, and styles, and extreme excess equipment contribute heavily to waste.

> THERE ARE APPROXIMATELY 6000 BRANDS OF PAPER, 50 per cent of which are more or less inactive. Duplication of brand serves no useful purpose and ties up money in unnecessary stock. As an example of the disregard of standard size, the Federal Reserve Bank check will not cut without waste from any regular paper sizes. A draft questionnaire issued during the war was of such nonstandard size as to require special filing cabinets. The Technical Publishers' Association on measuring 927 catalogs found 147 different sizes. A trim of one-quarter inch on a 6 × 9 page is equal to 7 per cent of the total cost of the paper. Among current magazines there are 18 variations in width and 76 in length of page or column. Among trade paper publications there are 33 variations in width and 64 in length. Among newspapers there are 16 in width and 55 in length. These variations cost the public not less than a hundred million dollars each year. Standardization of newspaper columns to one size would make possible an annual saving of $3,000,000 to $5,000,000 on composition and plates alone.
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> LACK OF EFFECTIVE PLANNING AND ADMINISTRATION in one large typical plant wastes one-fifth of the worker's time. A shoe factory having a capacity of 2400 pairs of shoes a day could turn out for a considerable period only 1900 pairs because of shortage of needed racks. Another factory had 50,000 pairs of shoes tied up in the fitting room instead of the normal 15,000 because of congestion of operations. In another case a factory producing 700 pairs of shoes a day had 36,000 pairs in its fitting room, or ten times the normal supply. An entire factory was held up for several days waiting for leather heels. From shop records it is found that the average loss in clothing factories during running time, not including shut down, is between 30 and 35 per cent. If we call 80 per cent running time the maximum readily attainable, this means a possible increase of nearly 20 per cent in productive capacity, and a similar increase in plant capacity.
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> Since most strikes occur in seasonable employments, it can be deduced that output is not necessarily penalized, for it is often possible to make up the losses incurred by strikes through increased production at other times. More coal was mined in 1910 than in 1911, although the former year witnessed many protracted strikes involving large numbers of employees. The year 1912, with 47 per cent of the entire labor force out on strike and with an average loss per man of 40 days, showed an increased output of coal per man, per day and per year, and six days more employment than in 1911, which was relatively strikeless.
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> Clothing factories are built 45 per cent larger than is necessary; printing establishments are from 50 per cent to 150 per cent overequipped; the shoe industry has a capacity of 1,750,000 pairs of shoes a day, and produces little more than half that number; throughout the metal trades, standardization of products would permit of large reductions in plant and equipment.
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> * * *
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> Practically all industries are seasonal. The clothing worker is idle about 31 per cent of the year; the average shoemaker spends only 65 per cent of his time at work; the building trade workman is employed only about 190 days in the year or approximately 63 per cent of his time; the textile industry has regular intervals of slack time; during the past 30 years bituminous coal miners were idle an average of 93 possible working days per year.
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> ABSURD LABOR UNION REGULATIONS CAUSE WASTE. As carpenters' helpers are prohibited from using carpenters' tools, carpenters are required to do such work as stripping forms from concrete, work that helpers could do more cheaply and as well. Hoisting engineers claim the right to run all types of engines, including automatic, gas driven pumps. On one job a contractor had to hire a union engineer at $8.00 per day simply to start a pump in the morning, oil it occasionally, and stop it at night.
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> THE PUBLIC IS RESPONSIBLE FOR ABOUT ONE-TENTH OF THE WASTE DISCLOSED. Excessive numbers of styles, combative rather than coöperative public opinion, and crowding manufacture and trade into short seasons by failing to standardize wearing apparel are among industrial sins of waste of which the public is guilty.

These citations from the report are sufficient to show its thoroughness and to bring to notice elements of waste that are plainly preventable.

UNDERLYING THE STUDY ARE FOUR FUNDAMENTAL PRINCIPLES THAT MERIT our serious attention. First, that humanity, whether management, labor or public, proceeds along the same ways in each industry in strict, readily discernible accordance with laws that are world-wide;

THAT PROFITABLE PRODUCTION AND SUPERIOR EFFICIENCY RESULT FROM COÖPERATION; while loss, interruption of industry, and discontent among employees and public spring from absence of coöperation;

THAT ACTION AND REACTION ARE EQUAL IN HUMAN INDUSTRIAL RELATIONS as they are in mechanics; and that the Golden Rule, which is one wording of the law of equal action and reaction, is not a mere soothing expression of a pleasing ethical theory, but that it is a primary law of self-preservation in industry, commerce, and all human relations;

AND FOURTH, THAT RESEARCH, by the methods of applied science and mathematical analysis which engineers and chemists have applied to machines and processes, is equally applicable to every phase of industry, commerce, and human affairs.

A main value of the Federated Engineers' study of waste in industry is this proof that all human relations are capable of interpretation and improvement by scientific research. "The future of civilization depends upon the widening spread and deepening hold of the scientific habit of mind," says John Dewey. Continuance of profitable industry in its readjustment to the conditions arising from the World War depends upon scientific research that will extend into all human relations of industry as deeply and thoroughly as it has delved into the applied sciences that yielded the automobile, moving pictures, aviation, by-product coke and contact sulfuric acid—industries of applied science that did not exist a half century ago. As the report says:

> While certain industries are ahead of the rest in plant research, the need for more intensive research activity is apparent in every industry. One industry which is backward in this respect is clothing. In the majority of men's clothing plants nothing approximating research is practiced to improve materials, processes, equipment, or product. The assertion probably will not be challenged that there is not a single individual throughout the entire industry who is solely engaged in research and is thus without operating duties. In the shoe industry there is lack of information as to market demands in this country and abroad. In all leather industries there is need for scientific research to aid in predicting the kinds and quantities of leather required.

INDUSTRIAL MANAGEMENT HAS PAID TOO LITTLE ATTENTION to waste and loss of profit arising from disregard of social industrial relations with employees and the public. Failure to realize that these human relations are responsive to scientific research has resulted in a large by-product of industrial ill will, ill will not only of employee but of the public; ill will reflected in types of taxation and government regulation as senseless and costly as the $8.00 engineer who starts and stops an automatic pump. Here, too, we find reaction equal to action.

THE REAL TEST OF INDUSTRIAL CONSOLIDATION IS TO COME IN THE NEXT TWENTY YEARS. The Federated Engineers say "There is probably direct connection between the increase in size of industrial plants, and the statement made by Bradstreet to the effect that, while 'incompetence' had always bulked large as a cause of business failures, by 1912 it had grown to be the chief cause and by 1919, 38.2 per cent of all failures were caused by it. During this period plants were rapidly increasing in size because of the growth of the country, and a higher standard of management was at the same time being required."

In my opinion the next phase of corporate industry will be reversion to its original units, operated by local, resident management in social harmony with their several communities; with present absentee management supplanted by coöperative management acting in close accord with mathematical or statistical information secured by research like that of the Federated Engineers.

"Underlying the balance sheet, the Ethical Factor—expression of fairness in all relations—must be distinctly plus, not minus, or any industry cannot survive," says Babson. Future industrial coöperative management will be characterized by extension of practical coöperation to employees and to the public, with proportionate elimination of the vast fund of antagonism and industrial ill will toward employers as a class.

THIS RESEARCH UPON WASTE IN INDUSTRY IS AN EARLY PROOF OF THE NEED OF SUCH COÖPERATION. Equally convincing proof is the widespread abandonment of humanitarian work by corporate management since the war, and the dropping of a large portion of scientific industrial research as well.

HUGE CORPORATE INDUSTRY HAS ENTERED THE THIRD GENERATION OF THOSE WHO FOUNDED ITS COMPONENT UNITS. They say in Japan—"The third generation makes or breaks a dynasty." As Lothrop Stoddard expresses it: "The melancholy trinity—David, Solomon, Rehoboam—has reappeared with depressing regularity throughout history." In American corporate industry we are witnessing, and enduring, the third generation stage. The ultimate result will return to more individualistic, local, resident management, under a national, coöperative rather than competitive system.

It is a principle of human progress that it works in circles; that inventions or great social movements begin in simple, rudimentary forms, advance through extreme complication and, in their ultimate perfection, come back to the simple, essential elements from which they started. Thus the steam engine was first Hero's revolving cups, and next the reciprocating engine of Watt. In the modern turbine engine it has returned to Hero's principle.

THIS SURVEY OF WASTE IN INDUSTRY IS AN INVALUABLE SERVICE TO COMMUNITY, STATE, AND NATION. It points the way to the return of our industries to their ultimate, yet original, form of single plant units, efficiently managed and harmoniously conducted by men and women who make each industry their life career in the city or town they adopt as their home. By that return to first principles we shall regain the immensely valuable social force of American individualism, strengthened by a system of nation-wide, coöperative industrial relations based upon laws which govern world-wide human relations; laws that chemists and engineers will reveal and apply by scientific industrial research. Thus we shall attain industrial, social, world-wide peace, with enduring prosperity through elimination of industrial and social waste.

NOTES AND CORRESPONDENCE

Liability for Laboratory Accidents

Editor of the Journal of Industrial and Engineering Chemistry:

The Court decision which awarded a Cornell woman student $25,000 damages because of alleged negligence on the part of the College Department of Chemistry, by which she lost the sight of one of her eyes, as reported in the November 1921 issue of THIS JOURNAL, certainly gives those of us who teach beginners food for serious thought. The outcome of the appeal to the highest court will be awaited with great interest.

I have long opposed the usual method of dispensing chemicals in laboratories where beginners in the subject are at work, namely, letting the student help himself from bottles on a side shelf or table. I have seen so much trouble, and so many accidents, result from this method that I long ago discarded it as dangerous and inefficient, and have substituted a "dispensing stockroom," where the responsibility for giving out the correct chemicals, and in right amounts, is upon the stock clerk. There are so many chances that a student will meet with accident, even with the proper chemicals, that we should strive to eliminate entirely the many chances of accident due to getting the wrong chemicals.

I have never yet seen chemicals left out within reach of students that were not contaminated, one by the other, and while the testimony of Professor Chamot states that no lime was found in the unused remainder of the mixture made for the experiment, and the case under consideration seems to be clearly one of carelessness on the part of the student, there is always the possibility of accident due to the presence of a chemical in a bottle labeled as containing some other.

A case in point, which happily did not end in disaster, occurred in my own laboratory when a stock clerk, too lazy to do as he had been told, let the students help themselves. The students had been pouring potassium chlorate from a wide-mouthed container into a test tube. This procedure naturally resulted in the spilling of much of the substance on to the table. Students are notoriously prone to leave bottles unstoppered, and on this occasion a bottle of powdered sulfur was receiving a very liberal addition of the chlorate. Prompt removal of this contaminated material is probably all that saved some one from a bad explosion. That particular stock clerk was eliminated from the staff.

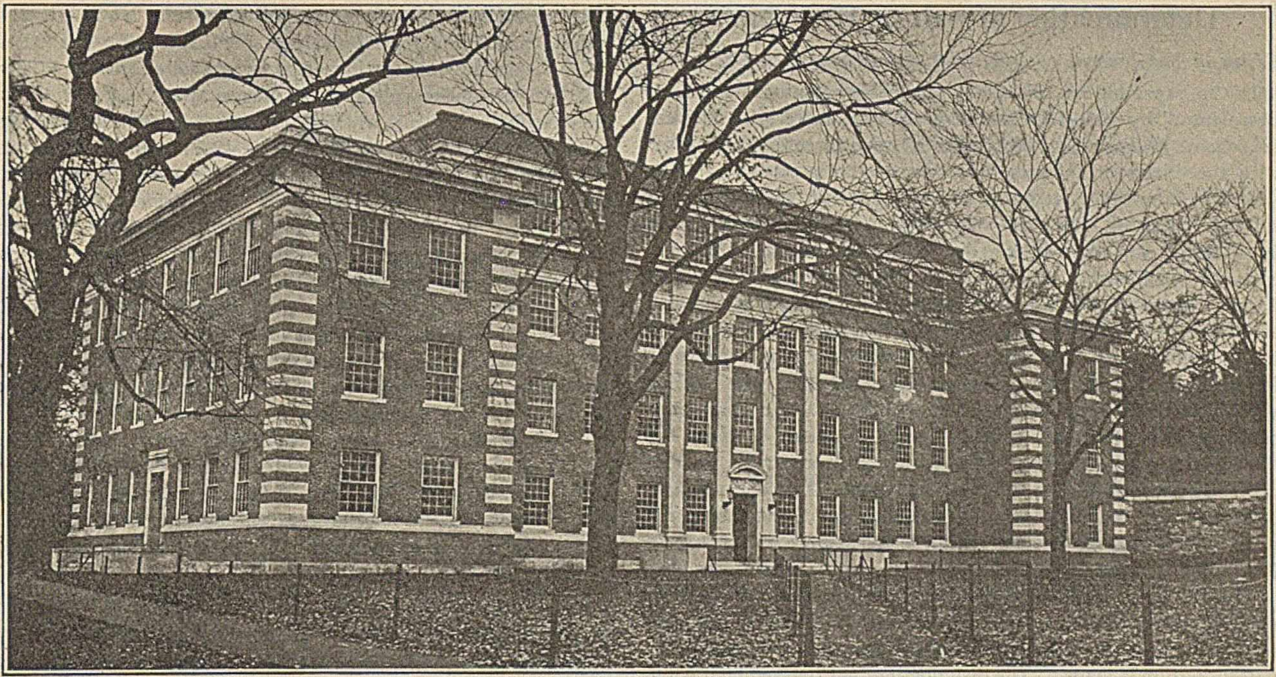
Contamination of fine chemicals by interchange of stoppers is also a frequent occurrence in a beginners' laboratory. This is especially true of solutions. I have had a class lose the work of nearly a whole laboratory period because a stock clerk (the same one, by the way) had let some student mix up stoppers on two bottles, one of which had contained a chemically pure substance in solution.

With free access to chemicals, foolhardy students will "try anything once." I have, when a student myself, seen another student take the opportunity, when the teacher had left the laboratory temporarily, to pour some material from nearly every bottle on the shelf into a beaker just to see what would happen. You may say that is the research spirit manifesting itself early, but I shudder to think that he might have produced hydrocyanic acid had he picked out *all* the bottles on that shelf. A kind Providence probably saved us all that day. The teacher wisely removed the potassium cyanide after hearing of this escapade.

If the ruling by the Court, that it is the duty of the Department of Chemistry to analyze all chemicals received from manufacturers before they are dispensed to students, is upheld by the higher Courts, colleges will feel required to make these analyses. This will add considerably to the expenses of instruction, and if the chemicals are bought in small containers the additional expense will be very large.

If the further ruling is upheld that it is the duty of the Department to ascertain by chemical examination whether the contents of all bottles in the student laboratories are in exact accord with their labels, a continuous run of analyses would have to be made on *all the bottles all the time* the students are present. This would seem to preclude the use of the system of dispensing where the students have access to the bottles, (for students are bound to contaminate the chemicals); otherwise the college must assume the liability incurred in neglecting to make such continuous analyses.

The case of the male student whose explosion was due to the fact that he had scraped up some white chemical that had been



STEELE CHEMISTRY BUILDING, DARTMOUTH COLLEGE

This new laboratory which was dedicated October 29, 1921, was in part the gift of the late Sanford H. Steele, formerly president of the General Chemical Co. At the dedication, Dr. Henry P. Talbot delivered an address on "Fifty Years of Chemistry: Our Heritage and Our Obligations."

spilled on the table, and which was evidently not "lime" which the experiment required, seems to me to be argument enough to persuade any teacher who has to supervise a beginners' laboratory that it is not wise to let these inexperienced students help themselves. Some students are always slovenly in pouring out chemicals and seem to care little how much they spill. It always seems to me that one slovenly student contaminates the others in the laboratory. They see that he "gets by" (as they say) without cleaning up what he has spilled, and they try to do likewise. This, if true, is another good argument for a controlled stockroom.

At Brown our "dispensing stockroom" opens directly into the laboratory, and a student assistant deals out the chemicals asked for by the students. Only dilute acids and ammonia are on the benches, and these are the only chemicals, outside of water, to which the students may help themselves. We are thinking seriously of eliminating all but the water.

While this system is not infallible, it is easier to find the source of trouble, and to place the responsibility for it.

Regrettable as it is that the Cornell student lost the sight in one eye, for which loss money alone can hardly be a recompense, it does not seem clear to me that the college should be held liable for the financial recompense in this case, which appears so clearly one of neglect on the part of the student.

If the higher courts sustain this verdict there seems to be nothing left for the colleges to do but to take out liability insurance to cover such cases. It is certain they cannot afford to make the analyses.

H. F. DAVISON

BROWN UNIVERSITY
PROVIDENCE, R. I.
November 14, 1921

Another Case of Spontaneous Combustion[1]

Editor of the Journal of Industrial and Engineering Chemistry:

At about 2:30 P. M. on July 15, 1921, a volume of white smoke was discovered arising from the top of a tank installed in the yard of the Experimental Kelp Potash Plant of the U. S. Department of Agriculture at Summerland, California. The tank being of wood, the impression created was that the tank itself was on fire, but it was immediately discovered that a cotton sack lying on top of the tank was burning vigorously and that this was giving rise to the smoke.

This sack, it developed—an ordinary white cotton flour sack—had been used in the filtration of crude sodium chlorate employed as a reagent in the manufacture of iodine from kelp potash brines, and when the iodine plant had been shut down two months previously, the sack had been thrown on top of the tank where it had remained ever since. Since the iodine plant was constructed out-of-doors, without a protecting roof, the top of the tank and the sack lying on it were exposed to the sun's rays, and it was so situated as to be exposed to the sun all the morning. The day in point was a brilliantly clear one, though not unusually warm.

The top of the tank is about 7 ft. from the floor, which fact would discount the idea that the fire could have had its origin in the carelessness of smokers. Furthermore, inasmuch as the plant was shut down and in a stand-by condition, no one entered it but the guards. The chances of the fire originating other than spontaneously, accordingly, seem negligible.

On the other hand, the facts that the sack in question was impregnated with sodium chlorate; that it was a second-hand flour sack and possibly had not been entirely freed from flour; that it accordingly was highly inflammable; that the sun's rays in this locality are highly actinic, all combine to substantiate the conclusion that the fire was another case of spontaneous combustion. It is believed that the reaction was started through the influence of the chemically active rather than the heat rays of the sun.

The phenomenon was witnessed by Mr. P. S. Shoaff, the superintendent, and Mr. H. G. Tanner, chief chemist, who concur in the above conclusion.

J. W. TURRENTINE

EXPERIMENTAL KELP-POTASH PLANT
U. S. DEPARTMENT OF AGRICULTURE
SUMMERLAND, CALIFORNIA
September 14, 1921

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[1] Published with permission of Secretary of Agriculture.

Determination of Salt in Petroleum

Editor of the Journal of Industrial and Engineering Chemistry:

In the paper on the subject of "Determination of Chloride in Petroleum," by Ralph R. Mathews[1] I have noted with interest his scheme of separating salt water by mixing acetone and water with the oil under examination.

In this laboratory we have for several years been estimating salt after burning off an oil. For rapid control we weigh from 10 to 20 g. of a fuel oil in a dry nickel dish of about 250-cc. capacity, and heat the dish and contents over a Bunsen gas flame. When the oil is fuming thickly, the gases over the dish are ignited with the Bunsen flame, and the heating is continued until the oil fumes burn out. The Bunsen flame is withdrawn for a minute, 75 cc. of water are added, and the mixture is boiled vigorously for a few minutes. The dish is cooled in a vessel of cold water until cool enough to handle, and the contents are filtered and washed several times with water, scrubbing out the dish. After the addition of a few drops of 1:10 potassium chromate solution, the filtrate and washings are titrated as usual with standard silver nitrate, and the results are calculated to NaCl.

There is left in the dish a mass of charred matter which, after sufficient washing, does not retain more than traces of salt, and need not be completely removed from the dish before another determination is made. The dish does not get to a red heat while the oil is burning off, and the charred mass provides a means of protecting NaCl from volatilizing. The nickel dish is not used for any other work.

If the oil contains an abnormal quantity of salt, it foams and spatters badly, and a lower flame is used for the first part of the heating operation.

Our specification on fuel oil for use in open hearth and forge furnaces does not permit the presence of more than 0.25 per cent of salt. However, it is only rarely that we have met with samples of oil running as high as 0.10 per cent. On the other hand, in composite samples from bunches of ten carloads we have never found a total absence of salt.

GEORGE T. DOUGHERTY

AMERICAN STEEL FOUNDRIES
CHICAGO, ILLINOIS
April 20, 1921

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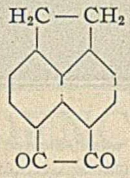
[1] THIS JOURNAL, 13 (1921), 325.

The Chemistry of Acenaphthene and Its Derivatives

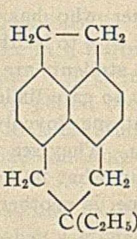
Editor of the Journal of Industrial and Engineering Chemistry:

The excellent summary of the chemistry of acenaphthene and its derivatives by D. A. Hahn and H. E. Holmes which appeared in the September number of THIS JOURNAL[1] undoubtedly will serve the purpose for which it was written and stimulate investigation in this interesting field. As, however, this paper was received on June 20, 1921, and it is stated that the synopsis represents all the references to the chemistry of acenaphthene and its derivatives which could be obtained from a fairly close search of the literature, new workers in this field may possibly overlook the most recent work. It appears of interest, therefore, to bring this subject up to date by the addition of a short note.

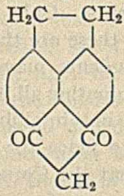
A. Zinke and E. Raith,[2] F. Mayer and W. Kaufmann,[3] F. M. Rowe and J. S. H. Davies,[4] K. Fleischer and P. Wolff,[5] and K. Fleischer, H. Hittel and P. Wolff[6] have described new derivatives of acenaphthene and, in some instances, have revised the melting points of derivatives previously known. New derivatives include pyridino-4,5-acenaphthene, melting at 67°[2] or 60° to 61°,[3] obtained by the action of concentrated sulfuric acid, glycerol and nitrobenzene on 5-aminoacenaphthene; tetrabromoacenaphthene, melting at 180° to 181°;[3] 5-ethylacenaphthene, boiling at 160°/20 mm.[3] or melting at 42.5° to 43°,[5] which forms a picrate, melting at 95° to 96°,[3] and is oxidized through 4-ethylnaphthalene-1, 8-dicarboxylic anhydride, melting at 180°,[3] to naphthalene-1,4,8-tricarboxylic acid; 5-nitroacenaphthenequinone, melting at 199°[3] or 218°,[4] forms a monophenylhydrazone, melting at 186°[3] or 234° to 235°,[4] and a diphenylhydrazone, melting at 148°, and is converted into the corresponding nitronaphthaldehydic acid, melting at 245° to 247°, by the action of concentrated potassium hydroxide; 5,6-dinitroacenaphthenequinone, melting above 300° with decomposition,[3,4] forms a monophenylhydrazone, melting at 287°; a diacetylacenaphthene, melting at 146°;[5] 5-acetylacenaphthene readily condenses with benzaldehyde to form crystalline benzylidene derivatives, the *o*-chlorobenzylidene compound melting at 113°;[5] 6-acetyl-5-ethylacenaphthene, melting at 110.5°;[5] 5,6-diethylacenaphthene, melting at 10° to 11° and boiling at 182°/14 mm.;[5] pyracenehemiquinone



melting at 226°,[5] obtained by the action of oxalyl bromide on acenaphthene in the presence of aluminium chloride; 5-bromoacetyl-acenaphthene, melting at 180°;[5] 2,2′-diethylperiacenaphthindane

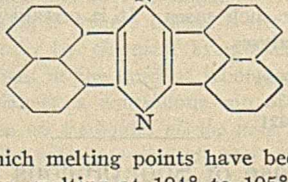


melting at 93° to 95°,[4] obtained by the reduction of 2,2′-diethylperiacenaphthindane-1 :3-dione; periacenaphthindanedione



melting above 300°.[6]

The substance regarded by Graebe[7] as acenaphthenequinoneimide has been shown by A. Schonberg and F. Nedzati[8] to be acenaphthylene-1,2-azine



Instances in which melting points have been revised are 5-aminoacenaphthene, melting at 104° to 105°;[4] 5-acetylaminoacenaphthene, melting at 238°,[4] for 192° given by Sachs and Mosebach;[9] 4-nitro-5-acetylaminoacenaphthene, melting at 255°[4]

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[1] THIS JOURNAL, 13 (1921), 822.
[2] *Monatsh.*, 40 (1919), 271.
[3] *Ber.*, 53 (1920), 289.
[4] *J. Chem. Soc.*, 117 (1920), 1344.
[5] *Ber.*, 53 (1920), 925.
[6] *Ibid.*, 53 (1920), 1847.
[7] *Ann.*, 276 (1893), 9.
[8] *Ber.*, 54 (1921), 238.
[9] *Ibid.*, 44 (1911), 2860.

for 253°;[9] 4-nitro-5-aminoacenaphthene, melting at 222°;[4] 4-nitronaphthalene-1,8-dicarboxylic anhydride, melting at 229° to 230°[4] for 220° given by Graebe.[10]

In conclusion it may be pointed out that the reason why the literature contains such a variety of melting points for certain derivatives of acenaphthene is that, in some instances, very numerous recrystallizations are required before a constant melting point is obtained, although the product may melt quite sharply after each crystallization.

FREDERICK M. ROWE

DYESTUFFS RESEARCH LABORATORY
COLLEGE OF TECHNOLOGY
MANCHESTER, ENGLAND
September 19, 1921

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[10] *Ann.*, **327** (1903), 77.

The Determination of Metallic Aluminium and Aluminium Oxide in Commercial Metal

Editor of the Journal of Industrial and Engineering Chemistry:

The paper of the above title in the September number of THIS JOURNAL warrants comment as to fundamental premises, logical development, and conclusions.

The density of hydrogen is assumed in the paper to be 0.08994, whereas the universally accepted value after Morley is 0.08987.

Apparently the weight of aluminium used was not reduced to the "*in vacuo*" basis. Adequate evidence is not adduced to indicate the purity of the hydrogen gas evolved in the reaction. However, it is in that portion of the paper headed "Data" that the logical development of the author's idea may be seriously questioned.

Column 1, Table I, shows the results obtained when it is assumed that 1 g. of "100 per cent pure" aluminium will displace 1.24068 liters of hydrogen (27.1 being the atomic weight of aluminium). The results obtained are quite at variance with what the author expected. Another chemist by other methods had determined the aluminium content to be 98.60 per cent. The author of the paper under discussion proceeds to accept these results of the other chemist and seeks to make his own results conform to them. Since the author finds 99.64 per cent, he assumes that the hydrogen equivalent (1241) employed by himself must be in error. He then solves the following proportion for X (the number of cc. of H equivalent to 1 g. aluminium):

$$X:1241 = 99.64:98.60$$

$$X = 1254.1$$

Now since a new value for the hydrogen equivalent of aluminium is obtained which confirms the other chemist's analysis, it is stated that a new atomic weight of 26.81 is indicated for aluminium. However, there is a failure to state that the value of 98.60 per cent found by the other chemist depends upon the atomic weight of aluminium being 27.1. If this chemist had used 26.81 as the atomic weight of aluminium instead of 27.1, he would have reported 98.36 per cent as the metallic aluminium content of the sample in place of 98.60 per cent actually reported. This in turn would lead the author of the paper under discussion into further difficulties, and he must perforce adopt still another value for the atomic weight of aluminium.

The author's statement that 1 g. of aluminium will displace 1254.1 cc. of hydrogen by reaction with a suitable reagent implies an atomic weight of 26.81 for aluminium. Since the author used as a basis of his calculation an analysis depending upon the atomic weight of aluminium being 27.1, we are forced to the conclusion that the proposed value of 26.81 is somewhat doubtful, depending as it does on the assumption that the atomic weight is 27.1.

The author has adduced no evidence to the effect that the accepted value for the atomic weight of aluminium is in error. Consequently, since the accuracy of his method, *i. e.*, the conformity of his results to those obtained by Rhodin, hinges on 26.81 being the atomic weight of aluminium, we are forced inevitably to the conclusion that the proposed method is unsound or that Rhodin's analysis is incorrect, or that both are in error.

As a matter of interest it may be pointed out that if the author's data for Run 106 are recalculated on the assumptions that the density of hydrogen is 0.08987, that the atomic weight after Richards and Krepelka is 26.963, and that the sample weight should be reduced to "*in vacuo*," we find a metallic aluminium content of 99.05 per cent. Again, if we summate Rhodin's analytical results for impurities other than Al_2O_3 we find them to total 0.95, which gives metallic aluminium content by difference of 99.05 per cent.

The author has not established the fact that oxide in metal is a serious problem, and no serious student of chemistry can agree with his conclusion that he has devised a method for the accurate estimation of metallic aluminium (and of oxide, indirectly) in commercial aluminium.

H. V. CHURCHILL

ALUMINUM COMPANY OF AMERICA
PITTSBURGH, PA.
September 20, 1921

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Editor of the Journal of Industrial and Engineering Chemistry:

The author frankly admits that in the paper under discussion he has inadvertently used what is probably a less accurate value of the weight of a liter of hydrogen than that of Morley, that no correction was made of weighing to the "*in vacuo*" basis, and that he failed to note the contradiction involved in his calculation of a new atomic weight of aluminium from data based on the present accepted value of 27.1.

He thanks Mr. Churchill for calling his attention to these matters and has corrected his data to conform to the suggested changes. After correcting weighings to "*in vacuo*" basis, using 0.8987 as the weight of a liter of H_2 and 27.1 as the atomic weight of Al, he obtains the figures shown in Column A below, which are placed along with Column I of the table as it appeared in the paper in question.

RUN		I	A
106		99.64	99.55
108		99.665	99.57
109		99.66	99.56
110		99.63	99.53
111		99.63	99.53
112		99.59	99.49
113		99.65	99.55
114		99.66	99.56
115		99.67	99.57
116		99.64	99.54
117		99.60	99.50
	Av.	99.64	99.54

The new figures are 0.1 per cent lower than the former ones, but are still far from agreeing even with the total aluminium of the metal sample. The discrepancy can be explained as due either to contamination of the hydrogen with air, to large errors in the analysis of the metal sample, or to the wrong value having been used (27.1) as the atomic weight of aluminium.

With regard to the hydrogen, such evidence as has been produced indicates that it carries no more gaseous impurities than were present in the apparatus at the start of a determination, to which attention was drawn in the original paper.

The analysis of the metal used has been checked in this laboratory with satisfactory closeness, considering the small amount of sample which was at hand, so that there is no doubt of the accuracy of the original analysis of Rhodin, within the limitations of the methods he used.

The author believes it is the atomic weight of aluminium which is at fault. Although Mr. Churchill says, "The author had adduced no evidence to the effect that the accepted value for the atomic weight of aluminium is in error," it is of interest to note that in Mr. Churchill's last paragraph but one, he himself has to use a value other than the accepted one in order to bring the "metallic aluminium content" into agreement with the figure which would be shown if aluminium had been found by difference.

Since the publication of this article some metal of much higher purity and more trustworthy analysis has been obtained, against which apparatus and method are to be checked up.

JULIAN H. CAPPS

BUREAU OF MINES EXPERIMENT STATION
PITTSBURGH, PENNSYLVANIA
October 31, 1921

Volume Increase of Compounded Rubber under Strain, and Recent Development in the Art of Rubber Microsectioning—Correction

In the articles by Henry Green of the above titles, appearing in the November and December 1921 issues of THIS JOURNAL, the following errors occur:

Page 1030, 1st column, 3rd line from bottom, "microscopically" should read "macroscopically."

2nd column, 3rd line from bottom, $V = 4/3\pi a \times a \times a$ should be written $V = 4/3 a \times a \times a$

Page 1131, 1st column, line 14, Fig. 1, *n* should read Fig. 1, *o*; line 18, *o* should be *n*.

Page 1132, 2nd column, line 2, "sulfur dioxide" should read "sulfur chloride."

SCIENTIFIC SOCIETIES

Fourteenth Annual Meeting of the American Institute of Chemical Engineers

The keynote of the meeting held at Baltimore, Md., December 6 to 9, 1921, was very obviously Gas Warfare and Chemical Preparedness. Most of the papers were on this general subject and the best attended and most interesting excursion was that to Edgewood Arsenal on the second day of the meeting.

The meeting opened on Tuesday morning at 9:15 at the Emerson Hotel with President David Wesson in the chair. The entire morning was devoted to a business session. The secretary reported the total membership as 529, an increase of 74 during the year. To meet the high cost of printing an assessment of $5.00 for active members and $2.50 for junior members had been voted by the Council for the coming year. After discussion the decision was reached not to make a permanent increase in dues. The Council also reported an amendment to the Constitution providing for Student Chapters similar to those affiliated with other engineering societies. By another resolution provision was made for the organization of local sections of the Institute.

Arthur D. Little, chairman of the Committee on Chemical Engineering Education, presented a very carefully prepared study of the courses in Chemical Engineering offered in all the technical schools and universities of the United States. Printing of this report was authorized, as was also the calling of a meeting of representatives of all institutions offering courses in Chemical Engineering, for the purpose of securing greater uniformity in courses offered.

The Committee on Atmospheric Pollution rendered a final report on pollution arising from sulfur dioxide fumes, stating that this problem had been solved by the investigation carried out by Dr. P. J. O'Gara, head of the Department of Agriculture and Smelter By-Products Investigation of the American Smelting and Refining Co., Salt Lake City, Utah. The results of this investigation will be published in the near future.

The election of officers for the coming year resulted as follows: Henry Howard, *president;* H. S. Miner, *third vice president;* John C. Olsen, *secretary;* F. W. Frerichs, *treasurer;* Chas. F. McKenna, *auditor;* Wm. H. Bassett, A. C. Langmuir, Alfred H. White, and A. E. Marshall, *directors.* By advance from second and third vice president, A. W. Smith became first vice president and Hugh K. Moore, second vice president.

The summer meeting is to be held in Buffalo and Niagara Falls in the latter part of June.

The most important resolutions passed were the following on the dye situation:

WHEREAS, the American Institute of Chemical Engineers assembled at its annual meeting at Baltimore, December 8, 1921, being convinced of the necessity of the embargo on dyes and synthetic organic chemicals as a measure essential for national defense and for the protection of the American Chemical Industry and holding, contrary to the belief of some, that this cannot be attained and regulated even by a very high protective tariff,

Therefore it hereby directs its officers to present this situation and this conclusion of the American Institute of Chemical Engineers to its representatives in Washington.

And the following on Chemical Warfare:

Be it resolved by the American Institute of Chemical Engineers in convention assembled in Baltimore, Md., December 8, 1921, that the following be sent to the American Delegation to the Conference on the Limitations of Armaments, the Advisory Committee thereof, and to our Senators and Representatives in Congress,

The campaign for the abolition of the use of gas in warfare is largely based on ignorance,

As Patriotic Americans, whose training and experience have been such as to enable us to better understand such technical matters, we state that chemical warfare is *now* much more humane than the older types. It is moreover the only type of warfare to which research and progress offer an almost certain promise of becoming still more humane,

We call attention to the fact that research in and preparation for gas warfare could be largely conducted secretly by an unscrupulous nation. The manufacture of many war gases is part of peace time industry. Effective chemical disarmament is therefore impossible,

In case of a life and death struggle between powers, we believe gases will be used, as gases represent real progress in the art of war, and you cannot arrest the hand of progress by rules and regulations,

We therefore urge for the proper defense of our country the imperative necessity of maintaining our Chemical Warfare Service.

President Wesson's address introduced the Symposium on Chemical Engineering and National Defense. In a paper on "Explosives and Fertilizers," Prof. Alfred H. White emphasized the urgent necessity of providing an adequate supply of fertilizers in order to maintain the fertility of our soils, which are rapidly being depleted. Dr. Raymond F. Bacon pointed out the humane aspects of gas warfare and the impossibility of its effective prohibition. The same point of view was taken by Maximilian Toch in a paper on "Chemistry and the Next War."

In discussing "Fundamental Research in Conservation and Defense," Mr. H. E. Howe called attention to a number of problems of fundamental importance which await solution. Dr. Robert M. Yerkes of the National Research Council explained the Research Information maintained under his direction.

In "The Chlorine Industry as an Essential Factor in our National Defense," Benjamin T. Brooks reviewed the capacity of the United States, for the production of chlorine, its uses, storage and transportation. Major Edward Holmes gave a similar survey of the lime industry.

In "Some New Products from Petroleum," Prof. J. H. James erported the results of a number of experiments on the distillation of low-grade petroleum products under oxidizing conditions.

A. E. Marshall discussed "Glass as a Material for Chemical Use," describing a number of installations in which this material has been successfully used and also the great possibilities for the employment of a glass having the properties of pyrex. In his paper on "Regenerative Evaporation," W. L. Badger presented a history of the attempts to utilize low pressure steam after compression in evaporators. Professor Badger pointed out the many difficulties to be overcome before this method would become commercially profitable.

Prof. Cavalier of France, exchange professor at the Johns Hopkins University, read a paper on the "Developments of the Chemical Laboratories in France," and showed a number of photographs of these laboratories under working conditions.

At a joint meeting with the Maryland Section of the American Chemical Society at the Johns Hopkins University on Thursday evening, Prof. J. C. W. Frazer explained the results obtained in the development of a catalyst by which carbon monoxide could be oxidized at room temperature to carbon dioxide. A gas mask had been developed utilizing this material. Prof. R. W. Wood showed a number of very interesting and very amusing applications of ultraviolet light.

The program of excursions was unusually complete; most of the chemical industries of Baltimore were open for inspection. On Wednesday afternoon the Curtis Bay industries were visited, including the plants of the U. S. Industrial Alcohol, The American Refractories, and the Davison Chemical companies. The greatest interest was shown in the experimental unit for drying air by means of silica gel and the freezing of water in a vacuum, the moisture being absorbed by silica gel.

More than 200 took the trip to Edgewood Arsenal. The entire morning was spent in inspection of the large installation of Nelson chlorine and caustic cells, the multiple effect evaporators, the gas mask factory, and the very extensive research laboratories. Luncheon at the Arsenal was followed by an address on Chemical Warfare by Brigadier General Amos A. Fries. After luncheon a field demonstration of all forms of gas warfare was witnessed with the greatest interest by the party.

On Friday afternoon a number of visits were made by small groups to various chemical plants, the largest party inspecting the large plant of the Baltimore Copper Works and the plant of the Standard Oil Company. At the latter plant the greatest interest was shown in the construction and operation of the improved Burton stills.

The social features of the meeting included a "Get-Together" at the Engineers' Club, at which a musical program was rendered, followed by dancing and a buffet supper. On Wednesday evening the ladies and members of the Institute and their guests attended a theater party tendered by the local committee and the local chemical industries. The subscription dinner was held on Friday evening at the Hotel Emerson.

In attendance and interest the meeting was the best which the Institute has ever held.

J. C. Olsen

Polytechnic Institute
Brooklyn, N. Y.

Officers of the Iowa and New York Sections of the A. C. S.

The officers of the Iowa Section for 1922 are as follows:

Chairman: Edward Bartow, Iowa City
Vice Chairman: R. W. Getchell, Cedar Falls
Secretary-Treasurer: L. Chas. Raiford, Iowa City
Councilor: J. N. Pearce, Iowa City

The recently elected officers of the New York Section are:

Chairman: Martin Hill Ittner
Vice Chairman: C. A. Browne
Secretary-Treasurer: B. T. Brooks
Executive Committee: R. H. McKee, Chas. H. Herty, J. E. Teeple, H. G. Sidebottom

Mr. Arthur H. Gallun

The following Resolution on the death of Mr. Arthur H. Gallun has been adopted by the Milwaukee Section of the American Chemical Society.

Whereas: In the death of Arthur H. Gallun, on November 9, 1921, the Milwaukee Section of the American Chemical Society recognizes the loss of one of its most valued members, who for the past eight years strove to make the Section an instrument of service for the general good, who by his substantial support assured the success of the work of its Library Committee, who was quick to aid the deserving and needy, who was active in the organization of the Leather Division of the American Chemical Society and had labored over plans for a tanning school that should bring about the coöperation of the best in both chemistry and industry, who was a staunch supporter of scientific research and encouraged the laboratories of his own plant to contribute to the development of chemistry, who generously endowed chemical research at Columbia University to be published without restriction, and who was a man much loved and admired by the Section.

Therefore, be it resolved that the Milwaukee Section of the American Chemical Society wishes to express its very deep sorrow on the loss of so valued a member and benefactor of science and to extend to his wife its most sincere sympathy.

The Birmingham Meeting of the American Chemical Society

The date at which the 63rd Meeting of the American Chemical Society will be held in Birmingham, Alabama, has been fixed as April 4 to 7, 1922.

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The Chairman and Secretary of the Cellulose Section are carefully considering the advisability of arranging for a meeting of that Section at Birmingham in April. The South is probably the largest cellulose-producing section of the country, and it should therefore be possible to have an enthusiastic meeting to listen to and discuss papers on cellulose and its derived products. It is requested that anyone planning to present a paper before this Section advise the secretary at once, even though the exact title may not be available until later. This request is made so that it can be ascertained whether a sufficient number who are interested in cellulose plan to attend the Birmingham Meeting of the Society to warrant holding a meeting of the Cellulose Section. The secretary's address is Gustavus J. Esselen, Jr., 248 Boylston St., Boston 17, Mass.

Nichols Medal for 1921

The Committee on the Nichols Medal Award met December 16 and decided not to award the medal for 1921. The retiring committee recommends to the 1922 committee that the last four numbers of the *Journal of the American Chemical Society*, which were not before them, be considered as a part of the 1922 chemical literature.

Calendar of Meetings

American Institute of Mining and Metallurgical Engineers—Spring Meeting, New York, N. Y., week of February 20, 1922.

American Ceramic Society—24th Annual Meeting, St. Louis, Mo., February 27 to March 2, 1922.

American Chemical Society—63rd Meeting, Birmingham, Ala., April 4 to 7, 1922.

A. C. S. Officers for 1922

The newly elected officers of the Society are:

President: Edgar F. Smith.

Directors: M. C. Whitaker, W. R. Whitney.

Councilors-at-large: A. M. Comey, E. C. Franklin, W. D. Harkins, W. Lee Lewis.

WASHINGTON LETTER

By WATSON DAVIS, 1418 Rhode Island Ave., Washington, D. C.

THE REDUCTION OF ARMAMENTS CONFERENCE

The Far-Eastern situation, one of the most important problems of the Washington conference, has been clarified, if not settled for the next ten years, by the Four-Power Treaty between the United States, England, France, and Japan, which the Senate has already begun to debate. The reduction of armaments proposal made by the American delegation seems to be near acceptance.

Chemical warfare, however, has not yet been considered by the conference itself, although the committee of technical advisers, which considered chemical warfare and made studies for the delegates to the conference, has practically finished its work. This committee consisting of Dr. Edgar F. Smith, President of the AMERICAN CHEMICAL SOCIETY, chairman; Brig. Gen. Amos A. Fries, Chief of the Chemical Warfare Service, U. S. A.; Col. W. H. Bartholomew, Great Britain; Prof. Charles Moureu and Prof. A. Mayer, France; Lieut. Col. N. Pentimalli, Italy; Maj. Gen. H. Haraguchi, Japan, has made its report to the heads of delegations but its recommendations probably will not be made public for at least a week.

While it is generally believed that the report of the technical committee on chemical warfare is favorable to that mode of fighting, current press reports state that it is understood that the complete abandonment of all forms of chemical warfare has been recommended to the American Arms Conference delegation by its official Advisory Committee. The Associated Press report says: "The Advisory Committee report was drawn by General Pershing and there is some intimation that it does not reflect the views of all other high army officials. In general, army officers are inclined to believe that poison gas or any other form of chemical warfare should be treated as any other military weapon." It is regarded as possible that the question of chemical warfare will not come directly before the conference, but that it will be referred to a continuing commission for study after the conference adjourns.

THE SENATE DYESTUFFS INVESTIGATION

The dyestuffs industry in the United States and the activities of importers of German dyestuffs will be investigated by the Senate Committee on the Judiciary as the result of a resolution introduced by Senator King of Utah, and passed by the Senate. The resolution directs the investigation of the alleged lobbying activities of both the American and German dye manufacturers. As originally introduced, it was directed at only the alleged American dyestuffs monopoly, but the insistence of Senator Frelinghuysen of New Jersey led to the inclusion of the importers of German dyestuffs. He charged that Germany is seeking by secret means to regain her control of the American dyestuffs market, and that a "carefully organized and strongly financed movement" is at work to this end. He urged a permanent embargo against German dyestuffs, and said that already there are in New York waters ships loaded with the German product waiting to unload, once the embargo provided for in the Emergency Tariff law is removed.

Senator Moses, in supporting the original King resolution, showed a large map with a circle containing the word "du Pont" located at Wilmington, Delaware. With radiating spider-like lines from this circle, he diagramed his conception of the extent of the control exercised by the alleged American dye monopoly.

"Representatives of the du Pont interests," said Senator Moses, "are connected with the League of Nations, the administration of the Versailles Treaty, the office of the Alien Property Custodian and other organizations." He also implicated various scientific societies and research organizations in and out of the Government.

SUSPENSION OF PUBLICATION OF GOVERNMENT PERIODICALS

A group of important scientific periodicals of the Department of Agriculture have suspended publication owing to the failure of Congress to give specific authority for their continuance after December 1, the date set by a provision of the Sundry Civil Act of March 4, 1921, for the suspension of all government department periodicals except those approved by Congress prior to December 1.

A resolution empowering the Congressional Joint Committee on Printing to authorize the continuance or discontinuance of these periodicals passed the Senate but did not come to a vote in the House before the adjournment of the last session of Congress. Therefore some forty-one publications issued by the government departments suspended publication, in most cases without even the customary obituary notice.

From a scientific standpoint, of those that are suspended, four Department of Agriculture publications are the most important: *The Experiment Station Record*, *The Journal of Agricultural Research*, the *Monthly Weather Review*, edited from the Weather Bureau, and *Public Roads*. Four other Department of Agriculture periodicals were doing a real service. The *Weekly News Letter* kept the 106,000 collaborators and employees of the department in touch with its activities and served to take current information to those especially interested in agriculture. Weather data were carried promptly by the weekly *National Weather and Crop Bulletin*. The weekly *Market Reporter* and the *Monthly Crop Reporter* went to those interested in agricultural statistics.

By the suspension of the forty-one periodicals, it has been estimated that from $500,000 to $1,000,000 will be saved each year. But scientists feel that this is false and mistaken economy. It is not inconceivable that even the temporary suspension of the quartet of periodicals mentioned may cause a much greater loss to the country than the supposed saving on the entire forty-one periodicals.

The inability to publish the results of important governmental researches, even excluding the suspension of the scientific periodicals, is becoming a serious situation. Printing appropriations of practically all governmental scientific bureaus have been badly cut and only the manuscripts that are most important can be published. Even these are usually many months in appearing.

HELIUM AS A BALLOON GAS

The flight of the navy dirigible, C-7, filled with helium, over Washington on December 5 was the first practical test of helium as a balloon gas on a large scale. This event will undoubtedly prove the beginning of a new era in lighter-than-air aviation, and it is a striking climax to four years of work by government chemists and engineers, largely directed by Dr. R. B. Moore of the Bureau of Mines. Helium has been raised from a chemical curiosity to a practical gas which surpasses hydrogen by being absolutely safe. The National Advisory Committee for Aeronautics, in its annual report, has just recommended that the Government acquire and seal for future use the best helium-producing gas fields, that the development of an efficient and economical process for the extraction and repurification of helium be continued, and that the Government inaugurate without delay the use of airships inflated with helium.

ANNUAL DEPARTMENTAL REPORTS

"The past year has been remarkable," says Brig. Gen. Amos A. Fries, Chief of the Chemical Warfare Service, in his annual report to the Secretary of War, "for the growth of understanding of the fundamental importance of chemistry in peace and war. With that growth has come a realization that the activities of peace and the activities of war are no longer capable of complete segregation." He pointed out that chemical warfare materials, as well as high explosives, are fundamentally bound up with the synthetic organic chemical industry.

The annual report of the Bureau of Chemistry of the Department of Agriculture tells of the work that has been done in studying processes used in industries related to agriculture. Some of the problems reported upon are: Making adhesives, cellulose, furfural, etc., from corncobs; manufacturing starch from potatoes; manufacturing a palatable sirup from the sweet potato; utilizing waste oranges and lemons; improving methods of tanning and testing leather; manufacture of rosin and turpentine; and study of the laws that govern the chemical reactions employed in the dye industry.

The annual report of the Commissioner of Patents for the fiscal year ending June 30, 1921, shows an increase of 34 per cent in the number of applications and an increase of 85 per cent in trade-mark applications. There were at the end of the fiscal year 49,334 patents awaiting action out of a total number of applications of 84,248. It also showed that the office had lost 163 scientifically and legally trained examiners, some of whom have been replaced by inexperienced men. The report as a whole pictured the deplorable condition of the Patent Office.

A new division in the Department of Commerce has been established to consider simplified commercial practices. It will be a subdivision of the Bureau of Standards, with William A.

Durgin of Chicago in charge. The work of the division will be devoted entirely to the elimination of waste as applied to commercial practices.

According to the latest figures there is a better trend in chemical exports of this country, but the volume of commodities in this group which are going abroad is still one-third of the volume for the corresponding period of a year ago. With the possibility of tariff legislation there has been a decided increase in the imports. The volume of trade, however, is still very much less than it was a year ago.

The Senate Finance Committee is at present considering individual schedules of the Tariff Bill and will continue to do so until some time next month. Further action on the chemical phases of the tariff cannot be expected until then or later.

It is believed here that the Secretary of War will recommend to Congress favorable action on Henry Ford's proposal to develop Muscle Shoals and that Congress will receive the definite plan shortly.

The Tariff Commission has been requested by the Senate Finance Committee to prepare for its use a volume similar to the Summary of Tariff Information compiled for the House Ways and Means Committee last January.

The U. S. Geological Survey's Commercial Atlas, Part II, will be issued about Jan. 1. This will give the distribution of developed and undeveloped water power throughout the world. Part III will deal with resources of mineral fuels and Part IV with the reserves of the principal metals.

December 14, 1921

LONDON LETTER

By Stephen Miall, 157 Haverstock Hill, Hampstead, N. W. 3, England

Industrial conditions here still form a large proportion of our thoughts, and we have now all made up our minds that a recovery is beginning and will be very slow and irregular in its growth. In this country and probably in this continent we can look forward to another year of poor trade and much unemployment. But all this is part of the natural cycle; riches beget pride, pride begets war, war begets poverty, poverty begets industry, industry begets riches, and so on. We are now in the state of poverty but here we are trying to live within our incomes and as a nation we shall succeed in doing it this year or next year or sometime. Our trouble is that some of our neighbors have not yet got so far as we have. Russia has ceased to have any income, Austria has so overspent her income that her currency is bought by the kilo, Poland can hardly buy anything and is not emerging yet from its considerable impecuniosity and Germany, formerly our best or nearly our best customer in many industries, seems to be going on the same path as Austria and Poland. Before the war Germany did not raise enough money to cover her national expenditure, during the war of course no effort was made to do this, and since the armistice she has probably been both unable and unwilling to make the attempt. The issue of paper money on a large scale is analogous in some respects to the issue of bonus share certificates by the company which is not very prosperous, and there is bound to come a time either in six months or some other number of months when this issue by Germany must stop. Five years ago it would have been incredible that Russian rubles should be worth only the paper they were printed on, and I suppose that Germany will at any rate stop printing marks when it costs more to print them than they will fetch. The time will surely come, and it seems to many of us not very far off, when the government of that country will find it impossible to carry on with the present financial methods. Then there will be political and labor troubles and Germany will find herself where we are now—poor, overtaxed, and faced with considerable unemployment. She is having her trade boom now; we had ours two years ago; both were overdone and to some extent unreal. How much of the profit or loss is a mere question of bookkeeping is hard to say. Ten years ago I owned ten houses worth £300 each, three years ago they were worth £550 each, now they are worth £450 each. Am I in fact any richer than I was? The same sort of delusion goes on in Germany at the present time; a man buys a ton of some chemical compound for say 20,000 marks, the next day it is worth 22,000 marks, and a fortnight afterward 30,000 marks. It may pass through many hands and everyone concerned makes a bookkeeping profit, and he and all his friends repeat the transaction to the utmost of their means and to their entire satisfaction. It seems as if the only way of avoiding a heavy loss in Germany is for each man to buy goods to the utmost extent of the credit he has, and he complacently thinks he is becoming richer. Surely one of these days they will wake up! I met recently in Geneva at the International Labor Conference some Germans whose expenses were about £3 sterling per day or at the present rate of exchange 30,000 marks per day. How long can the Germans continue to travel in other countries? Another man I heard of recently spent a holiday in Austria and had hard work to spend about £10 in three weeks, I mean he had to order expensive wines and luxurious dishes. We have become, whether we like it or not, a collection of more or less self-supporting states, and it is difficult to know whether, when we impose duties on chemicals imported from Germany, we are making the situation worse or merely making it easier for people to endure what is in fact a disagreeable necessity.

Organization of Federal Council

We are trying to do here what you seem to have done very efficiently in America, that is, so to organize British chemistry that chemist as a whole can make their voice heard and influence felt. The Chemical Society, the Society of Chemical Industry, the Association of British Chemical Manufacturers, the Faraday Society, the Public Analysts, the Dyers and Colorists and the other societies have appointed representatives to form a Federal Council, which is gradually getting into working order. But it is too recent a creation to make its influence felt in government circles; otherwise the Safeguarding of Industries Act—so far as chemicals are concerned—would have been very different. This country professes to be a democracy disguised as a monarchy; it is in fact a bureaucracy mainly recruited from an aristocracy; the officials who do the actual governing are usually about as sympathetic to science as stockbrokers or brigadier generals. In Parliament the men who understand chemistry and its needs could be numbered on one's fingers and most of these are naturally put into positions where their knowledge will not be liable to bias their views. Thus Sir Alfred Mond, who knows a good deal about the chemical industry, is in charge of the Ministry of Health; if Sir Joseph Thomson or Sir Ernest Rutherford were successful politicians we should probably find them Colonial Secretary and Director of Poor Law. The average politician seems to regard the chemist as something between an alchemist and a druggist—a clever crank, to be listened to with the courtesy the government official is accustomed to display, but who may be forgotten so soon as his back is turned. The Federal Council hopes that in time it may be able to keep the country on the right track in matters pertaining to chemistry.

November 15, 1921

Review of Scientific Instruments

A number of scientists have felt a need for adequate reviews and descriptions of scientific instruments. For some months the matter has been discussed by those interested, including the makers of apparatus, the National Research Council, the Bureau of Standards, and the Optical Society of America.

Arrangements have now been completed whereby the *Journal of the Optical Society of America* will add to its name *"and Review of Scientific Instruments,"* devoting a section to such reviews in addition to its regular editorial pages. The first number of the expanded journal is to appear April 15, 1922, and monthly thereafter.

Paul D. Foote, Bureau of Standards, is editor-in-chief, and F. K. Richtmyer, Cornell University, assistant editor-in-chief.

The Mineral Potash Corporation has been chartered under the laws of Maryland with a capitalization of $700,000 to begin the building and operation of a plant for the manufacture from powdered feldspar of an abrasive for polishing metals, enamels, and household goods. The lands upon which the feldspar deposits are located are at Ilchester, Howard County, Maryland.

OBITUARY

Joseph William Richards

Joseph William Richards was born in Oldbury, Worcestershire, England, on July 28, 1864. He came to this country in 1871, attended the public schools of Philadelphia, Pa., and subsequently received the following degrees from Lehigh University: A.C. (analytical chemist) in 1886; M.S. in 1891 and Ph.D. in 1893. In 1886 and 1887 he was employed in his father's metal refinery at Philadelphia, after which he was continuously employed in teaching at Lehigh University up to the time of his death. He was one of the founders of the American Electrochemical Society; its first president, 1902–3, and secretary 1907–1921. He held many offices in other societies and especially in the American Institute of Mining and Metallurgical Engineers, with which he was officially connected for more than a dozen years as councilor, director, and vice president; for seven years he was chairman of its Iron and Steel Committee. He was also appointed in several public capacities, such as member of the Engineering Council, Engineering Foundation, American Engineering Standards Committee, Engineering Division of the National Research Council, Naval Consulting Board; president of the Chemical Section of the Franklin Institute and its professor of electrochemistry for three years; member of the U. S. Assay Commission, member of the Jury of Awards, Department of Chemistry, National Export Exhibition, Philadelphia; member Jury of Awards and chairman of subjury on Metallurgy, Panama-Pacific International Exposition.

J. W. Richards

His most important books were a "Treatise on Aluminum," which is the established authority on this subject in English, and three small volumes on "Metallurgical Calculations" which have been translated into five foreign languages. He was also a voluminous contributor to technical literature by monographs and discussions.

His chief interest outside of his professional work was fondness for travel, a sympathetic taste for music and languages, and a deep interest in the study of religious and philosophic subjects. He was noteworthy for a seemingly tireless capacity for painstaking work, but in his relations to others he exhibited always a gentlemanly courtesy and an unselfish devotion to upbuilding the interests of engineers and chemists.

Bradley Stoughton

PERSONAL NOTES

President Edgar F. Smith, provost emeritus of the University of Pennsylvania, has been elected an honorary member of the Société de Chimie Industrielle, and also an honorary member of the Chemical, Metallurgical and Mining Society of South Africa.

Sir William Pope has been awarded the "Grande Médaille" and **Dr. F. G. Cottrell** has been elected an honorary member of the Société de Chimie Industrielle.

Dr. Ernest Fox Nichols has resigned the presidency of the Massachusetts Institute of Technology and his resignation has been accepted by the executive committee of the corporation. His decision resulted from the unfavorable condition of his health. Dr. Elihu Thomson, of Swampscott, chief consulting engineer of the General Electric Company, who served as acting president after the death of President Richard C. Maclaurin in January 1920, has again been appointed to that position.

Mr. Reuben L. Lindstrom, superintendent of the Point St. Charles Plant, Canadian Steel Foundries Ltd., died Dec. 12, 1921, at his home in Montreal. He left the Bettendorf Co., Bettendorf, Iowa, four years ago to become metallurgist with the Canadian Steel Foundries Ltd., a position which he filled until appointed superintendent of the St. Charles Works eighteen months ago.

Dr. J. A. Gunton has been appointed head of the chemistry department in Transylvania College, Lexington, Ky. Dr. Gunton recently received his doctorate of philosophy from the University of Illinois.

Mr. Lauchlin M. Currie resigned as research chemist with the Hooker Electrochemical Company at Niagara Falls to accept a position as assistant professor of mathematics in Davidson College, Davidson, N. C.

Mr. Paul R. Dawson, formerly teaching fellow in chemistry at the University of North Carolina, has accepted an appointment as assistant biochemist in the Soil Fertility Investigations, Bureau of Plant Industry, Washington, D. C.

Mr. W. S. Mahlie, formerly in the laboratory of the Buckeye Steel Castings Co., Columbus, Ohio, is at present employed as chemist and bacteriologist for the City of Fort Worth, Texas.

Mr. L. C. Humphrey has entered the graduate school at the University of Minnesota, Minneapolis, Minn., and will take advanced work in chemistry toward the doctorate degree. He will also do some assisting in the School of Chemistry. Mr. Humphrey, previous to September 1, was instructor in chemistry at Montana State College, and was also in charge of the Montana Oil Laboratory at Montana State College, Bozeman, Mont.

Dr. Austin Bailey, who has recently been employed as superintendent of the apparatus division of the Corning Glass Works, Corning, N. Y., has resigned his position to accept an assistant professorship in the physics department at Kansas University, Lawrence, Kans.

Mr. R. F. Remler, formerly assistant chemist in the nutrition department of the Ohio Agricultural Experiment Station, Wooster, Ohio, now holds an Industrial Fellowship at the Mellon Institute of Industrial Research, Pittsburgh, Pa.

Mr. R. E. Wilkin, after receiving his master's degree at the University of Iowa, Iowa City, Iowa, resigned his assistantship there to accept a position as instructor in chemistry at Kansas State Agricultural College, Manhattan, Kans.

Mr. John Jos. Gorrell, who has been connected with the Technical Direction Bureau of the Aluminum Company of America, New Kensington, Pa., has accepted a position as analytical chemist with the Cambria Steel Co., Johnstown, Pa.

Mr. S. G. Byam, chief chemist at the Fairfield Rubber Works of E. I. du Pont de Nemours & Co., has resigned from that position to become chief chemist with entire charge of the technical development at the Plymouth Rubber Co., Canton, Mass.

Mr. Parry Borgstrom, formerly research associate at the Research Laboratory of Applied Chemistry, Massachusetts Institute of Technology, Cambridge, Mass., is now instructor in physiological chemistry, Tulane University Medical School, New Orleans, La.

Mr. John H. Waldo has left Illinois, where he received his undergraduate work and master's degree, to assume the position of assistant professor in chemistry and physics in Morningside College, Sioux City, Iowa.

Dr. Clarence J. Monroe recently received his Ph.D. degree from the University of Chicago, Chicago, Ill., and has been appointed assistant professor in physical chemistry at the Missouri School of Mines and Metallurgy, Rolla, Mo.

Mr. Jas. A. Holladay was recently transferred from the Niagara Works of the Union Carbide and Electro Metallurgical Companies to take up work with the Union Carbide & Carbon Research Laboratories, Inc., Long Island City, N. Y.

Mr. Joseph P. Grennan, head of the department of chemistry in the Charles M. Schwab Laboratories at St. Francis College, Loretto, Pa., is now professor of analytical chemistry at Gonzaga University, Spokane, Wash.

Mr. A. C. Reed, who resigned as assistant materials engineer from the Navy Department, Bureau of Construction and Repair, last June, now holds a similar position with the department of maintenance and repair, Emergency Fleet Corporation, New York City.

Mr. Lincoln T. Work has been appointed instructor in chemical engineering at Columbia University for the year beginning October 1. Mr. Work completed three years of graduate work in this department at Columbia last June.

Miss Omega Hilton has discontinued work as chemist of the American Nitrogen Products Company to take a position as instructor in pharmacy at the University of Washington, Seattle, Wash.

Miss Ruth O'Brien recently returned to the chemistry department of Iowa State College, where she is associate professor of household chemistry, after a year's leave of absence which was spent working under Dr. Stieglitz at the University of Chicago.

Mr. D. B. Dill, who has been in charge of the San Diego branch of the Food Research Laboratory, conducting investigations in the canning of fish and the handling of fishery by products, has accepted a transfer to the Food and Drug Inspection Laboratory at Seattle, Wash., the Food Research Laboratory at San Diego having been discontinued.

Mr. L. J. Baney is at present superintendent of the Briggs Chemical Co., Amherst, Ohio, manufacturers of coal-tar products, having resigned from the Chemical Warfare Service at Edgewood Arsenal, Md.

Mr. Milton R. Louria, who completed his chemical engineering course at Columbia University last June, has been appointed instructor in chemistry at the University of Maine for the current year.

Mr. C. L. Hippensteel, following graduation from the School of Chemical Engineering of Purdue University, Lafayette, Ind., last June, accepted a position in the engineering department of the Western Electric Co., New York City.

Mr. F. H. Tucker has become associate chemist in the Bureau of Public Roads, Washington, D. C., having been connected with the Chile Exploration Company for the past year as research chemist in their New York laboratory.

Dr. Walter A. Lawrence, associate professor of chemistry at McMaster University, Toronto, has been appointed professor of chemistry and head of the department at Bates College, Lewiston, Me.

Mr. C. W. Botkin, who has been doing research on the refining of shale oil at the Colorado School of Mines for the past fifteen months, has accepted a position as head of the chemistry department in the New Mexico College of Agriculture and Mechanic Arts, State College, N. M.

Mr. E. Wertheim, formerly a graduate student at the University of Chicago, Chicago, Ill., has been appointed associate professor of organic chemistry at the University of Arkansas, Fayetteville, Ark.

Mr. Fred J. Allen recently received his M.S. degree from Purdue University and has returned to Corvallis, Ore., after a leave of absence, to resume his work as instructor in the chemistry department of the Oregon Agricultural College.

Mr. William U. Gallaher has been appointed chemist at the Illinois State Water Survey, Urbana, Ill., with the opportunity of pursuing further study at the University of Illinois. Mr. Gallaher received his degree of Master of Science from the University of Iowa last spring.

Mr. Frank Henry, formerly with the Dunlop Tire and Rubber Corp., Buffalo, N. Y., is at present with the Rochester Gas and Electric Corp., Rochester, N. Y., where he is doing research (chemical) work mainly on gas plant problems.

INDUSTRIAL NOTES

The executors of the estate of John C. Wiarda have sold the assets of their chemical manufacturing and jobbing business to Howard B. Bishop of 101 Park Ave., New York, who will continue the business under the name of John C. Wiarda & Co., Inc., and will enlarge and extend the manufacturing and jobbing facilities.

A special faculty research committee has been organized at Oberlin College to coöperate with the National Research Council. Dr. S. R. Williams, head of the department of physics, is chairman, while other members include members of the departments of mathematics, sociology, psychology, chemistry, and geology.

The main building of the Heyden Chemical Works plant at Garfield, N. J., was destroyed by fire on December 12, 1921, causing the death of four men and injuring several more. The fire was the result of an explosion, and within a few minutes the building was a mass of flames which spread to half a dozen other buildings and threatened nearby tanks of alcohol and explosive materials. The damage is estimated at more than $200,000. The plant was sold by the Alien Property Custodian about two years ago and purchased by A. A. Ryan for $1,500,000.

A huge pile of lava rock at Husum, Washington, which had for years harbored numbers of rattlesnakes was cleared recently by the use of mustard gas. The gas was freed in the porous formation through 150 ft. of garden hose and within half an hour the snakes blinded and half dead came out and were killed. Other communities have requested the gas for the same purpose.

The Dosch Chemical Co., organized in Delaware with a capital of $2,500,000, has purchased the property of the Bernheim Distilling Co., at Louisville, Ky., and will establish a large insecticide and spraying plant. The plant is to have four departments—manufacturing, research, public service, and advertising. Between 12,000,000 and 20,000,000 lbs. of low-grade tobacco will be used annually. A large variety of preparations used by agriculturists and horticulturists are to be produced, in addition to dusting machines and other equipment required in the use of insecticides. It is believed the plant will begin operations in January.

The building of the Calco Chemical Co., at Eggers' Station, N. J., was destroyed by fire recently, with an estimated loss of $50,000.

Statistics compiled by The Engineering Agency show that the number of inquiries for technical help in manufacturing construction, industrial and commercial work steadily decreased from February 1920 to June 1921, reaching a minimum in June, since when there has been a slow but comparatively steady increase. During the declining period many employers were forced to cancel their inquiries because of the falling off of their work, but since June there have been very few canceled inquiries.

After intensive research, the National Aniline and Chemical Company has established a rubber laboratory which will coöperate through consultation and advice with rubber factories. Through the efforts of this laboratory the National will be able to present products definitely standardized and especially adapted to rubber compoundings.

The Morris Fertilizer Company of Chicago has completed the construction and equipment of a modern high-grade hydraulic pebble phosphate mining plant at Bartow, Fla., where the company owns over 2000 acres of high-grade pebble phosphate running unusually low in its content of iron and aluminium. The company will specialize in the mining, washing, and drying of the material for export through the port of Tampa. Operations have already been begun and several cargoes have been shipped abroad. A complete laboratory and corps of chemists are maintained in order to have at all times analytical control of the rock mined and stored.

The Seydel Manufacturing Co., of Jersey City, N. J., has merged with the Nitro Products Corporation, Nitro, W. Va., to form the Seydel Chemical Co., the manufacturing base of which will be located at Nitro. The general offices and laboratories of the new company will be located at Jersey City. Herman Seydel, president of the Seydel Mfg. Co., is president of the Seydel Chemical Co.; the other officers are Paul Seydel and Frank C. Pitcher, vice presidents, and J. B. Pitcher, formerly president of the Nitro Products Co., secretary and treasurer.

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. Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Commerce Reports mailed weekly is $3.00 per year, payable in advance, to the Superintendent of Documents.

CONGRESSIONAL COMMITTEES

Metric System. Hearing before subcommittee on S. 2267, to fix metric system of weights and measures as single standard of weights and measures for certain uses. October 11–13, 1921. Part I. 50 pp.

TARIFF COMMISSION

Tariff Information Surveys. Revised edition, 1921.

C–16. On articles in paragraph 143 of Tariff Act of 1913 and related articles in other paragraphs. **Aluminium, magnesium, calcium, barium, sodium, and potassium, ores, metals, and manufactures.** 80 pp. Paper, 5 cents.

C–17. On articles in paragraphs 144 and 145 of Tariff Act of 1913 and related articles in other paragraphs. **Antimony, antimony alloys, and antimony salts.** 76 pp. Paper, 5 cents.

C–21. On articles in paragraphs 152 and 153 of Tariff Act of 1913 and related articles in other paragraphs. **Lead.** 63 pp. Paper, 5 cents.

FL–21. On articles in paragraphs 518–537 of Tariff Act of 1913 and related articles in other paragraphs. **Iron ore, pig iron, and scrap.** 103 pp. Paper, 10 cents.

N–20. On articles in paragraph 367 of Tariff Act of 1913 and related articles in other paragraphs. **Asbestos.** 56 pp. Paper, 5 cents.

C–19. On articles in paragraphs 147–150 of Tariff Act of 1913 and related articles in other paragraphs. **Copper and copper alloys.** 100 pp. Paper, 10 cents.

C–23. On articles in paragraph 155 of Tariff Act of 1913 and related articles in other paragraphs. **Nickel ore, matte, metal, and manufactures** 32 pp. Paper, 5 cents.

C–25. On articles in paragraphs 159 and 160 of Tariff Act of 1913 and related articles in other paragraphs. **Quicksilver.** 30 pp. Paper, 5 cents.

FL–6. On articles in paragraphs 403–408 of Tariff Act of 1913 and related articles in other paragraphs. **Arsenic and other articles.** 56 pp. Paper, 5 cents.

FL–10. On articles in paragraphs 447–457 of Tariff Act of 1913 and related articles in other paragraphs. **Coal and coke.** 56 pp. Paper, 5 cents.

FL–20. On articles in paragraph 517 of Tariff Act of 1913 and related articles in other paragraphs. **Platinum, platinum metals, gold and silver.** 70 pp. Paper, 5 cents.

WAR DEPARTMENT

Air Service

Thermometers. Laboratory test on Hartmann & Braun electric thermometer. Equipment Section Report. 4 pp. 1921. (Air Service Information Circular, Aviation, 3. No. 277, October 1, 1921.)

PUBLIC HEALTH SERVICE

An Occupational Dermatoconiosis among Zinc Oxide Workers. J. A. TURNER. Public Health Reports, 36 (November 4, 1921), 2727–32. The following conclusions are drawn from this study: Zinc oxide is considered a nontoxic substance, and from the chemical analysis it is evident that the adulterating substances are in insufficient amount to be harmful. It is a nonpoisonous material, but is capable of acting as a mechanical conveyor of bacteria. The zinc oxide, body debris, and bacteria are forced into the sebaceous glands, distending them. This action is aided by free perspiration and the rubbing together of two body surfaces. It is probable that the presence of the foreign substances, and the increased tension due to the retained secretion, produce sufficient irritation of the gland walls to allow an invasion of the bacteria and a resulting infection.

The Treatment of Leprosy with Chaulmoogra Oil. Public Health Reports, 36 (November 11, 1921), 2769–70. In regard to the treatment of leprosy with the ethyl esters of chaulmoogra oil it is stated that their use has resulted in the apparent cure of the disease in a considerable number of cases, but whether these "apparent cures" be permanent or not is a matter which requires time to determine. The results have, however, led to the belief that a therapeutic agent has been developed which surpasses in value everything which has been brought forward up to the present time.

DEPARTMENT OF THE INTERIOR

General Land Office

Potash Regulations under Act of October 2, 1917. Approved March 21, 1918. Reprint with slight changes, 1921. Circular 594. 21 pp. The circular contains rules and regulations governing the issuance of permits authorizing exploration of public lands for potassium; form of permit authorizing exploration of public lands for potassium; regulations pertaining to leases for lands containing potash; form of application for lease; form of lease of potash lands; regulations for permits for camp site and refining works; form of use permit for camp site or refining works; patents for lands containing potash, and quotes in full the act authorizing exploration for and disposition of potassium.

GEOLOGICAL SURVEY

Iron Ore, Pig Iron and Steel in 1919. E. F. BURCHARD. Separate from Mineral Resources of the United States, 1919, Part I. 32 pp. Published October 14, 1921. The problem that confronted leaders in the iron and steel industry in the United States at the beginning of 1919 was readjustment from war-time to peace-time conditions. Iron-ore production decreased 13 per cent, a decrease of 1.6 per cent as compared with the production of the last pre-war normal year.

Zinc in 1919. C. E. SIEBENTHAL AND A. STOLL. Separate from Mineral Resources of the United States, 1919, Part I. 12 pp. Published October 13, 1921. The primary zinc produced from domestic ores in 1919 was valued at $66,032,000, based on the average selling price, as compared with $89,618,000 in 1918—a decrease of 26 per cent. The quantity decreased 8 per cent.

Stone in 1919. G. F. LOUGHLIN AND A. T. COONS. Separate from Mineral Resources of the United States, 1919, Part II. 37 pp. Published October 18, 1921. About 65,539,000 short tons of stone were sold in the United States in 1919, 4 per cent less than in 1918, and 22 per cent less than in 1917. The total value of the stone sold in 1919 was $96,709,143, a value greater than any previously recorded.

Feldspar in 1920. L. M. BEACH. Separate from Mineral Resources of the United States, 1920, Part II. 2 pp. Published October 29, 1921. The quantity of feldspar marketed in 1920 was 114 per cent greater than in 1919 and 53 per cent greater than in 1918.

Abrasive Materials in 1920. L. M. BEACH AND A. T. COONS. Separate from Mineral Resources of the United States, 1920, Part II. 5 pp. Published October 28, 1921. The following table gives the value of all abrasive materials consumed in the United States, 1916–1920:

	1916	1917	1918	1919	1920
Natural abrasives	$1,664,339	$2,385,165	$2,864,332	$2,887,902	$4,299,812
Artificial abrasives	2,935,909	8,137,242	6,940,000[1]	5,019,779[2]	6,269,084[2]
Imports ...	555,850	812,303	1,187,632	2,237,077	4,425,409
	5,156,098	11,334,710	10,991,964	10,144,758[2]	14,994,305[2]
Exports ..	4,452,741	6,621,884	6,056,242	6,138,366	7,025,621
Apparent consumption....	703,357	4,712,826	4,935,722	4,006,392	7,968,684

[1] Estimated and not including entire production during second half of 1918.

[2] Not including production of one large company.

Mineral Waters in 1920. W. D. COLLINS. Separate from Mineral Resources of the United States, 1920, Part II. 6 pp. Published October 29, 1921. The term "mineral water" as here used applies to water that is bottled and sold in its natural state or only slightly altered from its natural state. The statistics given refer only to domestic mineral waters that have been sold. Three uses of mineral waters are recognized—table use, medicinal use, and use in the manufacture of soft drinks.

Gold and Silver in 1919. General Report. J. P. DUNLOP. Separate from Mineral Resources of the United States, 1919, Part I. 45 pp. Published October 31, 1921. Domestic smelters and refiners produced 2,918,628 fine oz. of gold and 56,682,445 fine oz. of silver from domestic sources in 1919, also 668,161 fine oz. of gold and 57,806,123 fine oz. of silver from foreign ores and bullion, an increase of 101,275 oz. of gold and 1,826,703 oz. of silver compared with the corresponding figures for 1918. The foreign ores came mainly from Mexico, Canada, and Peru.

Gold, Silver, Copper, and Lead in South Dakota and Wyoming in 1920. Mines Report. C. W. HENDERSON. Separate from Mineral Resources of the United States, 1920, Part I. 6 pp. Published November 3, 1921. The ore mined and treated yielded in recovered gold 0.1668 oz. or $3.45 a ton, as compared with $3.65 a ton in 1919. The mills of the state treated 1,356,079 tons of ore, which yielded as bullion $4,673,514 in gold and 87,319 fine oz. of silver, valued at $95,178, an average recovery per ton of $3.45 in gold and 0.064 oz. in silver, as compared with $3.62 in gold and 0.086 oz. in silver in 1919. The lead produced in South Dakota in 1920 was 19,735 lbs. less than in 1919. No gold, silver, or copper was produced at mines in Wyoming in 1920.

Sand and Gravel in 1920. L. M. BEACH. Separate from Mineral Resources of the United States, 1920, Part II. 10 pp. Published November 5, 1921. In spite of such hampering conditions as an insufficient supply of cars, the high cost of transportation, and the disorder of the local markets, the quantity of sand and gravel produced in the United States in 1920 increased 16 per cent and the value 43 per cent over 1919.

Lime in 1920. G. F. LOUGHLIN AND A. T. COONS. Separate from Mineral Resources of the United States, 1920, Part II. 11 pp. Published November 3, 1921. Although more lime was produced in 1920 than in 1919, the supply was not large enough to meet the demand. The shortage was not due to the inability of the plants to increase their output but to conditions beyond the control of the lime makers. Nearly all lime producers reported higher prices in 1920 than in 1919. There is every reason to predict better prospects for the lime industry.

Lead in 1920. General Report. C. E. SIEBENTHAL AND A. STOLL. Separate from Mineral Resources of the United States, 1920, Part I. 11 pp. Published October 14, 1921. The output of refined lead in the United States from domestic ores in 1920 was 476,849 short tons, valued at $76,296,000 at the average selling price of pig lead in New York, a gain, as compared with 1919, of 12 per cent in quantity and of 70 per cent in value.

Slate in 1920. G. F. LOUGHLIN AND A. T. COONS. Separate from Mineral Resources of the United States, 1920. Part II. 9 pp. Published October 12, 1921. The general industrial conditions in the slate industry in 1920 were seemingly somewhat better than in the three or four preceding years. Prices advanced for all slate products from 10 to 30 per cent, or enough to cover advances in labor and coal. The total quantity of mill stock sold in 1920 was an increase of 33 per cent over the quantity sold in 1919, but 24 per cent less than that sold in 1913, the record year.

Carbon Black Produced from Natural Gas in 1920. E. G. SIEVERS. Separate from Mineral Resources of the United States, 1920, Part II. 5 pp. Published October 13, 1921. The total quantity of carbon black produced from natural gas in the United States in 1920 decreased 1.4 per cent from 1919, notwithstanding an increase in the number of plants. In 1919 the plants were still operating at or near full capacity on account of the war, but since normal conditions have been restored the production has decreased. The output in 1920 was made by 19 producers. The prices received ranged from 4 to 27 cents a pound. The average daily production in 1918 was 119,178 lbs.; in 1919, 142,621 lbs.; and in 1920, 140,608 lbs.

BUREAU OF MINES

Selected Bibliography of Oil Shale. Compiled by E. H. BURROUGHS AND M. J. GAVIN. Reports of Investigations. Serial No. 2277. 66 pp. Published September 1921.

The Recovery of Unburned Fuel from Boiler Furnace Refuse. THOMAS FRASER AND H. F. YANCEY. Reports of Investigations. Serial No. 2281. 3 pp. Published September 1921. It is believed that the recovery of unburned fuel from boiler furnace refuse by the use of concentrating tables would pay only in large plants. Considering the present freight rates, the saving of transportation charges on fuel recovered at the plant is obvious. Experiments conducted by washing on coal-washing tables, however, show that continuous operation of a one-table unit would be possible at a power plant producing 120 tons of refuse per 24 hrs.

Natural Gas-Gasoline Blends. D. B. DOW. Reports of Investigations. Serial No. 2279. 2 pp. Published September 1921. The most common blending material now used in the Mid-Continent field is a naphtha ranging in gravity from 50°–52° B., with an end-point of 450° F. or less.

Hot High-Nitrogen Gas in a Metal Mine. G. E. MCELROY. Reports of Investigations. Serial No. 2282. 3 pp. Published September 1921.

The Utilization of Waste Slate as a Filler. OLIVER BOWLES. Reports of Investigations. Serial No. 2283. 5 pp. Published September 1921. All of the information available indicates that waste slate may be used to advantage as a filler in mechanical rubber goods and in some classes of oilcloths, floor coverings, and window shades. Apparently it is not adapted for use in rubber of a grade used in automobile tires. For plastic roofing and flooring products containing coal tar it has long been in use and constitutes a very satisfactory filler.

The Determination of Oxides of Nitrogen. V. C. ALLISON, W. L. PARKER, AND G. W. JONES. Technical Paper 249. 13 pp. Paper, 5 cents. 1921. This paper describes a method for determining small quantities of oxides of nitrogen, other than N_2O. It has been developed from the usual procedure of water analysis. With a 250-cc. sample as low as 10 parts of oxides of nitrogen (other than N_2O) per million parts of air can be determined with an accuracy of about 5 parts per million.

Production of Explosives in the United States during the Calendar Year 1920 with Notes on Mine Accidents Due to Explosives. W. W. ADAMS. Technical Paper 291. 44 pp. Paper, 5 cents. 1921. The production of explosives in the United States during the calendar year 1920 showed a marked recovery from the slump in 1919. The production (excluding exports) was 537,954,750 lbs., an increase of 120,320,280 lbs., or about 29 per cent, as compared with the preceding year. Of this 47 per cent was black blasting powder, 43 per cent high explosives other than permissible explosives, and 10 per cent permissible explosives. As compared with the year 1919, there was an increase of 41 per cent in the production of black powder, 15 per cent in "high" explosives, and 39 per cent in explosives classified as "permissibles."

Recent Articles on Petroleum and Allied Substances. Compiled by E. H. BURROUGHS. Reports of Investigations. Serial No. 2284. 32 pp. Issued October 1921.

Rate-of-Production Curve and Its Application to the Valuation of Oil Properties. W. W. CUTLER. Reports of Investigations. Serial No. 2285. 5 pp. Issued October 1921.

Bureau of Mines Experimental Tunnel for Studying the Removal of Automotive Exhaust Gas. A. C. FIELDNER AND J. W. PAUL. Reports of Investigations. Serial No. 2288. 3 pp. Published October 1921. In coöperation with the New York and New Jersey State Bridge and Tunnel Commissions, the Bureau of Mines has just completed the construction of an experimental tunnel in the Bureau's experimental mine at Bruceton, near Pittsburgh, Pa. The purpose of this tunnel is to make a final study of the ventilation problems arising in the adequate ventilation of vehicular tunnels for automobiles and trucks.

Bentonite. R. B. LADOO. Reports of Investigations. Serial No. 2289. 5 pp. Issued October 1921. Particular attention is directed to the commercial utilization of bentonite in paper making, as a filler in the manufacture of soap, as an ingredient in gypsum and lime plasters, as a superior adhesive paste, as a water softener, and its possible use to dewater crude petroleum.

Viscosities and Pour Tests of Typical Crude Oils from the Eastern and Rocky Mountain Producing Fields of the United States. E. W. DEAN, A. D. BAUER, AND W. B. LERCH. Reports of Investigations. Serial No. 2290. The figures which form a part of the report show that the crude oils from the eastern producing fields vary only moderately in viscosity and pour test. The pour test figures for the Rocky Mountain crude oils are noticeably variable.

Monthly Statement of Coal-Mine Fatalities in the United States, August 1921. W. W. ADAMS. 11 pp. Paper, 5 cents. 1921.

COMMERCE REPORTS

Statement comes from Chile that an agreement has been concluded between the Association of Nitrate Producers and European and American buyers and ratified by the producers on October 27, 1921, which set the prices of nitrate until July 1922. Shipments from Chile are not likely to increase greatly until the end of the year 1922 unless there is an improved demand for fertilizer in America and Europe. (P. 566)

There has been encouraging improvement in the British **tin-plate** trade. Total exports for August were the largest for any month since April. The local industry feels the competition of the United States in the foreign tin-plate markets, finding it difficult to combat owing partly to the high cost of production. (P. 569)

A market is reported in southern Sweden for **imitation leather.** This market is said to be able to import from the United States $268,000 worth annually. (P. 574)

The third series of articles on the **petroleum** industry in Mexico contains a list of the companies operating in Mexico, the production of oil by zones and companies, and the number and capacity of refineries, storage tanks, and pipelines. (Pp. 590–7)

The Czechoslovak Office of Foreign Trade has made the following reduction in export duties: Industrial **kaolin** not used in the manufacture of porcelain and ceramics reduced from one-half of 1 per cent to one-fourth of 1 per cent of the invoice price (Sept. 1, 1920). (P. 608)

The **copra** trade of the Pacific is reviewed, and the report is accompanied by tables showing the imports and exports of copra in tons for each of the importing and exporting countries of the Pacific, including British and Dutch Malaya. (Pp. 616–9)

The 1921 **olive** crop in southern Italy is estimated to be an increase of 50 per cent over that of last year. Ordinarily the proportion of oil varies from 20 to 40 per cent, according to the quality of the fruit. (P. 650)

The production of **olives** in the Cadiz district will be substantially the same as in 1920. The yield of olive oil will also be approximately the same as in 1920. (P. 651)

A decree recently issued by the Austrian government permits the importation of the following articles free of duty: **Coconut and palm oils, mineral oils,** and **lignite.** (Pp. 652–3)

By a decree of October 3, 1921, the duty of 1 cent per kilo shall be levied on **copper, bronze,** and **brass** when imported into Salvador in ingots as raw material for industrial purposes. (P. 654)

JAPANESE MINERAL PRODUCTION

Minerals	June 1920	 1921	January–June 1920	 1921
Gold, oz.	18,000	21,000	126,000	124,000
Silver, oz.	420,000	357,000	2,570,000	2,330,000
Copper, lbs.	11,900,000	10,200,000	73,100,000	61,000,000
Iron, metric tons	4,870	3,100	34,000	18,400
Coal, metric tons	2,220,000	1,840,000	13,400,000	11,900,000
Petroleum, gal.	7,040,000	7,480,000	44,400,000	45,100,000
Sulfur, metric tons	3,700	2,700	22,000	13,000

It is noted from these figures that Japan's production of **minerals** and **ores** during the first half of the current year decreased in all cases except that of petroleum, which registered a slight increase of 1.5 per cent, compared with the first six months of the preceding year. (P. 659)

A slight improvement in the Japanese **chemical market** is noted. (P. 660)

The production of **glycerol** in Japan and China's trade in it are described. (P. 660)

A New South Wales iron company has taken up large areas on the west coast of Tasmania, which contain deposits of high-grade **iron ore.** It is expected that at least 20,000 tons of iron ore monthly will be drawn from these deposits. (P. 661)

The **petroleum** industry at Baku is at a standstill as regards production, and refining is practically stopped from lack of soda and acid. (P. 663)

The corrected Mexican **mineral** statistics for the January–June 1921 period are as follows:

	Pounds
Gold	22,972
Silver	2,033,129
Copper	101,538,043
Lead	267,716,152
Zinc	31,665,104
Quicksilver	170,261
Antimony	3,466,475
Graphite	6,418,777
Tungsten	76,083
Tin	3,501
Arsenic	2,642,890
Manganese	1,848,849

(P. 666)

The following lists of Brazilian importers and dealers have been mimeographed and copies may be obtained from the Bureau of Foreign and Domestic Commerce:

Importers of chemicals and dyes
Importers of drugs
Importers and dealers in oils

(Pp. 667–8)

An English translation of two projects for **petroleum** legislation presented to the Argentine Republic by the President, September 23 and 25, 1919, and also a translation of the President's message of July 20, 1921, on the same subject, are on file at the Bureau of Foreign and Domestic Commerce. (P. 675)

A favorable market for American **paints** and **varnishes** is reported in South Africa. (P. 697)

Portugese East Africa also offers a market for **paints** and **varnishes.** (P. 697)

The **metal industries** of Finland are described and the report is accompanied by tables showing the imports and exports of metals and manufacture. (Pp. 699–702)

The discovery of a large deposit of high-grade **iron ore** on the shores of Lake Athabasca, Alberta, Canada, is reported. The ore is said to contain 64 per cent of metallic iron. (P. 702)

There is a large **radium** content in the uranium ore found at Jachymov, in Bohemia, near the frontiers of Saxony. Although the radium production in the United States is greater as to quantity, the ores of Jachymov are richer in quality. The known supply of radium in the Jachymov district will last for 20 yrs., at the present rate of production. There are several by-products of considerable importance. Uranium dyes are produced, eleven workmen being employed in the dye factory. (P. 726)

Mineral fertilizers are finding a growing market among the farmers and orchardists in southern Spain according to reports of the American consuls at Cadiz and Seville. A steady increase is noted, and 20,000 tons have been given as an estimate as the probable consumption this year in the Seville district alone. (P. 726)

A market for **copper sulfate** is reported in southern Italy. (P. 726)

An important meeting was recently held at Rome to discuss means of assisting the **sulfur** industry, which is at present undergoing a period of depression. There are 200,000 tons of sulfur unsold in Sicily. It has not been possible to find a market for it in competition with American sulfur, which is delivered in Europe at about 520 lire per ton. The meeting adjourned without having attained any results. (P. 727)

Reports from Buenos Aires state that the Argentine **oil** market is keenly competitive and it is advisable for any firm contemplating the establishment of an agency to send a thoroughly competent expert to study the whole oil situation. (P. 739)

A market for American **gasoline** is said to exist in Natal. (P. 778)

A copy of the new **petroleum** law for Ecuador may be examined at the Bureau of Foreign and Domestic Commerce. (P. 779)

French engineers are endeavoring to discover a substitute which may diminish to a certain degree the present dependence on German **coke.** The possibilities of the Saar-Lorraine coal for the manufacture of coke are being studied. (Pp. 780–1)

The Japanese **copper** industry seems to be in a tight place, and copper companies are now agitating for increased customs duties, which will save them from the disastrous effects of foreign competition. (P. 793)

The Japanese **chemical industries** are showing a willingness to combine with foreign concerns. The worst depression, however, is felt by the **dyestuff** manufacturers, who, unless something is done for them, are faced with the prospect of seeing German imports capture the entire market. (P. 793)

Practically the entire **zinc** and **lead** industry of Upper Silesia has passed to Poland. This industry is relatively very important, the output of raw zinc in Upper Silesia in 1912 having been 168,500 tons, which was five-eighths of the total production of Germany and more than one-sixth of the world production. (Pp. 798–9)

The governor of the Province of Jujuy has requested the Argentine Senate to take measures to protect the **metallurgical industry** recently established in the Provinces of Salta and Jujuy. (P. 802)

Paraguay offers a considerable source of supply of **palm oil** for the American market. (P. 803)

STATISTICS OF EXPORTS TO THE UNITED STATES

ITALY—(P. 650)
Olive oil
UNITED KINGDOM—(P. 728)
Salt, not table
Lead
Tin

CONSTANTINOPLE—(Pp. 661, 801)
Borate stone
Gum tragacanth
Attar of roses
Glue stock
Opium

BOOK REVIEWS

Engineering Instruments and Meters. By EDGAR A. GRIFFITHS. xxiv + 360 pp. D. Van Nostrand Co., New York, 1921. Price, $7.50.

The author limits himself to the measurement of the fundamental quantities of mechanical science; consequently instruments in the fields of electrical and chemical engineering are omitted. It would seem desirable for the author, in any future editions, to cover these fields also, thus making the subject matter as broad as the title.

The book consists of eight chapters, dealing with the measurement of length, screw threads, area, volume, velocity, force and masses, work, and temperature.

Chapter I includes an interesting historical account of length standards and their duplication. In addition to the description of the usual length gages there is a good description of Johanssen's block gages, whereby any standard of length between 0.2 inch and 10.0 inches in steps of 0.0001 inch may be obtained with the accuracy of ±0.00004 inch by means of a set of eighty-one blocks.

The chapter on the measurement of screw threads gives a well-developed account of the measurement and inspection of screw threads, especially by means of optical projection methods.

Of particular interest in the chapter on the measurement of area are the parts dealing with the accuracy of planimeters and the method of obtaining the mean ordinate for circular charts. No area measuring machines are described, such as are in use in this country, for the area measurement of hides. The chapter on the measurement of volume discusses such instruments as displacement meters, orifices, venturi meters and pitot tubes in a thorough manner, in the light of the comparatively recent English developments on the flow of fluids. The chapter also includes a section dealing with the usual types of steam flow meters, together with a section on the electrical measuring instruments, such as the Thomas. Usual and unique styles of depth gages are also described.

Chapter V gives a thorough account of all sorts of tachometers and speedometers, together with the methods for the measuring of train and aircraft velocity. Classifying pitot tubes, etc., as volume meters in the previous chapter and again as instruments for the measurement of velocity in this chapter makes the treatment somewhat scattered. Chapter VI, on the measurement of force and the comparison of masses presents a well worth while description of the variations in construction and shows how these variations affect the sensibility and durability of balances. The discussion of the measurement of work deals with indicators, their construction and errors, together with the construction and relative advantages of various types of dynamometers.

The final chapter is an abbreviated one on the measurement of temperature and is not up to the standard of the rest of the book. It contains a description of the usual types of thermometers and pyrometers. There is a lack of clearness and effectiveness in the treatment of pyrometry, since the author does not set forth clearly that the difference in temperature between a hot and cold junction of a pyrometer sets up an e. m. f., not a "current" proportional to the temperature difference. Errors in pyrometry and methods of correction, base metal couples other than iron-constantin, pyrometer construction, and protection tubes are inadequately discussed. Radiation pyrometry is overemphasized, as compared with the treatment of optical pyrometers.

Following each chapter is a complete and useful bibliography that will be highly useful to one particularly interested in any given type of meter. The index is very poor. For example, orifices, although adequately treated in the text, are not mentioned in the index. The index for Venturi tubes refer to their use in measuring aircraft speed, while the main development of these instruments in Chapter IV is not indexed at all.

This book covers, in a thorough and interesting way, an almost untouched field of utmost importance and will prove itself of value to engineers, constructors, and investigators whose equipment or problem requires the measurement of mechanical force.

R. T. HASLAM

The Electric Furnace. By J. N. PRING. xii + 485 pp. Longmans, Green & Co., 1921. Price, $10.50 net.

This is one of the monographs on industrial chemistry edited by Thorpe, whose preface points out that the object is to elucidate principles rather than to give technical details. The author's preface terms it a "general technical discussion of the position and prospects of high temperature industrial chemistry." The last four words would be as apt a title as the one used, for the author does better in dealing with the chemistry of the electric furnace than with the electric furnace itself.

Without the side-excursions into chemistry, the book, aside from being more recent, would not be of great value to the reader possessing Stansfield's work of the same title, which it closely resembles. With them, it is the best book so far available for a chemist who wishes a general survey of the electric furnace field, or for a student starting the study of electric furnaces.

It is written from the English viewpoint and with special reference to British conditions. The contents cover a historical discussion; laboratory furnaces (especially pressure furnaces); current supply; transformers; measurement of high temperatures; calcium carbide; fixed nitrogen; iron smelting; electric steel; ferro-alloys; nonferrous melting; zinc, copper and tin smelting; SiC, Si, Al_2O_3, graphite, P, and CS_2; Northrup and Hering furnaces; Al, Na, and Ca; refractories; heat losses, electrodes and electrode holders; power expenditure; water power developments (including India, Burma, and Tasmania, as well as the Severn tidal power project), and steam power stations. The chapters on nitrogen fixation are perhaps the best. The one on "current supply" is excellent.

The book is commendably free from descriptions of obsolete and merely "paper and patent" furnaces, though a few of them are included. In general the greatest weakness is not what has been put in but what has been left out. Notwithstanding that 500 pages are filled with close-packed, concisely written information, the electric furnace field is not covered at all fully, nor is the information at all up to date, especially as to American practice. Some fairly recent developments are touched on, such as the high-frequency furnace, preheating the charge for a Snyder steel furnace, the Fulton zinc furnace, and cyanide from cyanamide.

But a book aiming to cover the electric furnace field certainly ought to include the Ajax-Wyatt brass furnace and the Soderberg self-baking electrode, on which one reference each appears in the bibliography, but no mention in the text. The reader would not guess from the book that magnesium and phosphoric acid are commercial electric furnace products. What little information is given on electric brass melting is three years old and very sketchy. Synthetic cast iron is mentioned, but none of the recent progress in electric gray iron and semisteel. Electric annealing and heat-treating furnaces are entirely ignored. The section on ferro-alloys is rather inadequate.

The reviewer's conclusion is that a second volume of equal size would be required to cover, even as concisely as has been the case with the material dealt with, that which has been omitted and which is of equal importance.

There is a certain lack of perspective about the book. It is hard to tell the relative importance of what the author describes. A student taking up electric furnaces for the first time would as likely as not assume that induction furnaces are of equal importance in electric steel practice with direct arc furnaces. If he reads the tables of the number of furnaces of different types installed, and is of a sufficiently inquiring turn of mind to wonder why the direct arc type is so preponderant in steel, he will not find much to clear up the question in the text.

Glaring errors are rare. One occurs in quoting a figure of 168 kw. hr. per metric ton for melting red brass in a Rennerfelt furnace. This figure was once published, but is incorrect and not claimed to-day by the makers of the furnace.

A book of this type has largely to be written with a pair of scissors, of course, and the author intimates as much in his preface. Such a compilation is useful, and on the whole, this is well done, though neither complete nor entirely up to date.

H. W. GILLETT

Colorimetric Analysis. By F. D. SNELL. viii + 150 pp. D. Van Nostrand Co., New York, 1921. Price, $2.00.

An independent work on this subject is a desirable addition to the analyst's reference library. Somewhat of a Cinderella among analytical methods, it actually underwent the destined transformation in the evolution of spectroscopy. In fact the standard work on colorimetric methods (G. and H. Krüss, "Kolorimetrik und Spektralanalyse," L. Voss, Hamburg, 1909, 2nd Ed.) dwells largely with the phases of instrumental development from colorimeter to spectrophotometer. This preoccupation with instruments and principles leaves plenty of room for a book of the present type.

The first three chapters cover: conditions of use of colorimetric methods, apparatus and methods of using it, and figuring of results. The differentiation of colorimetric methods into those used for speed, with more or less sacrifice of accuracy, and those used for precision in the determination of very small quantities is clearly stated. The chapter on apparatus is adequate, if not exhaustive; it might have been more critical, and in particular have given some space to Dehn's contentions[1] with regard to optical distribution factors. The discussion on figuring results would be improved by reference to graphic methods, particularly in cases where speed is fundamental.

The essence of the book, however, is in Chapters IV to XVII, which contain valuable compendium of methods for the determination of Fe, Cu, C (in steel), Pb, Bi, As, Al, Cr, Ni, Co, Mn, Zn, K, Mg, Au, Ti, Vd, Wo, F, Cl, P, Si, B, O, S, beside oxides and acids of nitrogen, sulfur, selenium, etc. Several alternative methods are described wherever possible. Individual points invite some criticism, *e. g.*, in the estimation of iron by thiocyanate, the addition of a small amount of potassium persulfate to a solution is recommended (p. 33) to keep the iron oxidized if it is desired to preserve a sample or standard for several days. The reviewer's experience is that persulfate rapidly oxidizes the thiocyanate radicle, and that the ferrocyanide method (p. 36) is definitely preferable. In regard to Atack's estimation of Al by alizarin S,[2] the reviewer and his collaborators have been disappointed with this sensitive and promising method, as it does not seem to possess the immunity from interference by calcium and phosphates which is claimed for it. For the estimation of phosphorus and phosphate, the method of Taylor and Miller, as modified by Bell and Doisy[3] should be mentioned. It consists in the reduction of phosphomolybdate by a hydroquinol developer, giving a blue color, and is very satisfactory.

The last two chapters on colorimetry proper (color of water, oils, dyes) and on nephelometry are very meager. The former suffers from the total lack of any discussion of the nature of color, its specification, and measurement as such. Nephelometry is dismissed with a reference to P. Kober's paper.[4] Since the subject matter is explicitly limited by title to colorimetric methods, no criticism can be made of this, but since photometric and nephelometric methods are so closely allied to the colorimetric ones it may be hoped that some time they will be discussed together. The author's omission of all but one or two applications of colorimetry to the estimation of organic substances is less comprehensible. Not only are there many older applications in food, drug, etc., analysis, *e. g.*, for alcohols, acids, aldehydes, phenols, alkaloids, but more recently the number of special colorimetric methods in biochemistry has been greatly increased. The increasing importance of colorimetric methods for hydrogen-ion determination also remains unnoticed.

Taking these limitations into account, it appears that the book is essentially one on inorganic colorimetric analysis for the practicing analytical chemist. As such, it fills a need in a way helpful to every chemist who has occasion to speed up analytical procedure.

The book is clearly printed on paper free from excessive gloss, and is illustrated with cuts of various colorimeters.

S. E. SHEPPARD

The Chemical and Metallographic Examination of Iron, Steel, and Brass. By WM. T. HALL AND R. S. WILLIAMS. xiii + 501 pp. McGraw-Hill Book Co., 1921. Price, $5.00.

A few years ago Hall and Williams translated Bauer and Deiss with some additions of their own. The present volume retains emphasis on the necessity for accurate sampling, and other good features of Bauer and Deiss, but covers metallographic examination in somewhat greater detail, and the analytical methods are brought up to date, especially by a chapter and bibliography on electrometric methods.

The book stands out from the general run of laboratory manuals and reference books, because it is written from a broad viewpoint. We have too many such books written by analysts. This one is written by chemists. The young chemist who studies it cannot avoid understanding that proper sampling to take account of segregation, the use of accurate analytical methods, and consideration of the microstructure, are all equally important steps in answering questions as to the quality of a metal or alloy.

The book is written in an orderly fashion, clearly printed on good paper, and well indexed. The authors first discuss the chemical principles underlying each method of analysis, so that the essential precautions and the interferences are understood before the details of the method are given. Four or five methods are given for most of the common elements found in modern steels, but the relative advantages of each method are so clearly stated that the reader can make an intelligent choice. The limits of accuracy to be expected are usually given for each method, and analytical figures on the same material by different methods are often included. Methods are given for C, Mn, P, Si, S, Cu, Cr, Fe, Ni, Mo, W, V, Al, As, Co, Ti, Zr, N, and O in steel. The methods for nonferrous alloys are less complete, but standard methods for common determinations of elements in bearing metal, brass, and bronze are given. The light aluminium alloys are not covered either in the chemical or metallographic sections.

Only minor criticisms occur to the reviewer. Since methods involving separation of ferric chloride by ether are numerous in the book, it would have been well to point out that one can make this separation with a beaker, a stirring rod and a siphon without having to use the Rothe shaking funnel and increase

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[1] "Fallacies in Colorimetry," *J. Am. Chem. Soc.*, **39** (1917), 1392.

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

[3] *J. Biol. Chem.*, **44** (1920), 55.

[4] THIS JOURNAL, **10** (1915), 843.

the volume of the solution by washing out the original beaker. Since methods for zirconium are included, it would have been well to point out that both zirconium and titanium interfere with evolution of sulfur even in an annealed sample, and that the cupferron method given for zirconium is often more applicable for titanium than the methods given under that element.

"Peptonization" (p. 309) might better be peptization, in the interests of "economy and efficiency" in spelling and pronunciation.

The statement (p. 248) that in steel "oxygen is present chiefly as ferrous oxide dissolved in the crystals of ferrite" may be correct, but in view of the differences of opinion on this subject among metallurgists, the statement seems a bit positive.

The metallographic end of the book is a trifle sketchy and elementary compared with the chemical end, but covers the essentials clearly. The reviewer would prefer fuller references to the literature.

If you have an analyst in your laboratory whom you wish to have analyze whatever samples are handed to him without question as to history of the sample, or application of the analysis, don't let him use this book, for it might lead him to become a chemist instead of an analyst.

H. W. GILLETT

Naval Stores—History, Production, Distribution, and Consumption. Compiled by THOMAS GAMBLE. 286 pages. Review Publishing & Printing Co., Savannah, Ga., 1921. Price, $3.25, postpaid.

Certain industries require a special treatment and that given to the naval stores industry in this volume is extremely appropriate. The illustrations are profuse and there is a wealth of introductory historical matter that would compel the interest of the layman who might not know the meaning of the name on the title page; even the immortal Samuel Johnson has contributed his mite: "I remember I used to think tar dirty, but when I knew it to be only a preparation of the juice of the pine, I thought so no longer."

Every corner of the earth that grows a pine capable of producing naval stores has been ransacked. All phases of the industry, such as methods of production, marketing, standards, uses, statistics on production, exports and prices, and future sources of supply receive consideration. The chapters bearing on wood turpentine and rosin are especially valuable. This phase of the industry, after many vicissitudes, is on a sound basis and has the promise of an increasingly great future.

It is a striking fact that the first great improvement in the industry resulted through the introduction of the cup and gutter system in 1901 through the energy of Dr. Herty, and this step to-day remains the high-water mark of advancement. Another fine piece of work was performed by Miss Eloise Gerry of the Forest Service. A microscopical study of tapped trees showed clearly the nature of resin flow, and, aside from the investigations of Tschirch, furnished the first really scientific information on which a rational method of tapping could be based.

Not so many years ago turpentine was the valuable product, the rosin being frequently run to waste. To-day the condition is reversed. The chief use of turpentine continues to be in paints and varnishes, but many manufacturers consider that only enough is necessary to give their finished products a "smell." Rosin has highly desirable properties for certain soaps and is practically indispensable in the sizing of the cheaper grades of paper.

In the settlement of a new country it is difficult to decide how much waste is compatible with proper economic development. There is no question, however, but that the exploitation of our forests has gone beyond the bounds of reason, and that the future must receive serious consideration. So many futile predictions have been made regarding the approximate time at which the present stands of timber will cease to be the largest factor in naval stores production, that it is useless to hazard a guess; but the end is just as certain as it is indefinite. Consequently it is gratifying to know that steps have been taken to perpetuate the industry through the growing of long leaf and Cuban pines, the latter being particularly desirable from the standpoint of rapidity of growth and resin production.

Great credit is due Mr. Thomas Gamble. While he has refrained from calling it a "labor of love," it could hardly have been otherwise.

A. W. SCHORGER

The Silver Bromide Grain of Photographic Emulsions. By A. P. H. TRIVELLI AND S. E. SHEPPARD. 143 pages. D. Van Nostrand Co., New York, 1921. Price, $2.50.

This is the first volume of a series of monographs on the theory of photography from the Research Laboratory of the Eastman Kodak Company. Each is intended to be complete in itself, and to include not only work done at the research laboratory of the company, but also that available in the literature of the subject. If the standard of the initial volume is maintained, the series will be invaluable to students of the science of photography.

Since the silver halide grains are of very small size and precipitated in a colloid medium, they have usually been treated simply as colloid aggregates. In the present volume, however, a detailed study is made of these grains. It is established that they are definitely crystalline and belong to the regular system, though of widely different final shapes. The questions of their alteration by mechanical strains and of the modification of the gelatin structure are discussed. A study of the course of development of the silver halide emulsion by ammonia leads to the conclusion that the process is primarily a recrystallization of the silver halide as a halide-ammonia complex on nuclei furnished by the visible photochemical image; the hypothesis of mechanical disintegration by light therefore becomes unnecessary. This is contrary to the widely urged hypothesis of Lüppo-Cramer.

The formation of grains in the emulsion is studied in the light of the dispersion theory of von Weimarn, according to which the grain-subdivision of the initial precipitate is determined by the concentration of the solutions and by other physical conditions. The changes of this "dispersity" are now found to be connected with changes in the content of adsorbed impurities present. Crystallization catalysis by nuclei is suggested as an explanation of some of the effects produced by the admixture of silver iodide and silver bromide in an emulsion.

A bibliography is appended, and there are many references to original papers. The study of the relation between the sizes of grains and their photographic properties is reserved for a future monograph.

L. DERR

Statistical Supplement to the Final Report of the Nitrogen Products Committee of the Ministry of Munitions. By J. A. HARKER, O.B.E., D.S.C., F.R.S., Director of the Nitrogen Research Laboratory, Ministry of Munitions, London. 22 pages. H. M. Stationery Office, Imperial House, Kingsway, W. C. 2. Price, One Shilling.

The above pamphlet supplements the statistical data published in the Final Report of the Nitrogen Products Committee of the Ministry of Munitions early in 1920 and should be obtained and bound with that Report, which is one of the best compilations on nitrogen fixation and the world nitrogen situation that has been published in any language. The present pamphlet simply brings the statistics of the nitrogen industry as nearly up to date as possible and covers all phases of the industry, including Chile nitrate, nitric acid, by-product ammonia, and the synthetic nitrogen industry. As always, Dr. Harker's work has been done well.

CHARLES L. PARSONS

NEW PUBLICATIONS

Agricultural Chemistry: Chimie Agricole. C. André. 3d edition. 3 Vol. 1213 pp. Price, 20fr. J.-B. Baillière & Fils, Paris.

Analytical Chemistry. Vol. I, Qualitative Analysis. F. P. Treadwell and William T. Hall. 5th English edition. 597 pp. Price, $4.50 net. John Wiley & Sons, Inc., New York.

Atomic Theories. F. H. Loring. 218 pp. Price, 12s. 6d. Methuen & Co., London.

Biochemistry: A Manual of Selected Biochemical Methods—as Applied to Urine, Blood and Gastric Analysis. Frank P. Underhill. 232 pp. Illustrated. Price, $3.00 net. John Wiley & Sons, Inc., New York.

Catalogue of British Scientific and Technical Books. Prepared by a committee of the British Science Guild, London. 376 pp. Price, 10s. net.

Chemistry. G. H. J. Adlam. Price, 3s. 6d. James Thin, Edinburgh.

Coal: Practical Chemistry of Coal. A. F. Findley and R. Wiggington. 140 pp. Price, 12s. 6d. Benn Brothers, Ltd., London.

Confectioners' Raw Materials; Their Sources, Modes of Preparation, Chemical Composition, the Chief Impurities and Adulterations, Their More Important Uses and Other Points of Interest. James Grant. 173 pp. Price, $3.00. Longmans, Green & Co., New York.

Explosives: Manufacture and Uses of Explosives. R. C. Farmer. 116 pp. Price, 2s. 6d. net. Sir Isaac Pitman & Sons, Ltd., London.

Explosives: Technical Records of Explosives Supply 1915–1918. No. 3. Sulfuric Acid Concentration. No. 4. The Theory and Practice of Acid Mixing. Ministry of Munitions and Department of Scientific and Industrial Research. Price, 12s. each. H. M. Stationery Office, London.

Flotation: A Manual of Flotation Processes. Arthur F. Taggart. 192 pp. Price, $3.00. John Wiley & Sons, Inc., New York.

Forensic Chemistry. A. Lucas. 258 pp. Price, $5.25 net Longmans, Green & Co., New York.

Graphical Analysis: A Textbook on Graphic Statics. William S. Wolfe. 374 pp. 713 illustrations. Price, $4.00. McGraw-Hill Book Co., Inc., New York.

Hydraulique Générale et Appliquée. Denis Eydoux. (Encyclopédie du Génie Civil et des Travaux Publics.) 504 pp. Illustrated. Price, 50 fr. J.-B. Baillière & Fils, Paris.

Inorganic Chemistry: A Textbook of Inorganic Chemistry. A. F. Holleman. 527 pp. Price, 19s. net. Chapman & Hall, London.

Laboratory Manual of General Chemistry. Harry N. Holmes. 115 pp. Price, $1.60. The Macmillan Co., New York.

Medical Chemistry: Chemistry and Analysis of Drugs and Medicines. Henry C. Fuller. 1072 pp. Illustrated. Price, $10.00. John Wiley & Sons, Inc., New York.

Medical Chemistry: Précis de Chimie Médicale. Desgrez. 476 pp. Illustrated. Price, 25fr. J.-B. Baillière & Fils, Paris.

Metallurgical Plants: Nos Usines Métallurgiques Dévastées 1914–1918. Monographies de quelques Grandes Usines Métallurgiques Francaises Détruites par les Allemands. Introduction by Léon Guillet. 234 pp. Illustrated. Price, 25 fr. La Revue de Métallurgie, Paris.

Microbiologie Agricole. E. Kayser. 4th edition. 2 vol. 715 pp. 98 figures. Price, 20fr. J.-B. Baillière & Fils, Paris.

Mineralogy: A Manual of Determinative Mineralogy. Charles H. Warren. 163 pp. Price, $2.00. McGraw-Hill Book Co., Inc., New York.

The Mineral Industry. Vol. XXIX. 1920. Edited by G. A. Roush and Allison Butts. 938 pp. Illustrated. Price, $10.00. McGraw-Hill Book Co., Inc., New York.

Mining Physics and Chemistry. J. W. Whitaker. 268 pp. Price, 9s. Edward Arnold & Co., London.

Modern Gasworks Practice. Alwyne Meade. 2d edition. 815 pp. Price, 55s. net. Benn Brothers, Ltd., London.

Organic Chemistry: Résumé Analytique du Cours de Chimie Organique. Paul Cazeneuve and Albert Morel. 2d edition. 432 pp. Price, 25fr. J.-B. Baillière & Fils, Paris.

Organic Medicaments: Préparation des Médicaments Organiques. E. Fourneau. 350 pp. Illustrated. Price, 25fr. J.-B. Baillière & Fils, Paris.

Paint and Color Mixing. A Practical Handbook for Painters, Decorators, Paint Manufacturers, Artists, and All Who Have to Mix Colors. Arthur S. Jennings. 6th edition. 253 pp. Illustrated. Price, $5.00. D. Van Nostrand Co., New York.

Practical Refrigeration. Compiled by Editorial Staff of *Power*. 283 pp. Illustrated. Price, $2.00. McGraw-Hill Book Co., Inc., New York.

Quantitative Analysis: A Course of Instruction in Quantitative Chemical Analysis for Beginning Students. George McPhail Smith. Revised edition. 218 pp. Price, $2.25. The Macmillan Co., New York.

Quantitative Analysis: An Introductory Course of Quantitative Chemical Analysis with Explanatory Notes. Henry P. Talbot. 6th edition, completely rewritten. 203 pp. Price, $2.25. The Macmillan Co., New York.

Radioactivity and Radioactive Substances. J. Chadwick. 111 pp. Price, 2s. 6d net Sir Isaac Pitman & Sons, Ltd., London.

Tanning: Practical Tanning: A Handbook of Modern Practice and Processes as Applied in the Manufacture of Leather and Allied Products. Allen Rogers. New edition, completely rewritten. 900 pp. 125 illustrations. Price, $10.00. Henry Carey Baird & Co., Inc., New York.

Textile Chemistry: Introduction to Textile Chemistry. H. Harper. 189 pp. Illustrated. Price, $1.25. The Macmillan Co., New York.

Vegetable Oils: Les Huiles Végétales. H. Jumelle. 495 pp. 125 figures. Price, 15fr. J.-B. Baillière & Fils, Paris.

Vitamine Manual: A Presentation of Essential Data about the New Food Factors. Walter H. Eddy. 121 pp. Price, $2.50. Williams & Wilkins Co., Baltimore.

RECENT JOURNAL ARTICLES

Bleaching of Cotton. J. Merritt Matthews. *Color Trade Journal*, Vol. 9 (1921), No. 5, pp. 172–76.

Chemical Elements of Living Matter. Ingo W. D. Hackh. *American Journal of Pharmacy*, Vol. 93 (1921), No. 11, pp. 745–56.

Dyes: Organic Acids for Printing and Dyeing. A. J. Hall. *Textile Colorist*, Vol. 43 (1921), No. 515, pp. 741–43.

Dyes: La Naphtaline au Point de Vue Scientifique et Industriel. M. E. Noelting. *Revue Générale des Matières Colorantes de la Teinture, de l'Impression et des Apprêts*, Vol. 26 (1921), No. 298, pp. 145–51.

Enamels: Some Relations of Composition to Solubility of Enamels in Acids. Homer F. Staley. *Journal of the American Ceramic Society*, Vol. 4 (1921), No. 9, pp. 703–17.

Glass: The Development of Various Types of Glass. Parts XII, XIII, XIV, XV, XVI. C. J. Peddle. *Journal of the Society of Glass Technology*, Vol. 5 (1921), No. 19, pp. 201–268.

Heat Balance in the Kier Boil. Paul A. Merriam. *American Dyestuff Reporter*, Vol. 9 (1921), No. 19, Sec. 2, pp. 13–18.

Leather: The Microscope as Applied in the Manufacture of Leather. Robin Bruce Croad and Fini G. A. Enna. *Journal of the American Leather Chemists Association*, Vol. 16 (1921), No. 12, pp. 690–95.

Leather: Recovery of Acetic Acid during the Evaporation of Tanning Extracts. Georges Vie. *Journal of the American Leather Chemists Association*, Vol. 16 (1921), No. 11, pp. 641–44. Translated from *Le Cuir*, 10 (1921), 329.

Naval Stores: The Manufacture of Naval Stores from the Dead Wood of the Southern Pines. C. M. Sherwood. *Chemical and Metallurgical Engineering*, Vol. 25 (1921), No. 22, pp. 994–98.

Oil: The Relation between Alcohol-Water Solubility and Spontaneous Ignition Temperatures. W. R. Ormandy and E. C. Craven. *Journal of the Institution of Petroleum Technologists*, Vol. 7 (1921), No. 28, pp. 325–34.

Photomicrographic Method for the Determination of Particle Size of Paint and Rubber Pigments. Henry Green. *Journal of the Franklin Institute*, Vol. 192 (1921), No. 5, pp. 637–66.

Polariscope as an Aid in the Identification of Alkaloids. A. G. Murray. *Journal of the American Pharmaceutical Association*, Vol. 10 (1921), No. 10, pp. 736–42.

Porcelain: Use of Special Oxides in Porcelain Bodies. R. F. Geller and B. J. Woods. *Journal of the American Ceramic Society*, Vol. 4 (1921), No. 10, pp. 842–54.

Potash: Les Gisements de Potasse d'Alsace et l'Etat de leur Exploitation. Camille Matignon. *Chimie et Industrie*, Vol. 6 (1921), No 4, pp. 440–64.

Rubber: The Discontinuity of Vulcanization in the Presence of Organic Accelerators. D. F. Twiss. *Journal of the Society of Chemical Industry*, Vol. 40 (1921), No. 20, pp. 242*t*–48*t*.

Rubber: The Problem of Solvent Recovery. P. Wilson Gumaer. *The Rubber Age*, Vol. 10 (1921), No. 3, pp. 85–87.

MARKET REPORT—DECEMBER, 1921

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

INORGANIC CHEMICALS

	Dec. 1	Dec. 15
Acid, Boric, cryst., bbls..........lb.	.12$^3/_4$	.12$^3/_4$
Hydrochloric, com'l, 20°.....lb.	.01$^1/_2$	.01$^1/_2$
Hydriodic..................oz.	.19	.19
Nitric, 42°..................lb.	.06$^3/_4$	.06$^3/_4$
Phosphoric, 50% tech.......lb.	.12	.12
Sulfuric, C. P...............lb.	.07	.07
Chamber, 66°..........ton	17.00	17.00
Oleum 20%............ton	22.00	22.00
Alum, ammonia, lump...........lb.	*.03$^1/_2$	*.03$^3/_4$
Aluminium Sulfate (iron-free).....lb.	.03	.03
Ammonium Carbonate, pwd......lb.	*.07	*.07
Ammonium Chloride, gran.......lb.	*.07$^1/_2$	*.07
Ammonia Water, carboys, 26°....lb.	.07$^1/_2$	.07$^1/_2$
Arsenic, white..................lb.	.06	.05$^1/_2$
Barium Chloride ....ton	*50.00	*50.00
Nitrate...................lb.	*.07	*.07
Barytes, white..................ton	28.00	28.00
Bleaching Powd.,35%, works, 100 lbs.	2.25	2.25
Borax, cryst., bbls..............lb.	.05$^3/_4$	.05$^3/_4$
Bromine, pure..................lb.	.20	.20
Calcium Chloride, fused, f. o. b. N. Y.....................ton	28.75	28.75
Chalk, precipitated, light.........lb.	.03$^1/_2$	.03$^1/_2$
China Clay, imported...........ton	18.00	18.00
Copper Sulfate.............100 lbs.	5.30	5.55
Feldspar.......................ton	8.00	8.00
Fuller's Earth.............100 lbs.	1.00	1.00
Iodine, resublimed..............lb.	3.50	3.80
Lead Acetate, white crystals......lb.	.12	.12
Nitrate...................lb.	.15	.15
Red American..........100 lbs.	.08	.08
White American........100 lbs.	.06$^1/_2$	.06$^1/_2$
Lime Acetate..............100 lbs.	1.75	1.75
Lithium Carbonate..............lb.	1.50	1.50
Magnesium Carbonate, tech.......lb.	.06	.06
Magnesite.......................ton	72.00	72.00
Mercury flask..............75 lbs.	*45.00	*52.00
Phosphorus, yellow..............lb.	*.28	*.28
Plaster of Paris............100 lbs.	1.50	1.50
Potassium Bichromate...........lb.	.10$^1/_2$	.10$^1/_2$
Bromide, imported.........lb.	*.14	*.14
Carbonate, calc., 80–85%....lb.	.04$^1/_2$	.04$^1/_2$
Chlorate, cryst............lb.	*.06	*.06
Hydroxide, 88–92%.........lb.	*.05$^1/_2$	*.05$^1/_2$
Iodide, bulk...............lb.	2.60	2.90
Nitrate...................lb.	.08	.08
Permanganate, U. S. P.......lb.	*.16	*.15
Salt Cake, bulk.................ton	17.00	17.00
Silver Nitrate..................oz.	.45$^1/_2$	.44$^1/_4$
Soapstone, in bags..............ton	12.00	12.00
Soda Ash, 58%, bags........100 lbs.	*2.00	*1.85
Caustic, 76%...........100 lbs.	*3.90	*3.85
Sodium Acetate.................lb.	.04	.04
Bicarbonate............100 lbs.	2.25	2.25
Bichromate...............lb.	.08	.08
Chlorate..................lb.	.07$^1/_2$	.07$^1/_2$
Cyanide..................lb.	*.27	*.27
Fluoride, technical..........lb.	*.10	*.10
Hyposulfite, bbls.......100 lbs.	3.50	3.50
Nitrate, 95%...........100 lbs.	2.25	2.25
Silicate, 40°...............lb.	.01$^1/_2$	.01$^1/_2$
Sulfide, 60% fused ....lb.	*.04$^1/_4$	*.04$^1/_4$
Bisulfite, powdered..........lb.	.04$^1/_2$	.04$^1/_2$
Strontium Nitrate...............lb.	*.11	*.11
Sulfur, flowers..............100 lbs.	3.00	3.00
Crude................long ton	20.00	20.00
Talc, American, white...........ton	18.00	18.00
Tin Bichloride..50% sol'n.......lb.	.09$^3/_4$	.09$^3/_4$
Oxide.....................lb.	.38	.38
Zinc Chloride, U. S. P...........lb.	.35	.35
Oxide, bbls................lb.	.08	.08

ORGANIC CHEMICALS

	Dec. 1	Dec. 15
Acetanilide......................lb.	*.29	*.29
Acid, Acetic, 28 p. c.........100 lbs.	2.50	2.50
Glacial................lb.	.10	.10
Acetylsalicylic..............lb.	.65	.70
Benzoic, U. S. P., ex-toluene..lb.	.65	.60
Carbolic, cryst., U. S. P., drs..lb.	.10	.10
50- to 110-lb. tins.......lb.	.21	.21
Citric, crystals, bbls.........lb.	*.45	*.44
Acid (*Concluded*)		
Oxalic, cryst., bbls...........lb.	.14$^1/_2$	.14$^1/_2$
Pyrogallic, resublimed.......lb.	1.75	1.75
Salicylic, bulk, U. S. P.......lb.	.22	.24
Tartaric, crystals, U. S. P....lb.	*.27	*.26
Trichloroacetic, U. S. P......lb.	4.40	4.40
Acetone, drums.................lb.	.12$^1/_2$	.12$^1/_2$
Alcohol, denatured, complete....gal.	.44	.46
Ethyl, 190 proof...........gal.	4.85	4.85
Amyl Acetate..................gal.	2.15	2.15
Camphor, Jap, refined...........lb.	.90	.90
Carbon Bisulfide................lb.	.06$^1/_2$	.06$^1/_2$
Tetrachloride..............lb.	.10$^1/_2$	.10$^1/_2$
Chloroform, U. S. P.............lb.	*.36	*.36
Creosote, U. S. P...............lb.	.40	.40
Cresol, U. S. P..................lb.	.17	.17
Dextrin, corn..............100 lbs.	2.45	2.45
Imported Potato...........lb.	.08$^1/_2$	.08$^1/_2$
Ether, U. S. P., conc., 100 lbs....lb.	.14	.14
Formaldehyde..................lb.	.10$^1/_2$	.10$^1/_2$
Glycerol, dynamite, drums.......lb.	.12$^1/$	.14
Methanol, pure, bbls...........gal.	.85	.85
Pyridine......................gal.	1.75	1.75
Starch, corn................100 lbs.	1.88	1.88
Potato, Jap................lb.	.08	.08
Rice......................lb.	.18	.18
Sago......................lb.	.04	.04

OILS, WAXES, ETC.

	Dec. 1	Dec. 15
Beeswax, pure, white............lb.	.35	.33
Black Mineral Oil, 29 gravity....gal.	.22	.22
Castor Oil, No. 3................lb.	.10$^1/_2$	.10$^1/_2$
Ceresin, yellow. ....lb.	.08	.07$^1/_2$
Corn Oil, crude, tanks, mills......lb.	.07$^3/_4$	.07$^3/_4$
Cottonseed Oil, crude, f. o. b. mill..lb.	.06$^7/_8$	.07
Linseed Oil, raw (car lots)......gal.	.67	.67
Menhaden Oil, crude (southern).gal.	.33	.33
Neat's-foot Oil, 20°.............gal.	1.25	1.25
Paraffin, 128–130 m. p., ref.......lb.	.06	.06
Paraffin Oil, high viscosity.......gal.	.45	.45
Rosin, "F" Grade, 280 lbs.......bbl.	5.60	5.40
Rosin Oil, first run.............gal.	.35	.35
Shellac, T. N...................lb.	.65	.65
Spermaceti, cake................lb.	.30	.30
Sperm Oil, bleached winter, 38°..gal.	1.73	1.73
Stearic Acid, double-pressed......lb.	.10	.10
Tallow Oil, acidless............gal.	.82	.82
Tar Oil, distilled...............gal.	.60	.60
Turpentine, spirits of...........gal.	.80	.81

METALS

	Dec. 1	Dec. 15
Aluminium, No. 1, ingots........lb.	.17	.17
Antimony, ordinary.........100 lbs.	4.55	4.55
Bismuth........................lb.	1.55	1.65
Copper, electrolytic.............lb.	.13$^5/_8$	.13$^7/_8$
Lake......................lb.	.13$^1/_2$	.13$^3/_4$
Lead, N. Y......................lb.	.04$^3/_4$	.04$^3/_4$
Nickel, electrolytic..............lb.	.41	.41
Platinum, refined, soft...........oz.	80.00	78.00
Quicksilver, flask.........75 lbs. ea.	45.00	52.00
Silver, foreign ....oz.	.66$^1/_4$	.65$^3/_4$
Tin............................lb.	.30	.32
Tungsten Wolframite.......per unit	2.50	2.50
Zinc, N. Y.................100 lbs.	5.10	5.25

FERTILIZER MATERIALS

	Dec. 1	Dec. 15
Ammonium Sulfate, export...100 lbs.	2.60	2.60
Blood, dried, f. o. b. N. Y.......unit	3.50	3.50
Bone, 3 and 50, ground, raw.....ton	30.00	30.00
Calcium Cyanamide, unit of Ammonia........................	2.25	2.25
Fish Scrap, domestic, dried, f. o. b. works......................unit	3.25 & .10	3.25 & .10
Phosphate Rock, f. o. b. mine:		
Florida Pebble, 68% ....ton	5.00	5.00
Tennessee, 78–80%............ton	8.00	8.00
Potassium Muriate, 80%.......unit	.75	.75
Pyrites, furnace size, imported..unit	.14	.14
Tankage, high-grade, f. o. b. Chicago....................unit	3.00 & .10	3.00 & .10

*Resale or Imported (not an American maker's price).

COAL-TAR CHEMICALS

Crudes

		Dec. 1	Dec. 15
Anthracene, 80–85%	lb.	.75	.75
Benzene, pure	gal.	.27	.27
Cresol, U. S. P.	lb.	.17	.17
Cresylic Acid, 97–99%	gal.	.80	.80
Naphthalene, flake	lb.	$.06^{1}/_{2}$	$.06^{1}/_{2}$
Phenol, drums	lb.	.10	.10
Toluene, pure	gal.	.28	.28
Xylene, 2 deg. dist. range	gal.	.45	.45

Intermediates

		Dec. 1	Dec. 15
Acids:			
Anthranilic	lb.	1.10	1.10
Benzoic tech	lb.	.50	.50
Broenner's	lb.	1.55	1.55
Cleve's	lb.	1.50	1.50
Gamma	lb.	2.25	2.25
H	lb.	1.00	1.00
Metanilic	lb.	1.60	1.60
Monosulfonic F	lb.	2.40	2.40
Naphthionic, crude	lb.	.65	.65
Nevile & Winther's	lb.	1.35	1.30
Phthalic	lb.	.40	.38
Picric	lb.	.30	.30
Sulfanilic	lb.	.27	.27
Tobias'	lb.	2.00	2.00
Aminoazobenzene	lb.	1.15	1.15
Aniline Oil	lb.	$.17^{1}/_{2}$	17
Aniline Salt	lb.	.26	.26
Anthraquinone	lb.	1.50	1.50
Bayer's Salt	lb.	1.00	1.00
Benzaldehyde, tech	lb.	.45	.45
U. S. P.	lb.	1.25	1.25
Benzidine (Base)	lb.	1.00	.90
Benzidine Sulfate	lb.	.75	.70
Diaminophenol	lb.	5.50	5.50
Dianisidine	lb.	4.75	4.75
p-Dichlorobenzene	lb.	.15	.15
Diethylaniline	lb.	1.10	1.00
Dimethylaniline	lb.	.42	.40
Dinitrobenzene	lb.	.21	.21
Dinitrotoluene	lb.	.25	.25
Diphenylamine	lb.	.65	.60
G Salt	lb.	.70	.70
Hydroquinol	lb.	.90	1.35
Metol (Rhodol)	lb.	3.00	3.00
Monochlorobenzene	lb.	.10	.10
Monoethylaniline	lb.	1.00	1.00
a-Naphthylamine	lb.	.30	.30
b-Naphthylamine (Sublimed)	lb.	1.50	1.50
b-Naphthol, dist	lb.	.30	.30
m-Nitroaniline	lb.	.85	.85
p-Nitroaniline	lb.	.77	.77
Nitrobenzene, crude	lb.	.10	.10
Rectified (Oil Mirbane)	lb.	$.11^{1}/_{2}$	$.11^{1}/_{2}$
p-Nitrophenol	lb.	.75	.75
p-Nitrosodimethylaniline	lb.	—	—
o-Nitrotoluene	lb.	.15	.15
p-Nitrotoluene	lb.	.70	.70
m-Phenylenediamine	lb.	1.10	1.10
p-Phenylenediamine	lb.	1.70	1.60
Phthalic Anhydride	lb.	.38	.38
Primuline (Base)	lb.	3.00	3.00
R Salt	lb.	.60	.60
Resorcinol, tech	lb.	1.50	1.50
U. S. P.	lb.	2.00	2.00
Schaeffer Salt	lb.	.70	.70
Sodium Naphthionate	lb.	.70	.70
Thiocarbanilide	lb.	.40	.40
Tolidine (Base)	lb.	1.20	1.20
Toluidine, mixed	lb.	.30	.30
o-Toluidine	lb.	.20	.20
p-Toluidine	lb.	1.25	1.25
m-Toluylenediamine	lb.	1.10	1.10
Xylidine, crude	lb.	.45	.45

COAL-TAR COLORS

Acid Colors

		Dec. 1	Dec. 15
Black	lb.	.80	.80
Blue	lb.	1.50	1.50
Fuchsin	lb.	2.00	2.00
Orange III	lb.	.50	.50
Red	lb.	1.00	1.00
Alkali Blue, domestic	lb.	4.50	4.50
Azo Carmine	lb.	4.00	4.00
Azo Yellow	lb.	1.50	1.50
Erythrosin	lb.	7.50	7.50
Indigotin, conc.	lb.	2.50	2.50
Paste	lb.	1.50	1.50
Naphthol Green	lb.	1.60	1.60
Ponceau	lb.	.80	.80
Scarlet 2R	lb.	.70	.70

Direct Colors

		Dec. 1	Dec. 15
Black	lb.	.70	.70
Blue 2B	lb.	.60	.60
Brown R	lb.	.85	.85
Fast Red	lb.	2.35	2.35
Yellow	lb.	1.50	1.50
Violet, conc.	lb.	1.10	1.10
Chrysophenine, domestic	lb.	1.10	1.10
Congo Red, 4B Type	lb.	.90	.90
Primuline, domestic	lb.	3.00	3.00

Oil Colors

		Dec. 1	Dec. 15
Black	lb.	.70	.70
Blue	lb.	1.25	1.25
Orange	lb.	.95	.95
Red III	lb.	1.65	1.65
Scarlet	lb.	1.00	1.00
Yellow	lb.	1.25	1.25
Nigrosine Oil, soluble	lb.	.90	.90

Sulfur Colors

		Dec. 1	Dec. 15
Black	lb.	.20	.20
Blue, domestic	lb.	.70	.70
Brown	lb.	.35	.35
Green	lb.	1.00	1.00
Yellow	lb.	.75	.75

Chrome Colors

		Dec. 1	Dec. 15
Alizarin Blue, bright	lb.	5.00	5.00
Alizarin Red, 20% paste	lb.	.60	.60
Alizarin Yellow G	lb.	.85	.85
Chrome Black, domestic	lb.	.65	.65
Chrome Blue	lb.	.75	.75
Chrome Green, domestic	lb.	1.50	1.50
Chrome Red	lb.	1.75	1.75
Gallocyanin	lb.	2.30	2.30

Basic Colors

		Dec. 1	Dec. 15
Auramine, O, domestic	lb.	1.80	1.80
Auramine, OO	lb.	3.00	3.00
Bismarck Brown R	lb.	.70	.70
Bismarck Brown G	lb.	1.00	1.00
Chrysoidine R	lb.	.75	.75
Chrysoidine Y	lb.	.75	.75
Green Crystals, Brilliant	lb.	3.50	3.50
Indigo, 20% paste	lb.	.45	.45
Fuchsin Crystals, domestic	lb.	3.00	3.00
Magenta Acid, domestic	lb.	2.00	2.00
Malachite Green, crystals	lb.	2.25	2.25
Methylene Blue, tech	lb.	1.50	1.50
Methyl Violet 3 B	lb.	1.75	1.75
Nigrosine, spts. sol	lb.	.70	.70
Water sol., blue	lb.	.60	.60
Jet	lb.	.90	.90
Phosphine G., domestic	lb.	2.50	2.50
Rhodamine B, extra conc	lb.	8.50	8.50
Victoria Blue, base, domestic	lb.	5.40	5.40
Victoria Green	lb.	2.00	2.00
Victoria Red	lb.	7.00	7.00
Victoria Yellow	lb.	7.00	7.00